Blend Compatibility of Waste Materials—Cellulose Acetate (from Sugarcane Bagasse) with Polystyrene (from Plastic Cups): Diffusion of Water, FTIR, DSC, TGA, and SEM Study

Carla da Silva Meireles,[1] Guimes R. Filho,[1] Rosana M. N. de Assunção,[1] Mara Zeni,[2] Kátia Mello[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

ABSTRACT: In this article, the compatibility of blends produced from recycled materials—cellulose acetate (from sugarcane bagasse) and polystyrene (from plastic cups)—was studied using diffusion of water, Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analysis, and scanning electron microscopy. With these techniques, it was possible to confirm the existence of miscibility microregions in blends produced according to what has already been pointed out in a previous paper (Filho et al., J Appl Polym Sci 2005, 96, 516). In addition, all the results present a transition occurring in blends containing 30% polystyrene. This composition indicates the starting limit for a possible inversion between the matrix and the disperse phase in the system. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 909–914, 2007

Key words: compatibility; blends; cellulose acetate; polystyrene; recycling

INTRODUCTION

Brazil is one of the most important producers of sugar and alcohol from sugarcane. This industrial activity generates a huge amount of residue, the sugarcane bagasse. We have previously demonstrated that it is possible to aggregate value to this industrial residue through chemical recycling for producing membranes of regenerated cellulose and cellulose acetate (CA).[1–3]

From these possibilities of chemical recycling, the production of CA must be highlighted because this material is an important input, which may be used in a broad range of applications, such as reverse osmosis, hemodialysis, controlled release of drugs, etc.[4–7]

In a recent paper,[8] we studied the water flow through blends composed of recycled materials: CA from sugarcane bagasse and polystyrene (PS) from plastic cups. The water flow results were approximately the same as those obtained for commercial membranes, particularly the ones used in nanofiltration. Through differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR),

it was possible to identify miscibility regions in those blends, in which the van der Waals forces predominate.

The formation of a miscible polymer blend requires the presence of specific interactions between the two polymers. Miscibility concerns interactions at the molecular level. A miscible blend forms a homogeneous mixture and presents a single glass transition temperature, while an immiscible one results in a heterogeneous mixture and the T_gs are similar to the isolate materials T_g. Even a partially miscible blend usually presents a heterogeneous, dispersed phase structure, and presents intermediate values of T_g when compared with the isolate materials. The concept of compatibility is related to the degree of heterogeneity and dispersion between the blend components.[9,10] For example, a partial miscible blend could show compatibility.

In the present article, we studied the miscibility of CA/PS blends using diffusion of water, FTIR, DSC, and thermogravimetric analysis (TGA). The scanning electron microscopy (SEM) was used to investigate the compatibility of the blends. The obtained results corroborate those found previously.[8] Moreover, they also indicate a transition that could be associated to a possible inversion between the matrix and the disperse phase. This transition starts in blends containing 30% PS.

EXPERIMENTAL

Production of CA

CA was produced through homogeneous acetylation, using acetic anhydride as acetylating agent, acetic acid as solvent, and sulfuric acid as catalyst.[8] The degree of substitution of the produced material was 2.79; thus, the material is characterized as cellulose triacetate.

Viscosimetric molecular weight

The molecular weights of the materials were determined by measuring the intrinsic viscosity, which is directly related to its molar weight according to Mark–Houwink–Sakurada equation, in eq. (1), as follows:

$$[\eta] = K(M_v)^a \tag{1}$$

where K and a are the solvent constants. The solvent system used for CA was dicloromethane/ethanol (8/2, v/v) in which $K = 13.9 \times 10^{-3}$ and $a = 0.834$. For PS, toluene was used as solvent, in which $K = 3.8 \times 10^{-5}$ and $a = 0.630$. M_v was determined as 48,000 g mol^{-1} for CA and 96,398 g mol^{-1} for PS.[11,12]

Production of membranes

One gram of CA and 1 g of PS were dissolved in 25 mL of dichloromethane for producing a CA50%/PS50% blend. These amounts were changed to obtain CA90%/PS10%, CA70%/PS30%, and CA10%/PS90% blends. Membranes containing only CA and only PS were also produced. The mixture was stirred for 24 h and then cast onto a glass plate to a uniform wet thickness of 200 μm. The membranes were produced using 1–8 successive castings, to obtain membranes of distinct thicknesses. The time of solvent evaporation between each cast was 90 s. After the casts, the glass plate was immersed in distilled water to detach the membrane from the glass plate.

FTIR, DSC, and TGA experiments

The FTIR experiments were performed in a Perkin–Elmer, Spectrum 1000 equipment, with 4 cm^{-1} resolution. Thirty two scans were performed. The DSC experiments were performed in a DSC-50, Shimadzu, at a heating and cooling rate of 10°C min^{-1} and nitrogen flow of 50 cm^3 min^{-1}. The TGA was performed in a TGA-50, Shimadzu, the samples were heated from room temperature to 600°C at a rate of 10°C min^{-1} under nitrogen atmosphere.
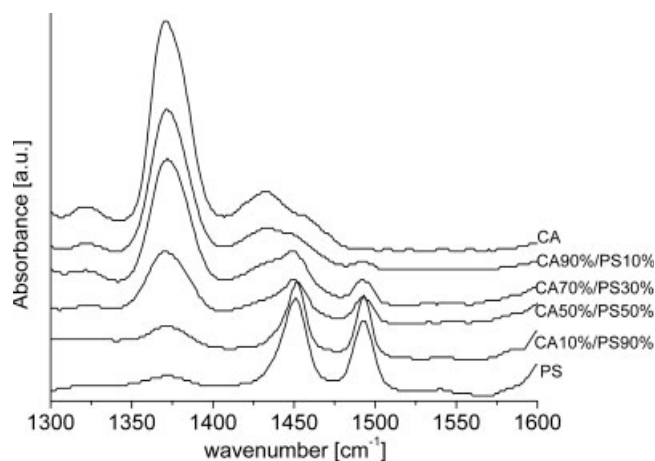
Figure 1 Typical infrared spectra for CA 90%/PS10%, CA70%/PS30%, CA50%/PS50%, CA10%/PS90% blends, cellulose acetate (CA), and polystyrene (PS).

Scanning electron microscopy

The samples were initially gold-coated in a Bal-Tec SCD-050, and the morphology of the surfaces was studied in a Jeol/Scaning Eletron Microscope, JSM 6060, operated at 10 kV.

Water sorption measurements

A piece of membrane was weighted and put in direct contact with water inside a glass tube. The system was immersed in a thermostated bath at 25°C. The membranes were periodically weighted until they reach their saturation condition.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy

Figure 1 presents the FTIR spectra of CA, PS, and blend films, in distinct compositions. All the films were 10-μm thick.

The results show that the band attributed to the bending vibration of the CH$_2$ group (1429 cm^{-1})[8] is almost inexistent for blends containing 30% or more PS. This result not only corroborates those previously reported by us[8] but also evidences the 30% PS composition as a limit for occurring an inversion between the matrix and the disperse phase. Besides, the observed changes in the cited region of the FTIR spectra confirm the existence of miscibility regions in the blends. In these regions, van der Waals forces would predominate.

DSC and TGA

Figure 2 presents the DSC first scan thermograms of 40-μm thick films of CA and blends. According to
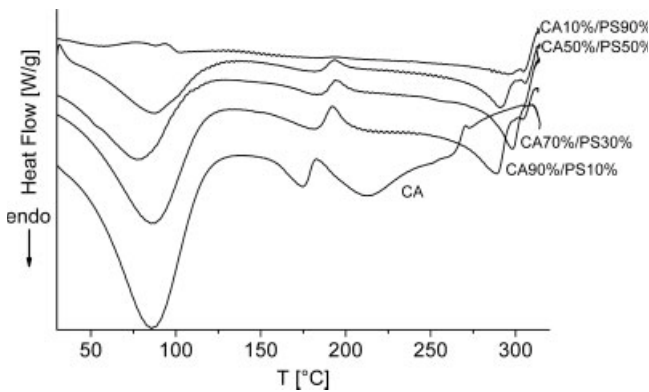
Figure 2 Typical DSC thermograms in the first scan for CA 90%/PS10%, CA70%/PS30%, CA50%/PS50%, CA10%/PS90% blends, and cellulose acetate (CA).

Figure 4 Enthalpy of fusion versus % PS.

previous DSC results,[8] we may observe in Figure 2 the phenomena related with morphological changes, which were presented in Figure 1.

A sharp increase of about 50°C in the temperature of fusion may be noticed when PS is added to CA. This phenomenon is attributed to some kind of plasticizer effect caused by the PS, which causes an increase in the mobility of the macromolecule chains, conducting to a more perfect crystalline pattern. According to Figure 3, this effect starts at the blend containing 10% PS and becomes approximately constant.

Figure 4 presents a plot of the real ΔH_m (melting enthalpy minus the enthalpy of crystallization) versus the percentage of PS in the blends. It is observed that the PS effect reaches a maximum at 30%. These results confirm those indicated by FTIR about the existence of miscibility microregions in the blends. Also, these results show a region of transition, which could not be observed in our previous paper.[8]

Figure 5 presents the DSC second scan thermograms of 40-μm thick films of CA, PS, and blends.
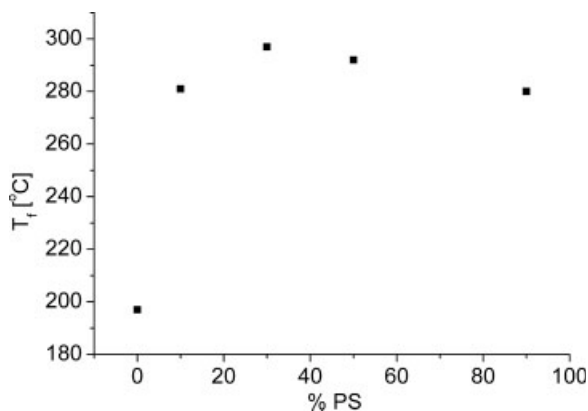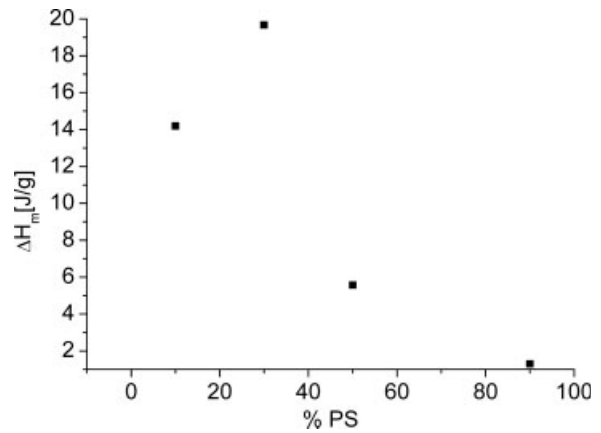
On DSC second scans, the endotherm of fusion and the exotherm of crystallization are shown again, indicating that the material was crystallized during the DSC experiment. However, since their enthalpies of fusion and crystallization present nearly the same values, the materials are amorphous. We can observe the two T_g of the materials. However, we call for attention to the sharp shift of CA T_g for high temperature value when PS is added, which shows the partial miscibility of the blends. Even though partially miscible blends present intermediate T_g values when compared with the isolate materials,[9,10] the shift on T_g of CA, in this case, for values higher than pure CA, indicates the existence of interaction between the polymers in a short extension. These interactions occur in molecular level and indicate the existence of miscibility regions.

Figure 6 presents the TGA curves of membranes CA, PS, and blends. For CA membrane, it is observed that a loss of mass in the range from 180 to 240°C could be assigned to acetoxyl groups condensation. Moreover, another loss of mass occurs in the range from 300 to 400°C due to rupture of the chains. PS
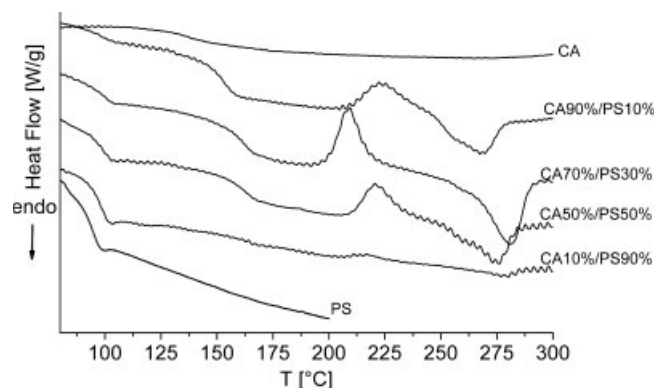

Figure 3 Temperature of fusion versus %PS.

Figure 5 Typical DSC thermograms in the second scan for CA, 90%/PS10%, CA70%/PS30%, CA50%/PS50%, CA10%/PS90% blends, and cellulose acetate (CA).
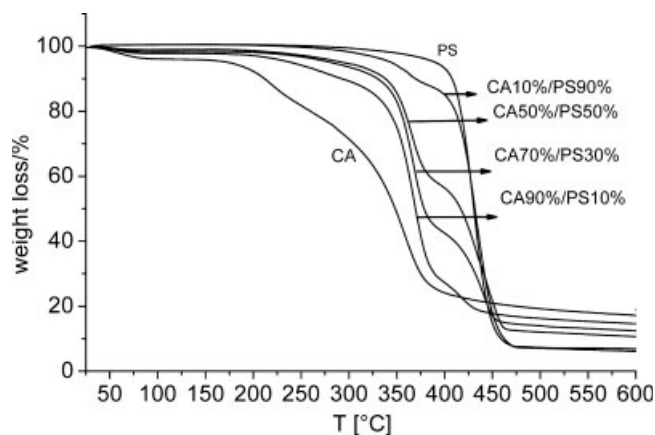
Figure 6 TGA curves of CA 90%/PS10%, CA70%/PS30%, CA50%/PS50%, CA10%/PS90% blends, cellulose acetate (CA) and polystyrene (PS).

TGA curve presents a weight loss in the range between 370 and 480°C, also due to rupture of chains.[13] For the blend TGA curves, we must highlight that in the region where the endothermic peaks are seen in the DSC first scan, we cannot observe any weight loss event. This confirms that the peaks are actually related to a phenomenon of fusion.

Scanning electron microscopy

Figure 7 presents the morphologies of CA and blend surfaces. The surfaces of pure CA and blends are visually similar, except for 70/30 blend. The change in the structural aspect of 70/30 blend in relation to the other films is reflected on the results found for other evaluated properties. For 90/10 blend, we observed a nearly continuous phase, which is also
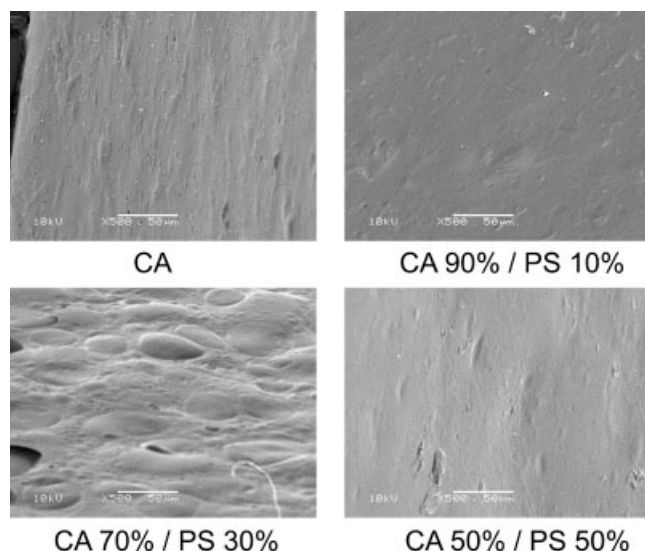

Figure 7 SEM surfaces morphologies of CA membranes and blends CA90%/PS10%, CA70%/PS30%, CA50%/PS50%. Size of the bar is 50 μm.

observed for 50/50 blend. A different behavior is observed for 70/30 blend, where we verified the presence of structures such as disperse bubbles over the matrix. As this phenomenon is only observed for this blend composition, it suggests a possible phase transition. This phase transition may be related to a restructuring of the polymeric blend that results in a separation of domains with different sizes.
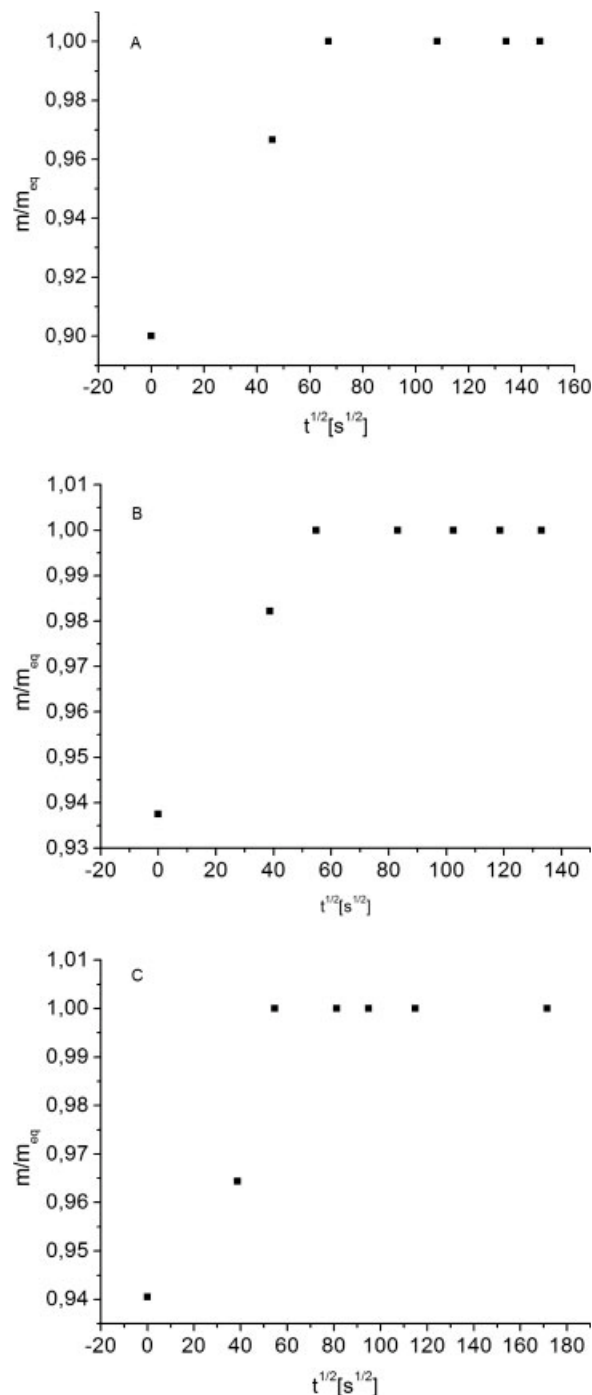

Figure 8 Typical curves of m/m_{eq} versus $t^{1/2}$ for CA50%/PS50% blends (A = $L - 10$ μm, B = $L - 40$ μm, C = $L - 80$ μm).

SEM results corroborate the discussion that there is a region of phase transition, which occurs at 30% PS.

Diffusion of water

Figure 8 presents typical plots of m/m_{eq} versus $t^{1/2}$ for various thicknesses. It shows a typical Fickian behavior, and the coefficient of diffusion was obtained from the linear portion of the curve according to eq. (2).

$$D = \left[(\Delta m_t/m_{eq})/\Delta t^{1/2} \right]^2 l^2 \pi/16 \qquad (2)$$

in which D is the average diffusion coefficient, t is the time, and l is the membrane thickness.[14]

The obtained diffusion coefficients were plotted in function of the PS composition, which is shown in Figure 9. According to this, there is a transition occurring at 30% PS and a change on the curve concavities starting at 40-μm films, being the concavity faced down until 40-μm films and faced up for films thicker than 40 μm.

The diffusion coefficient values range from about 10^{-12} cm^2 s^{-1} for the blend membranes (varying with the blend composition) to 10^{-11} cm^2 s^{-1} for the membranes of pure CA. This last value contradicts the value of around 10^{-8} cm^2 s^{-1} found in the literature[15] for CA. According to Perrin et al.,[15] the difference inn the values should be credited to the method used for producing the membranes. Other important factor that can contribute to decrease in D is the change in crystallinity that was observed in the DSC experiments. This change could be attributed to a kind of plasticizing effect already mentioned, because of the presence of PS. PS may provide mobility to CA in a way that it would have time to reorder and produce crystalline structures.

When using the thickness of the blend films as a parameter of study, we observed that the diffusion
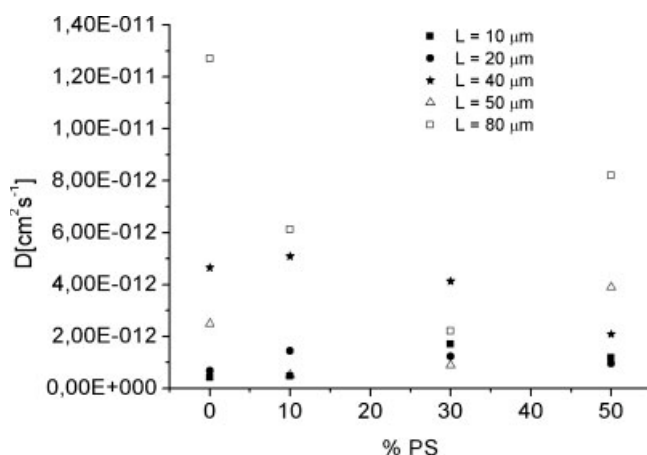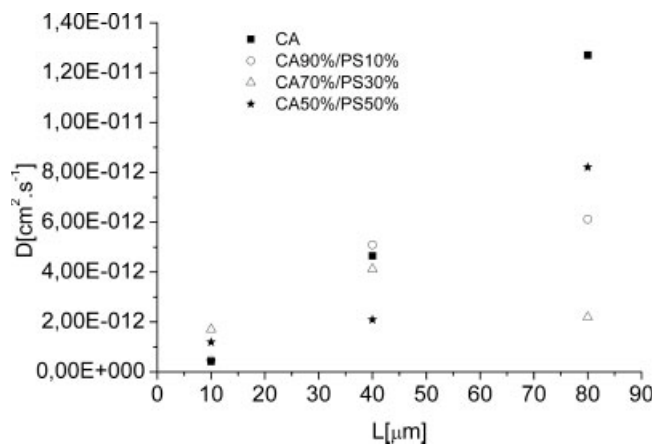
Figure 10 Diffusion coefficient versus thickness for CA 90%/PS10%, CA70%/PS30%, CA50%/PS50% blends and cellulose acetate (CA).

coefficient varies with the thickness, and again, we verified a transition occurring around the thickness of 40 μm, as shown in Figure 10.

The variation of the diffusion coefficient with the thickness, according to Perrin et al.,[15] may be interpreted, considering that, in a vitreous polymer as CA, the stress generated by the material preparation procedure induces a certain frozen organization and results in materials with different properties. The films may remain in some intermediate metastable states in sorption experiments, owing to the low segment mobility in glassy polymers. Besides CA, we also used another vitreous polymer, the PS, which contributes even more for reinforcing this hypothesis. Thus, our results suggest that the physical structure of the blend films is dependant on their thickness.

In spite, the detection of a transition through this technique, but using another variable, confirms the existence of microregions of miscibility on the produced blends.

CONCLUSIONS

From FTIR, DSC, TGA, SEM, and water diffusion results for CA/PS blends in several proportions, it was possible to confirm the existence of miscibility microregions, as already shown in a previous paper.[8] This partial miscibility is not enough for generating blend compatibility.

SEM results showed a phase transition occurring at 30% PS in the blends, which has also been pointed out through the other techniques.

Figure 9 Diffusion coefficient versus %PS.

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