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Synthesis and properties of polyaniline–cellulose acetate blends: The use of sugarcane bagasse waste and the effect of the substitution degree

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ABSTRACT

Membranes of blends of polyaniline (PANi) and cellulose acetate (CA) produced from sugarcane bagasse with different degrees of substitution were produced and characterized using various techniques. Results showed that incorporation of PANi into the CA matrices leads to significant alterations of the blend morphologies, with phase separation, and that these differences are less significant for PANi/cellulose triacetate blends. The blends also showed a significant increase in electrical conductivity, with that of PANi/cellulose diacetate demonstrating an almost 200-fold increase.

1. Introduction

Polyaniline (PANi) is a conjugated polymer with interesting properties which allows it to be used in a wide spectrum of applications, including biomedical uses (such as artificial muscles) (Guimard, Gomez, & Schmidt, 2007), electronics (Morrin et al., 2008), textiles (Kim, Koncar, & Dufour, 2006), corrosion protection (Alam, Riaz, & Ahmad, 2008), electrochromic devices (Hong, Hwang, & Chen, 2008), synthesis of polyaniline nanocomposites, as well as in the development of chemical sensors and biosensors (Arora, Prabhakar, Chand, & Malhotra, 2007; Lange, Roznyatouskaya, & Mirsky, 2008; Prabhakar, Arora, Singh, & Malhotra, 2008; Valente et al., 2005a), fuel cells and nanocomposites (Wu et al., 2008). However, this polymer has very poor mechanical properties, limiting its use in the pure form. A methodology to solve this problem is to produce blends with neutral polymers which have good mechanical and processing properties. Cellulose derivatives and, in particular cellulose acetate, are quite often used as matrices for PANi, and have the important advantages of neutral character, capacity for transparent film formation and low cost. Several studies focusing on the chemical and physical properties of PANi and cellulose acetate blends have been reported (das Neves & De Paoli, 1998; Ebrahim, Kashyout, & Soliman, 2007; Marques, Brett, Burrows, Monkman, & Retimal, 2002; Planes et al., 1998; Pron, Nicolau, Genoud, & Nechtschein, 1997; Valente et al., 2005a).

In this paper, two different issues will be addressed: the use of sugarcane bagasse to synthesize cellulose acetate with different degrees of substitution and the study of the physical-chemistry properties of PANi/sugarcane based cellulose derivatives blend membranes.

Since blend properties are dependent on the nature of the polymeric matrix, and in this paper, the effect of the degree of substitution (DS) of cellulose acetate on the blend properties is reported. The DS of cellulose is the average number of hydroxyl groups that may be substituted on the glycosidic rings, and may take any value from 0 (cellulose) to 3 (completely substituted cellulose). DS affects various characteristics, such as the polymer crystallinity (Barud et al., 2008; Samios, Dart, & Dawkins, 1997) and solubility in different solvents. For example, pure cellulose (DS = 0) is insoluble in most common solvents, but upon increasing the DS of cellulose through formation of acetate esters or other derivatives, the solubilities in different types of solvents (S) change ($DS \approx 1$, S: water; $DS \approx 2$, S: tetrahydrofuran and acetone; $DS \approx 3$, S: dichloromethane and chloroform) (Heinze & Liebert, 2004).

Cellulose acetate samples with two distinct DS's were produced. Initially, cellulose triacetate was synthesized using cellulose extracted from sugarcane bagasse, through a homogeneous acetylation route. The cellulose triacetate was then deacetylated to produce cellulose diacetate. The use of sugarcane bagasse stems from the urgent need of finding uses for this waste product. With the increase in the demand for biofuel over the last years, there has been a marked increase in the production of ethanol from sugarcane, increasing also the generation of residues from this activity. Usually, sugarcane bagasse is burnt to produce the electricity required by the sugar mills and, in some cases, excess energy is even

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sold in the electricity market. However, a great amount of bagasse is still wasted, and several options for recycling it have been studied, such as the hydrolysis of cellulose for producing ethanol (Sanchez & Cardona, 2008), the use of lignin for producing phenolic resins (Effendi, Gerhauser, & Bridgwater, 2008), the production of cellulose derivatives such as carboxymethylcellulose (Ruzene, Goncalves, Teixeira, & De Amorim, 2007), methylcellulose (Rodrigues Filho et al., 2007a; Viera et al., 2007) and cellulose acetate (Cerqueira, Rodrigues Filho, & Meireles, 2007; Filho, Da Silva, Meireles, De Assuncção, & Otaguro, 2005; Filho et al., 2000; Meireles, Filho, Assunção, Zeni, & Mello, 2007; Rodrigues Filho et al., 2007b). The aims of this work are to see if this recycled material can be used in advanced materials, and to study the properties of blends produced with it and polyaniline.

2. Experimental

2.1. Materials

Sugarcane bagasse from the 2007 harvest was provided by Usina Caeté, from Delta, Minas Gerais, Brazil. High purity polyaniline in powder form as its emeraldine form was prepared by chemical polymerization (Adams, Laughlin, Monkman, & Kenwright, 1996). Ethanol was purchased from Merck, poly (ethylene glycol) from Fluka, sodium hydroxide and DMSO-d6 from Sigma–Aldrich, and dichloromethane from Riedel-de-Haën. All the other reagents and solvents were purchased from Panreac. All reagents and solvents were used as received.

2.2. Cellulose extraction

Extraction of cellulose from sugarcane bagasse was carried according to the following methodology (Rodrigues Filho et al., 2000): a mixture of 76 mL NaOH (0.25 M) and 4 g of dry, ground bagasse was kept at room temperature for 18 h. Then, this mixture was filtered, washed with distilled water and refluxed with a HNO_3/ethanol solution (20% v/v) for 3 h, changing the alcoholic solution every hour. After the reflux, the bagasse was washed with distilled water to remove the acid and oven dried at 105 °C for 3 h.

2.3. Preparation of cellulose acetate

Cellulose triacetate was produced according to the methodology described elsewhere (Cerqueira et al., 2007). A brief description is presented below:

A mixture consisting of 1 g cellulose from bagasse and 25 mL acetic acid was stirred for 30 min. A solution composed by 0.08 mL H_2SO_4 and 9 mL acetic acid was then added to the system, which was stirred for 25 min. The mixture was filtered and 32 mL acetic anhydride was added to the filtrate. This solution was returned to the recipient containing bagasse and stirred for a further 30 min. After this time, the mixture was allowed to stand for 14 h at room temperature.

To isolate the cellulose triacetate (CTA), this mixture was filtered to remove undissolved particles and water added to the filtrate to stop the reaction and precipitate cellulose triacetate. This was filtered and washed with distilled water to remove acetic acid, and then dried at room temperature overnight.

To produce the cellulose diacetate (CDA), a mixture containing 10 mL acetic acid, 10 mL water and 0.75 mL sulfuric acid was slowly added to the reaction medium, and the flask was then immersed in a bath at 80 °C for 10 min. Next, water was added to the mixture to precipitate cellulose diacetate, which was filtered, washed to remove the excess of acetic acid, and then dried at room temperature overnight.

The substitution degrees of cellulose acetates were determined by NMR spectroscopy (Varian Unity 500 NMR spectrometer, Palo Alto, CA) and calculated by integration of the ^{1}H NMR resonances assigned to methyl groups and those to the hydrogen atoms bonded to the glycosidic group (Biswas, Saha, Lawton, Shogren, & Willett, 2006). The calculated DS of the cellulose acetates were 2.60 and 2.88 for CDA and CTA, respectively; these values are in close agreement with those obtained by acid–base titration: 2.65 (±0.04) and 2.94 (±0.06).

2.4. Membrane preparation

The membranes were prepared using a solvent mixture, composed of dichloromethane (60%), ethanol (10%) and formic acid (30%). In order to prepare the membranes, cellulose acetate (CDA, CTA or both) was initially dissolved in dichloromethane/ethanol and PANi was dissolved in formic acid. After complete dissolution of both polymers, they were mixed together and stirred for 24 h. Next, the solution was cast on a glass plate using a casting knife (*Braive*) set at 100 μm. After complete evaporation of solvent, at room temperature (20 °C) for 30 min, films were removed from the glass plate with the help of water. Membranes without PANi were also produced for comparison.

The chemical compositions of the different prepared membranes are shown in Table 1.

2.5. Membrane characterization

The samples were analyzed by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). DSC tests were carried out on a DSC Q100, TA instruments, using about 4 mg of each sample at a heating rate of 10 °C/min from 25 to 320 °C, using modulation of 0.8 °C at every 30 s and nitrogen purge (50 mL/min). For TGA, 4 mg of each sample was heated from 25 to 700 °C using nitrogen purge (50 mL/min).

The surface morphologies of cellulose acetate membranes and cellulose acetate/PANI blends have been analysed by scanning electron microscopy (SEM) with a JEOL model 5310 scanning microscope operating under low vacuum at 15 kV. The membranes were previously freeze dried (*Free Zone 4.5 – Labconco*) overnight before coating with gold.

Visible absorption spectra of films were obtained over the wavelength range 400–800 nm, with a bandwidth of 0.5 nm, using a Shimadzu UV-2100 spectrophotometer by directly inserting the CA/PANI blend sample in the beam.

The porosity (P%) of blends was measured by mercury porosimetry (*Micromeritics* Poresizer 9320), according to the method described by Palacio, Pradanos, Calvo, and Hernandez (1999).

2.6. Percentage of water uptake

To determine the percentage of water uptake, various samples of each membrane were cut, immersed in water, and left in this medium until the sample weight reached an equilibrium value M_{eq} Subsequently, the membranes were dried in oven at 100 °C un-

Table 1
Chemical composition of membranes.

Membrane	CDA (% w/w)	CTA (% w/w)	PANi (% w/w)
M1	8	–	–
M2	8	–	0.02
M3	4	4	–
M4	4	4	0.02
M5	–	8	–
M6	–	8	0.02

til constant weight, M_0. The weight/weight (w/w) water concentration in the membrane, C_w, was calculated from Eq. (1)

$$C_w = \frac{M_{eq} - M_0}{M_{eq}} \tag{1}$$

All gravimetric measurements on water sorption were made (to 0.1 mg) using an ADA 120LE balance.

2.7. Water permeation

The diffusion coefficients of water in the different polymer membranes were measured using a previously described technique (Lobo, Murtinho, Gil, Garcia, & Valente, 1996; Valente, Polishchuk, Burrows, & Lobo, 2005b). This uses a cell with two compartments, A, completely filled with distilled water and B, with poly(ethylene glycol), with a 1.950 cm diameter membrane separating them. The variation of water volume during the diffusion studies is measured by a capillary positioned in the upper side of the cell. The poly(ethylene glycol) (molecular weight 400, Fluka, purum) in compartment B is continuously stirred to maintain the concentration of water in the bottom of the membrane equal to zero.

All the membranes were immersed in water 24 h before the beginning of the experiment in order to attain equilibrium rapidly.

The water diffusion coefficients (D_w) were determined using an adaptation of Fick's first law equation

$$\rho_0 \frac{dh}{dt} = C_w D_w \left(\frac{s_m}{a_c}\right) l^{-1} \tag{2}$$

where ρ_0 is the water density, dh/dt is the variation of the height of column of water in the capillary tube with time, C_w is the weight/weight water concentration in the membrane surface in contact with water phase, l is the thickness of the membrane, s_m is the area of membrane surface and a_c is the capillary area.

2.8. Conductimetric measurements

Conductimetric measurements were carried out using a technique similar to that described by Nouri, Dammak, Bulvestre, and Auclair (2002). The conductimetric cell is made up of two polyethylene parts, and a cylindrical shape. On the cylinder base there are two platinum electrodes both parallel to the bases of the cell. The electrodes are the basis of an imaginary cylinder, containing NaCl (0.1 M), whose electrical resistance was measured with (R_a) and without (R_s) the membrane, using a Wayne Kerr LCR 4265 operating at 1 kHz. Before the measurement, the system was kept for 24 h in a thermostat at 25.0 ± 0.1 °C for complete equilibration, after which the values of electrical resistance and impedance are similar.

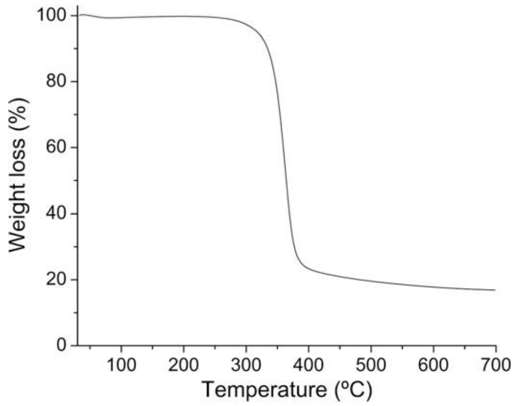

Fig. 1. TGA of M1 sample.

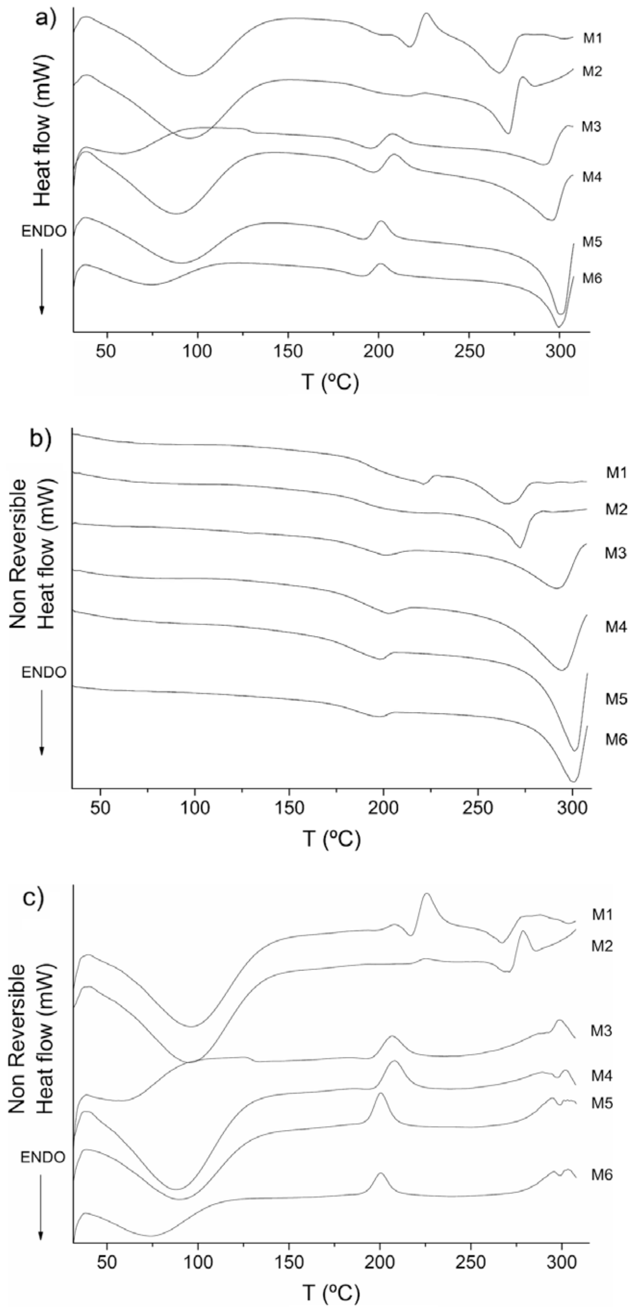

Fig. 2. mDSC for the blends. (a) heat flow, (b) reversible heat flow and (c) nonreversible heat flow.

Table 2
Enthalpies of crystallization and fusion, and percentage of crystallinity of the produced membranes.

	ΔH_c (J/g)	ΔH_f (J/g)	%C (%)
M1	5.8	8.3	4.2
M2	0.7	8.4	13.1
M3	1.5	10.3	15
M4	5.3	20.7	26.2
M5	3.7	21.1	30
M6	7.8	27.9	34.2

From the measurement of the electrical conductance of the NaCl equilibrating solution between Pt electrodes with (G_T) and without (G_s) the membrane, the membrane conductance, G_m, can be calculated using the following equations

$$G_m = \frac{G_T G_s}{G_s - G_T} \tag{3}$$

and the electrical conductivity of the membrane (κ_m) is given by:

$$\kappa_m = G_m \frac{l}{A} \tag{4}$$

where l and A are the thickness and the area of the polymer membrane, respectively.

3. Results and discussion

3.1. Characterization of the produced materials

All samples, with and without PANi, showed a very similar degradation pattern in their TGA. Typical results for membrane M1 are shown as an example in Fig. 1. These involved a mass loss, corresponding to the release of a small percentage of water at around 100 °C and a degradation peak around 360 °C, which starts around 320 °C. Fig. 2 shows the mDSC thermograms for cellulose acetate membranes (with different hydrolysis degrees) and blends containing PANi. All cellulose acetate samples are semi-crystalline, presenting an exotherm resulting from crystallization around 200 °C, and a melting endotherm with temperatures ranging from around 275 °C for M1 to 300 °C for M5. Thermograms also present an endotherm corresponding to dehydration. Crystallinity of the cellulose acetate samples increases with the increase of DS, which is likely to be a consequence of better chain packing, since the higher DS values lead to a more homogeneous chain, in agreement with the reversible heat flow DSC shown in Fig. 2b (Barud et al., 2008). The real enthalpy of fusion is calculated from the net value between the enthalpies of fusion and crystallization (Table 2).

From the results on the thermal behavior of the blend membranes, it is possible to conclude that crystallization increases by

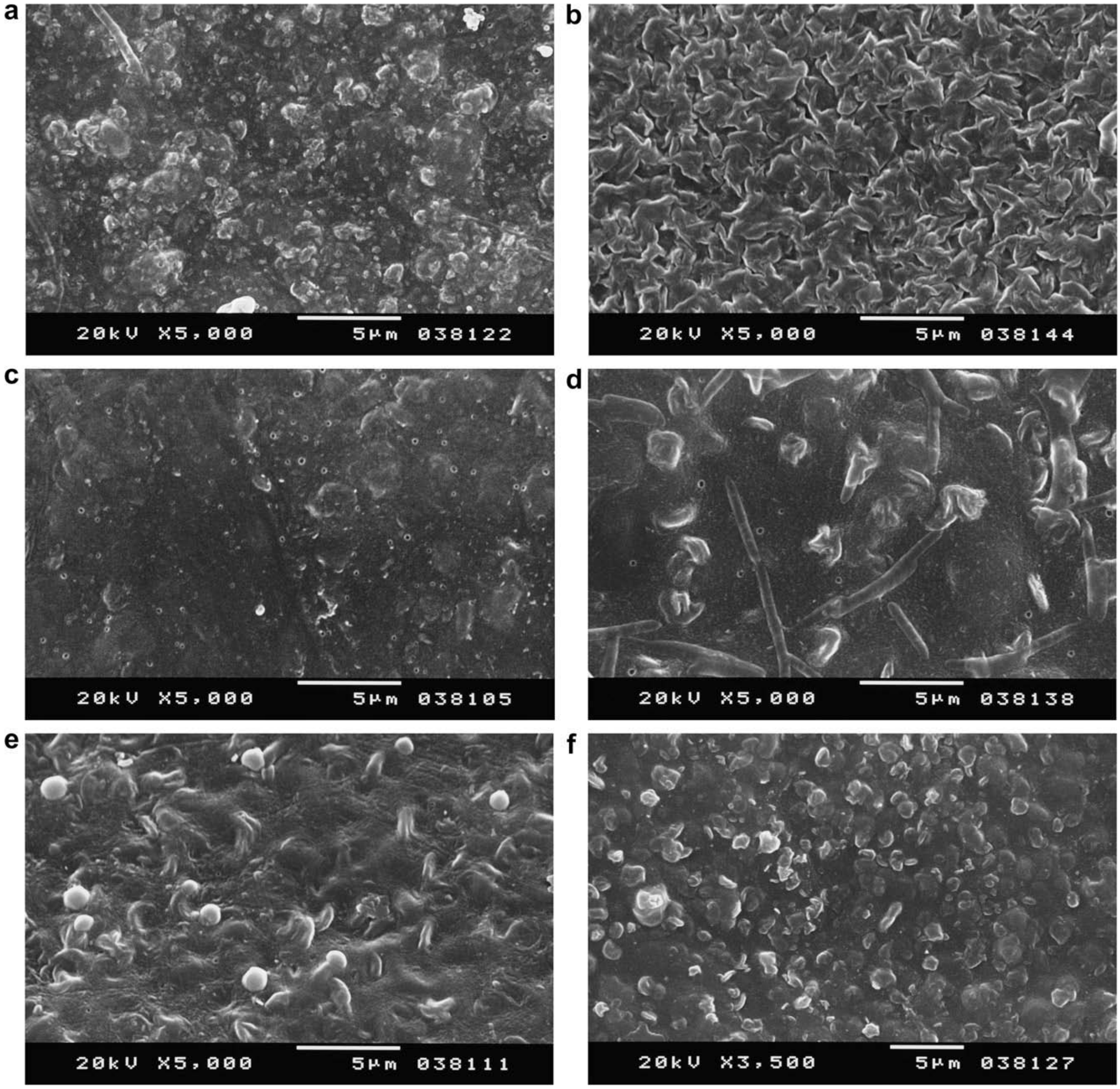

Fig. 3. SEM micrographs of the surface of (a) M1, (b) M2, (c) M3, (d) M4, (e) M5 and (f) M6.

increasing the DS of the CA, clearly suggesting that the CA plays the major role in the thermal and structural properties of the blend. However, the degree of crystallinity (%C) of blend membranes is higher than in membranes of pure CA; this effect is most marked in the case of CDA, where the incorporation of PANi leads to a 3-fold increase of %C, and becomes less pronounced upon increasing the DS of the CA (the percentage of variation of the %C in the CTA without and with PANi is only 13%). The CDA membrane is typically amorphous; consequently, it may be anticipated that PANi incorporation might induce the crystallization of the CA amorphous phase (Zheng et al., 2005); in the case of membranes M3 and M5, which show higher crystallization degrees, the incorporation of PANi shows a less significant effect. It should be noted that the degradation temperatures of cellulose acetate membranes observed at 362 °C, as measured by TGA, do not show any alteration either with the DS or with PANi incorporation. These values are slightly higher than those corresponding to the fragmentation of the macromolecular structure of cellulose acetate reported by Hanna et al., 330 °C (1999), but are smaller than those found for blends of cellulose acetate and polyaniline, with a higher content of PANi (greater than 10% w/w, around 380 °C) (Al-Ahmed, Mohammad, & Rahman, 2004).

Confirmation of modifications in the polymeric structure in PANi-modified cellulose acetate membranes also came from SEM analysis. Fig. 3 shows the micrographs of the different polymer films with a magnification of 5000×. Comparing the micrographs of CA with different DS, it is possible to observe that the surface morphology is essentially non-porous, with different degrees of roughness, and that some phase separation can be found. Upon PANi incorporation, the surface morphology changes in all CAs. In particular, the surface of M2 changes drastically when compared with membrane M1, in agreement with modifications seen in the DSC analysis, showing in a distinct way a two-phases surface and becomes more diffuse (Valente, Burrows, & Lobo, 2006); with other DS CA blends membranes the surface heterogeneity is enhanced.

From the analysis of membrane cross-section it is possible to conclude that cellulose acetates show an anisotropic arrangement with a preferential orientation in the plane of the film, in a very similar fashion to that which characterizes PANi membranes; therefore, it can be observed that the incorporation of PANi in cellulose acetate may induce some compaction of the polymeric structure by enhancing lamellar structures (Fig. 4b). The exception is the membrane M6 in which dense cross-section morphology can be seen (Fig. 4d). However, the loss of the lamellar structure and consequent formation of a more dense M6 structure is only a surface phenomenon. The apparent density, d_{ap}, of M6 is around 13% lower than that of the membrane M5 (Table 3). The analysis of porosity and density of different membranes also supports the reported alterations found by alteration of DS and incorporation of polyaniline. For cellulose acetate membranes (M1, M3 and M6), d_{ap} increase by increasing the degree of substitution, in agreement with the other results on the greater degree of crystallinity obtained by DSC; these changes occur with a concomitant slight decrease in the average pore diameter (φ_{av}); however, the apparent density of blend membranes follows a reverse order: d_{ap} (M2) > d_{ap} (M4) > d_{ap} (M6). Therefore, the incorporation of PANi results in a phase separation, which is less significant in the case of cellulose triacetate membranes and has a strong effect in the case of cellulose diacetate, where a difference of around 44% in d_{ap} is found. These values are in close agreement with changes in the surface morphology as seen by SEM.

Other important physical properties that contribute to shed light on the polymeric structural modification provoked by DS

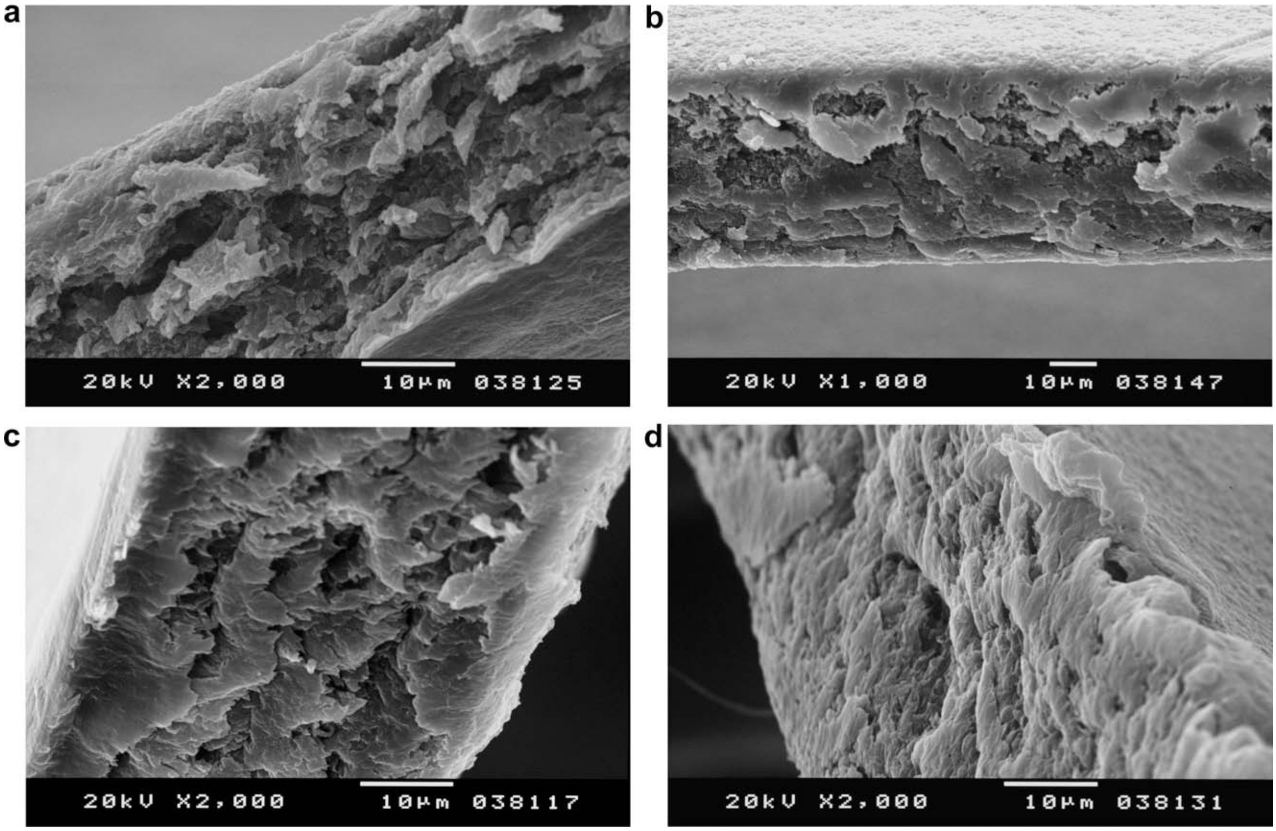

Fig. 4. SEM micrographs of the cross-section area of (a) M1, (b) M2, (c) M4 and (d) M6.

Table 3
Some physical properties of the blends.

	ϕ[a] (%)	d_{ap}[b] (g mL^{-1})	$ø_{av}$[c] (nm)	C_w[d] (g g^{-1})	D_w[e] (10^{-13} m2 s^{-1})	κ_m[f] (s cm^{-1})
M1	18.0	0.774	14.0	0.015	6.88	4.1×10^{-5}
M2	18.5	1.377	11.9	0.017	4.83	8.0×10^{-3}
M3	21.0	1.308	13.2	0.041	3.17	5.7×10^{-5}
M4	25.9	1.150	26.3	0.030	26.34	3.0×10^{-4}
M5	11.1	1.136	9.7	0.013	10.72	1.1×10^{-4}
M6	16.6	0.992	10.0	0.013	29.17	2.2×10^{-4}

[a] ϕ porosity.
[b] d_{ap} apparent density.
[c] $ø_{av}$ average pore diameter.
[d] C_w water concentration.
[e] D_w water diffusion coefficient.
[f] κ_m electrical conductivity.

and PANi incorporation are the percentage of water uptake and the water diffusion coefficients, D_w, (Table 3).

Comparing the different cellulose derivatives, it is possible to note that the percentage of water uptake, C_w, is not linearly dependent on the degree of substitution, and that the most dense membrane (M3) also has the highest water concentration. Thus, the water concentration increases upon increasing the polymer volume fraction (Naghash & Okay, 1996). These results are consistent with the analysis of water diffusion coefficients; that is, there is a decrease of D_w with an increase of C_w. These experimental results are similar to those reported elsewhere (Valente et al., 2005b), and can be explained according to the cluster model for water diffusion. This model is based on the reasonable suggestion that interactions between water molecules exceed polymer–water interactions (Polishchuk & Zaikov, 1997). A possible justification is that the decrease of hydroxyl groups of cellulose will stabilize the water molecules by allowing the formation of water clusters.

For the PANi-containing blends (M2, M4 and M6), to a first approximation no regular patterns in behavior, can be found, suggesting that the structure alterations of the cellulose matrix as due to the presence of PANi are not comparable; however, it is noteworthy that water diffusion coefficients, which are an order of magnitude higher than those found for cellulose derivatives, increase linearly with a decrease of polymer density. This behavior, although not completely understood, suggests that in the case of CA/PANi blends the most relevant parameter for the water transport is not the water concentration but the obstacles caused by the polymeric structure.

One of the crucial physical properties of the polyaniline for practical applications is its proton conductivity (Kang, Neoh, & Tan, 1998). The effect of DS of cellulose derivatives on the electrical conductivity of the PANi–cellulose blend films is shown in Table 3. It can be seen that the incorporation of PANi leads to an increase of the A.C. electrical conductivity of the resulting blend; however, the most drastic increase in the electrically conductivity was found for DCA/PANi where an increase of the electrical conductivity of almost 200 times was observed. It should be stressed that such a drastic increase in the κ_m is observed for an incorporation of only 0.02% (w/w) of PANi in the blend and that this shows very good nominal values when compared with other PANi blends (Bae, Jo, & Park, 2003; Pan, Yang, Li, & Jiang, 2005). As the degree of substitution of cellulose increases the electrical conductivity of cellulose membranes also increases and the effect of incorporation of PANi, on the blend electrical conductivities, decreases. Comparing the electrical conductivities of CTA and CTA/PANi the increase of κ is only a factor of two resulting from PANi incorporation. A possible justification for this can be found from the analysis of the visible spectra of different membranes (Fig. 5). Upon the incorporation of PANi, an absorption band in the visible spectra is observed. For the membranes M4 and M2, the absorptions are well defined and show maximum absorbance wavelengths at 750 and 800 nm, which is characteristic of PANi in its emeraldine form with some degree of protonation (Pereira et al., 2009). However, the M6 blend shows a flat absorbance band with a maximum wavelength at 650 nm; this band is characteristic of the presence of a leucoemeraldine base (Kang et al., 1998), a fully protonated polyaniline. This completely reduced polyaniline has less possibilities for electrical conduction, which explains the small electrical conductivity increase observed between membranes M5 and M6.

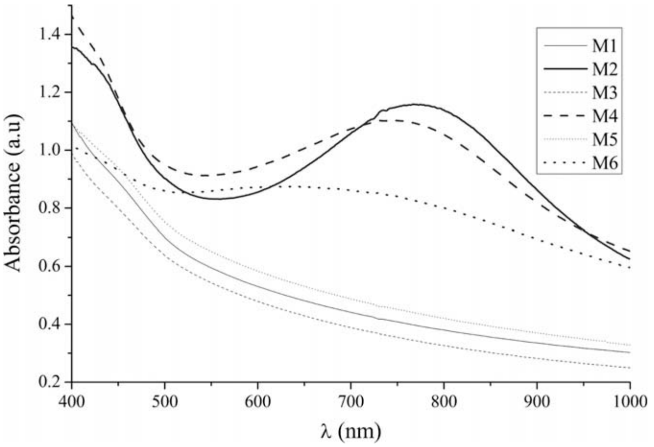

Fig. 5. Visible absorption spectra of CA/PANi blends.

4. Conclusions

PANi incorporation to cellulose acetate matrices led to significant alterations in the blend morphologies. For example, DSC showed that the crystallinity of the membranes increase when PANi is incorporated to the matrix, and that this increase is more effective for the material with the lower DS. Furthermore, SEM showed that the incorporation of PANi into the CA matrices led to possible phase separation, which was corroborated by the porosimetry results.

The PANi/cellulose diacetate blends also showed a significant increase in electrical conductivity, which was up to 200 times greater than in the pure matrix. The electrical conductivity of the other blends was not as significant, since PANi remained protonated after the membrane preparation.

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