Water Flux through Blends from Waste Materials: Cellulose Acetate (from Sugar Cane Bagasse) with Polystyrene (from Plastic Cups)

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ABSTRACT: In the present work we blended cellulose acetate (taken from sugar cane bagasse) (CA) with polystyrene (taken from postconsumer plastic cups) (PS). The blends were produced in the following ratios (w/w) of the polymers: CA 50%/PS 50%, CA 90%/PS 10%, and CA 10%/PS 90%, using dichloromethane as solvent. The blends were characterized by Fourier transform infrared spectroscopy, differential scanning calorimetry, and wide-angle X-ray diffraction. The results show that the presence of polystyrene hinders the organization of regions responsible for the crystallinity originally existing in pure cellulose acetate.

We also made measurements of water flux through blends, using the Payne cup technique. The flux properties were compared with those obtained for commercial membranes by Osmonix: nanofiltration (SG) and reverse osmosis (CG). The results show that the blend CA 90%/PS 10% presents water vapor flux comparable with that of commercial membranes for nanofiltration (SG). © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 516–522, 2005

Key words: blends; cellulose acetate; polystyrene; amorphous; membranes

INTRODUCTION

Cellulose acetates are broadly used as membranes in separation processes such as hemodialysis, reverse osmosis, and gas separation. Acetates are cellulosic derivatives obtained from cellulose acetylation. The cellulose acetylation reactions are classified as homogeneous (acetylation, in which acetic anhydride is used as acetylating agent, acetic acid is the solvent, and sulfuric acid or perchloric acid is used as catalyzer) and heterogeneous (in this kind of acetylation, toluene is used as a nonswelling agent, responsible for keeping the original characteristics of the fibers). The acetate obtained from heterogeneous acetylation is more crystalline than that obtained from the homogeneous process. Cellulose acetates have distinctive degrees of substitution (DS) (average number of acetyl groups that substitute the hydroxyl groups on the glucosidic units of cellulose). The DS influences the transport properties as well as the biodegradation of these cellulosic derivatives. This is fundamentally related to the cristallinity in acetates. The cristallinity and bio-

degradation in acetates decrease according to the following order: cellulose triacetate, cellulose diacetate, cellulose monoacetate (CA). Cellulose acetates have limitations concerning their mechanical properties, even though they are tough materials.

Polystyrene is a thermoplastic material obtained from styrene. Polystyrene presents, in general, good mechanical, thermic, and electric resistance, as well as low density. Due to these properties, it is used to produce discardable materials such as cups and food trays. Polystyrene can be produced with distinct regularities: atactic, isotactic, and syndiotactic.

On isotactic and syndiotactic materials, the phenyl groups are distributed regularly way throughout the polymeric chain, so that such materials are crystallizable. On the other hand, on atactic polystyrene this regularity practically doesn't exist, and the polymer is mainly amorphous. Most polystyrene commercial products are made of this amorphous polystyrene.

The polystyrene properties make this material suitable for investigating blend formation with cellulose acetate to overcome the deficiencies in the mechanical properties of acetates.[1,2]

Brazil is one of the biggest world producers of sugar and alcohol from sugar cane. This industrial activity generates sugar cane bagasse as the main residue. Recycling industrial and urban residues then becomes

very important in order to preserve the environment and also to aggregate value to the industrial residue according to the economic point of view.

Thus, recently we demonstrated the ability to produce cellulose acetate membranes from sugar cane bagasse.[3] The membranes were analyzed by Fourier transform infrared (FTIR) spectroscopy, wide-angle X-ray diffraction (WAXD), and differential scanning calorimetry (DSC) techniques, and the water flux through the membranes was measured by Payne's cup technique. However, one problem observed was the difficulty in handling the membranes in Payne's cup because the membranes were fragile. To improve the workability of the membranes we began to study blends of cellulose acetate with polystyrene (obtained from waste plastic cups).[4] The blend composition used was 50% w/w. A reduction of water flux was observed due the presence of polystyrene; however, the main result was improvement in the quality of the membrane in relation to workability.

Edgar et al.[5] presented a review of the literature relative to cellulose ester blends and, surprisingly, did not find instances where polystyrene was mixed with cellulose esters. The paper of Uesaka et al.[6] corroborates this perspective. This may be attributed to the fact that blends of cellulose acetate and polystyrene are fundamentally incompatible.[1] Furthermore, there is a paucity of literature about blends of cellulose acetate with polystyrene. Kesting[7] has looked at this mixture primarily with regard to the grafting of cellulose acetate polymer with styrene. Recently, Meenakshi et al.[2] have reported that cellulose acetate obtained from banana stem when mixed with polystyrene results in a material that presents high stability.

In the present work, based on our previous results,[4] we have produced blends in distinct compositions (CA 50%/PS 50%, CA 90%/PS 10%, and CA 10%/PS 90%, from industrial (sugar cane bagasse) and urban (plastic cups) wastes. The resulting materials have been characterized using FTIR, WAXD, and DSC techniques. The water vapor flux through the blends was measured using Payne's cup technique. The water vapor flux was measured also with commercial membranes by Osmonix (SG, nanofiltration, and CG, reverse osmosis) for comparison. The blends obtained are basically incompatible and amorphous. However, the amorphous character resulted from morphological changes that indicate the hindrance of the CH_2 bending vibrations,[8] at 1429 cm^{-1}, at the crystalline regions of cellulose acetate due to the presence of the polystyrene. This band is associated with the neighboring group of C-6, for example, the formation or rupture of intramolecular hydrogen bondings involving the O-6. Thus, the blends also present some regions of compatibility generated mainly by van der Waals forces.

EXPERIMENTAL

Cellulose acetate was produced from the homogeneous acetylation reaction[9] of cellulose obtained from sugar cane bagasse. The bagasse had been purified in accordance with the procedure described by Filho et al.[3] Homogeneous acetylation was chosen because, in accordance with Sassi and Chanzy,[9] it produces a more amorphous material than that obtained by heterogeneous acetylation. The degree of substitution of cellulose acetate was 2.80. The intrinsic viscosity of the materials was measured with an Ostwald viscometer at 25°C for polystyrene (toluene as solvent, $[\eta] = 34$ mL·g^{-1}) and at 30°C for cellulose acetate (dichloromethane/methanol mixture 9/1 v/v, $[\eta] = 44$ mL·g^{-1} as solvent). The blends were produced as follows:[4] cellulose acetate (1 g) and polystyrene (1 g) were dissolved in 25 mL of dichloromethane to produce a blend CA 50%/PS 50%. For the other blend compositions, the weight ratios were modified to produce CA 90%/PS 10% and CA 10%/PS 90% blends. The mixture was agitated until all solutes were dissolved (over a 24-h period). Membranes were produced by casting the solution on a cleaned glass surface. After total evaporation of the solvent, the plates with the membranes were immersed in distilled water at ambient temperature, approximately 27°C. The detached membranes were left to dry at ambient temperature and stored in a desiccator with silica gel for later use. For comparison, individual membranes of polystyrene (from cup plastic) and cellulose acetate (from sugar cane bagasse) were also produced under the same conditions of the blends in our laboratory. The FTIR, WAXD, and water flux experiments were carried out under the same conditions described in Ref. 3 but the DSC experiments were executed at a velocity of 10°C/min.

RESULTS AND DISCUSSION

FTIR

Figure 1 presents the infrared spectrum of the cellulose acetate membranes. Figure 2 presents the infrared spectrum of polystyrene, while Figure 3 presents part of the infrared spectra of CA 50%/PS 50% blend.

The 1300 to 1600 cm^{-1} region of the spectrum was chosen because it is where the main morphological changes were observed. In Figure 1, we want to highlight the band at 1429 cm^{-1}, which is attributed to the bending vibration of the CH_2 group. This band is associated with the neighboring group of C-6, for example, the formation or rupture of intramolecular hydrogen bonding involving the O-6.[8] In the case of the blend, as shown in Figure 3, the band practically does not appear. This means that the presence of polystyrene caused morphological alterations in the crystalline region of cellulose acetate. This also occurs for the
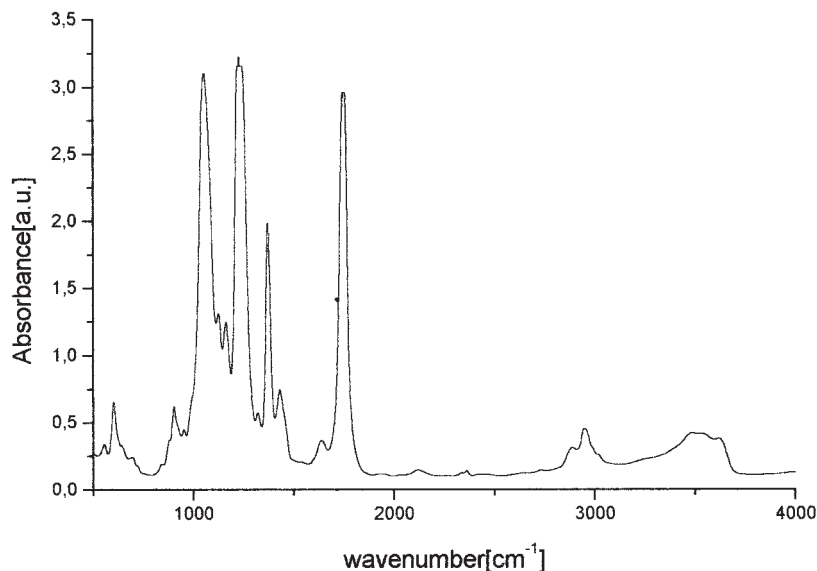
Figure 1   Typical infrared spectrum of cellulose acetate membrane.

band at 1321 cm^{-1}, CH$_2$ wagging. These alterations indicate that, while blends are basically incompatible, due to the individual characteristics of each material observed in Figures 1 and 2, which are also kept in the blend (Figure 3), there are regions of miscibility in the produced material. In this way we can consider a blend of CA/PS as being partially miscible. This partial miscibility could occur in microregions in the formed blend. The partial miscibility could be explained by the van der Waals forces, e.g., Puleo et al.[10] discuss that the alterations on the dipole–dipole forces (van der Waals forces) among the acetyl groups that are not hydrogen bonded can be weakened by solvents and also in polymer blends where one of the

constituents has at least a carbonyl group. The authors also mention that similar phenomena were also reported for PMMA upon the addition of styrenic polymers. These literature observations are based on a small displacement (about 5 cm^{-1} to a higher frequency) on the carbonyl band, located around 1748 cm^{-1}, on the FTIR results of the studied materials. Nevertheless, in our study the changes are drastic and more significant for the band at 1429 cm^{-1}, which involves the carbon C^6 vicinity and, consequently, the pendants acetyl groups. Corroborating with this hypothesis that the van der Waals forces could explain our results, recently Zhang et al.[11] showed that there is miscibility for blends of poly(ether imide)/polycar-
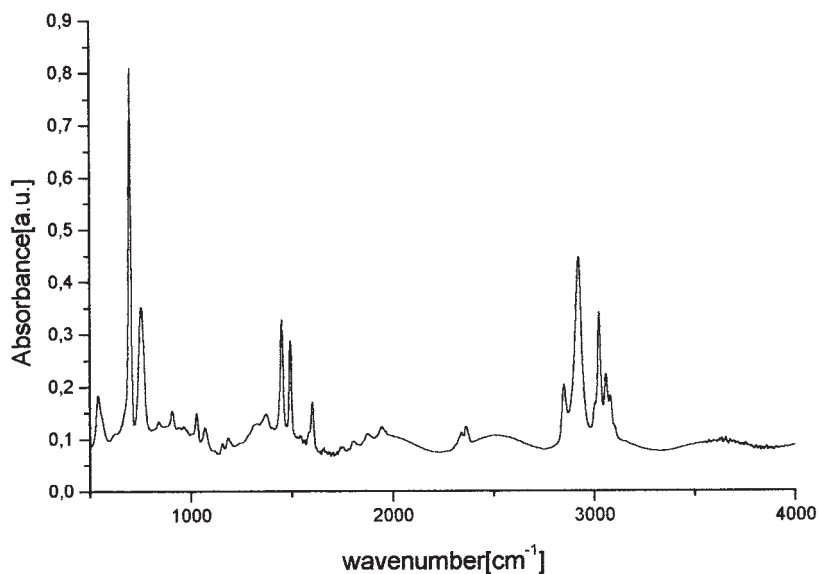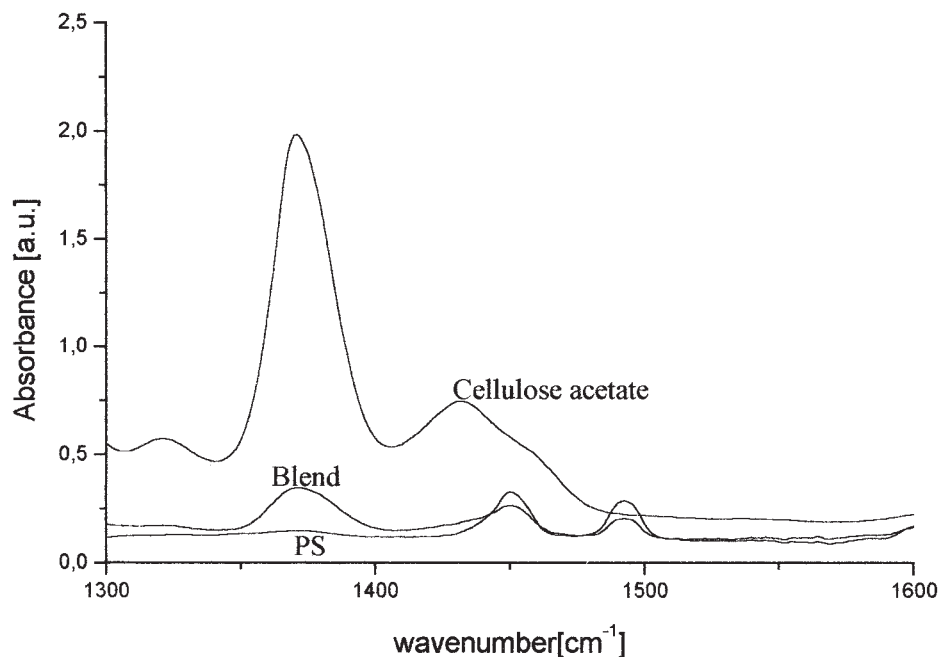

Figure 2   Typical infrared spectrum of polystyrene membrane.

Figure 3 Typical infrared spectra, in the range of 1300 to 1600 cm^{-1}, for blend AC 50%/PS 50%, cellulose acetate (CA), and polystyrene (PS).

bonate, even though they are fundamentally immiscible. This partial miscibility of the PC phases in PEI occurred for 80 wt % of PEI and was attributed by the authors to the van der Waals forces and is related to the fact that the Flory–Huggins interaction parameter, χ, reached a minimum value at 80 wt % poly(ether imide). So, for the CA/PS blend the van der Waals forces between CA and PS are consistent with the low value for the Flory–Huggins interaction parameter $\chi_{CA/PS} = 0.057$ calculated by Silva et al.[1]

WAXD

If our analysis in the FTIR study is correct, then it is possible that X-ray experiments would show some changes in the diffraction pattern of the blends. In this way, Figure 4 presents the X-ray diffractograms of cellulose acetate, polystyrene, and 50% w/w blend membranes.

We conclude that the cellulose acetate membrane is semicrystalline because it presents in 2θ a maximum at
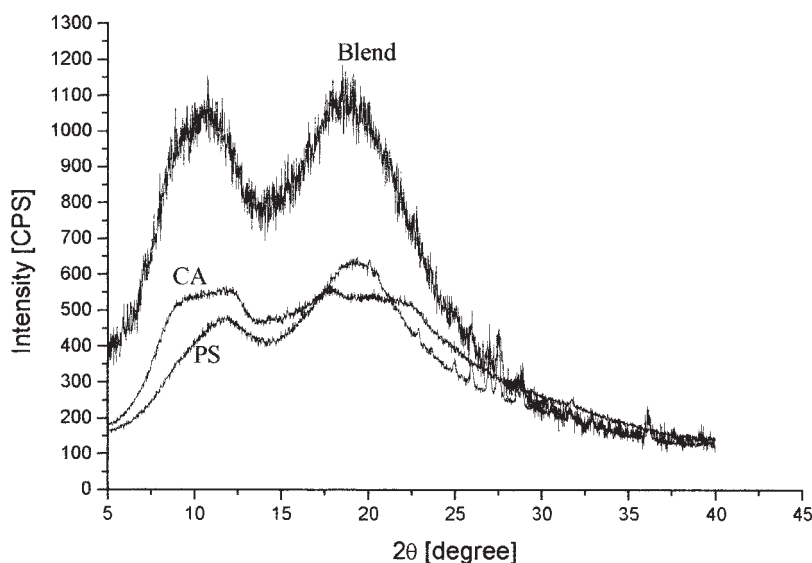
Figure 4 X-ray diffractograms of cellulose acetate, CA, polystyrene, PS, and CA 50%/50% PS blend.
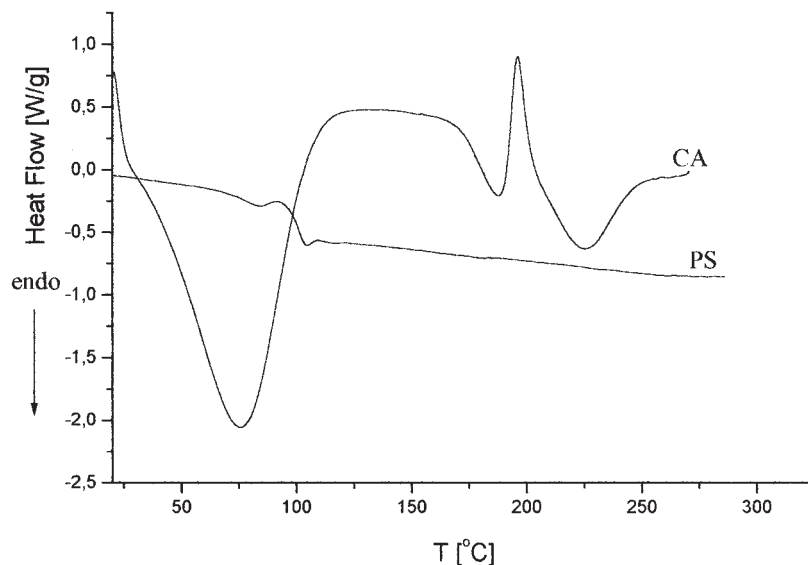
Figure 5   Typical DSC thermograms in the first scan for cellulose acetate, CA, and polystyrene, PS.

approximately 17.5° and two maxima approximately at 10° (low van der Waals maximum) and 20° (van der Waals maximum). The PS diffractograms present two maxima, the first at approximately 12° (low van der Waals maximum) and the other at 20° (van der Waals maximum). In the blend, the two maxima are located at approximately 10° (low van der Waals maximum) and at 20° (van der Waals maximum). The mixture of polystyrene with cellulose acetate resulted in a basically amorphous diffraction pattern. These results are in agreement with the comments on the FTIR analysis.

DSC

The data of FTIR and WAXD suggest that alterations would also be observed by the DSC technique. To this end, Figure 5 introduces the DSC thermograms, for the first scan, for cellulose acetate and polystyrene membranes.

We observed that the cellulose acetate possesses, in addition to the endotherm of water, at approximately 85°C[10,12] one crystallization exotherm, around 200°C, and one endotherm of fusion, localized around 220°C. Based on results of the WAXD, we can affirm that the cellulose acetate membranes are a material of very low crystallinity. On the other hand, PS presents only the T_g at approximately 95°C, being therefore a totally amorphous material.

Figure 6 presents the DSC thermograms, for the same materials of Figure 5, for the second scans. We notice the T_g of cellulose acetate appears around 130°C and the exotherm of crystallization at around 195°C. The T_g on the second scan is located at a value lower than that obtained in the first scan, 170°C, vide Figure 5. This could mean that the existing microcrystals

added rigidity to the material and when they disappeared in the second scans, the T_g appeared at a lesser value. Attention must also be given to the value of the crystallization enthalpy in the second scan, which was 5.26 J/g in comparison with 12.2 J/g in the first scan. The difference implies that there is still material capable of crystallizing during the DSC experiment.

Figure 7 shows the DSC thermograms of the 50% w/w blend in the first and second scans.

The main characteristics present in Figure 7 are as follows:

(i) The endotherm of water exists at 85°C; however, its value of enthalpy is diminished to 44 J/g, compared with 101 J/g of pure cellulose acetate in the first scans, vide Figure 5. This may be explained by the fact that polystyrene is a hydrophobic material and therefore caused a reduction in the water content of almost 50%.

(ii) The exotherm of crystallization at approximately 190°C has a lesser value (about 3.90 J/g) than that found for pure cellulose acetate (12.9 J/g, in Fig. 5). This result indicates that the presence of polystyrene reduces the capacity of crystallization of cellulose acetate. This comment is in agreement with the results obtained for FTIR and WAXD.

(iii) In comparison to pure cellulose acetate (vide Fig. 5), in the blend the endotherm of fusing at 220°C is barely present despite the material having an exotherm of crystallization at around 190°C. This indicates that there is a trend toward the amorphous state due to the presence of polystyrene.

(iv) We note in the second scan that the T_g values of the PS and cellulose acetate suffer almost no alterations in relation to those positions observed in Figure 5. Cellulose acetate still has the presence of the exo-
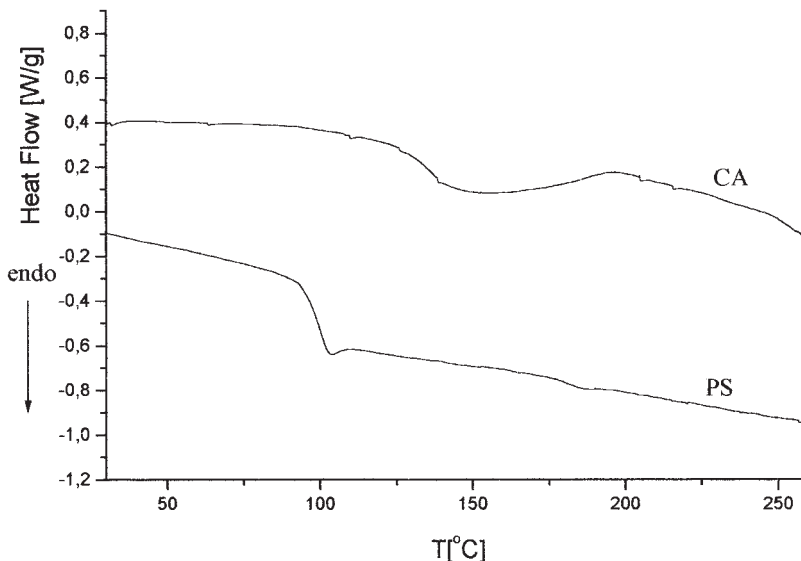
Figure 6 Typical DSC thermograms in the second scan for cellulose acetate, CA, and polystyrene, PS.

therm of crystallization at approximately 190°C, and the value of the enthalpy associated with this exotherm is 1.37 J/g, which confirms the trend of polystyrene in diminishing the capacity of crystallization of cellulose acetate.

Water flux

Table I presents the results of the normalized, by thickness, water flux for cellulose acetate blends with polystyrene beyond those of the pure materials. The results obtained with commercial membranes are also presented and are used for comparison.

The results show that cellulose acetate blended with polystyrene in the ratio of 50% w/w presents flux about three times less than the membrane produced with pure cellulose acetate. The reduction in flux may indicate that the flux occurs preferentially for the matrix of cellulose acetate. This reduction, taking into account experimental error, is in agreement with what we observe through the DSC results when the value of 12.9 J/g of the exotherm of crystallization of pure cellulose acetate (from sugar cane bagasse) is compared to that of the blend, 3.90 J/g, in the first scan. The results show also that blends of CA 90%/PS 10% present water vapor flux comparable with that of commercial membranes for nanofiltration, SG. This could be related to the way the blends had been produced, that is, solution casting with total evaporation of solvent.
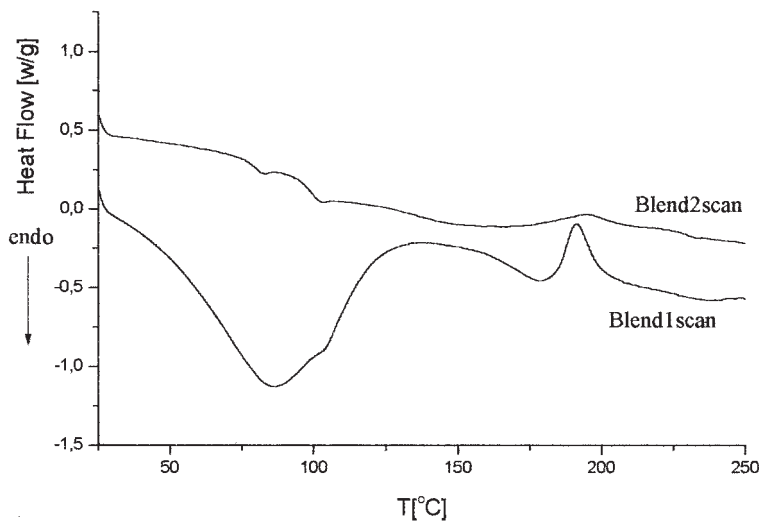

Figure 7 Typical DSC thermograms in the first, blend 1scan, and second, blend 2scan, scans for CA 50%/50% PS blend.

TABLE I
Water Flux through the Materials

Materials	L (μm)	$JL/10^{-4}$ (g s^{-1} cm^{-2} μm)
Blend CA 50%/PS 50%	50	0.25
Blend CA 90%/PS 10%	49	0.76
Blend CA 10%/PS 90%	51	0.058
Acetate bagasse	63	0.76
Polystyrene cup	56	0.030
CG	160	9.0
SG	168	2.0

CONCLUSIONS

The results show that blends CA 90%/PS 10% presented water vapor flux, measured by Payne's cup technique, comparable with that of commercial membranes for nanofiltration (SG). PS improves the workability of the membranes. This could be related to the compatibility microregions. These microregions could have cocontinuous morphology as observed by Silva et al.[1]

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