

Hybrids of Cellulose Acetate and Sol–Gel Silica: Morphology, Thermomechanical Properties, Water Permeability, and Biodegradation Evaluation

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Received 15 November 2000; accepted 14 August 2001

ABSTRACT: Hybrids based on cellulose acetate (CA) and SiO₂ were prepared by hydrolysis of tetraethoxysilane (TEOS). More rigid films were obtained with an inorganic phase incorporation. The thermal stability of the hybrids was similar to pure CA. Composite membranes were prepared by casting of CA/TEOS mixtures onto a poly(vinylidene fluoride) support. The water permeation decreased with the incorporation of the inorganic phase. Hybrid membranes were able to retain solutes with a molar mass of ≈ 9000 g/mol ($\approx 98\%$ retention). Hybrids were submitted to biodegradation tests. The presence of the inorganic phase did not inhibit the growth of *Thricoderma harzianum* fungi. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2196–2205, 2002

Key words: sol–gel process; hybrids; cellulose acetate

INTRODUCTION

Cellulose acetate (CA) is a thermoplastic polymer produced from cellulose, which is a renewable feedstock. CA has applications in many areas such as supports for fibers, plastics, photographic films, and coatings for pharmaceuticals. In the area of membrane separation processes, CA is often employed to separate solutes dissolved in water because it is highly hydrophilic. Other characteristics must be considered such as the mechanical and chemical resistance, thermal and dimensional stability, pos-

sibility of sterilization, and costs.¹ Sometimes the CA utilization can become limited, mainly because of its poor mechanical resistance and organic solvent attack.² Another limitation that can prejudice its utilization is the facility of microorganisms growing in special fungi on its surface. Thus, different procedures have been described to modify CA properties, such as the blending of CA with other organic polymers and, more recently, the preparation of hybrid organic–inorganic materials.^{3,4}

The incorporation of inorganic materials into organic polymers to improve their thermal stability and mechanical properties is a very common practice. Large amounts of silica, alumina, and other kinds of mineral fillers are mixed with an organic polymeric matrix to produce more rigid materials; in many cases, this mixture is made for economic reasons. The relatively large size of the particle mineral fillers can also interfere with the

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Contract grant sponsor: FAPESP; contract grant number: 95/9506-4 and 95/3636-3.

Journal of Applied Polymer Science, Vol. 84, 2196–2205 (2002)
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opacity, conductivity, and permeability of different compounds into the final material.

The preparation of hybrid organic–inorganic materials using the sol–gel process has been investigated. Using the sol–gel process it is possible to grow an inorganic phase into an organic polymeric matrix with a very fine dispersion of the inorganic component, sometimes reaching molecular levels. The polymerization of the inorganic phase occurs by hydrolysis and polycondensation of metal alkoxides in the sol state.

The incorporation of metal oxides into CA was described with the aim of producing chemically and mechanically resistant hybrid films with a high degree of dispersion of the metal oxide. Composite membranes of Nb₂O₅ and CA were prepared from NbCl₅. The thermal stability of these membranes is slightly decreased in relation to the pure membrane with the incorporation of the metal oxide into the matrix. Scanning electron microscopy coupled with X-ray energy dispersive spectrometry (EDS) showed that the metal oxide particles were homogeneously dispersed into the matrix. It was also verified that dispersed oxide possesses a mainly Lewis acid character.³ These membranes were used to adsorb hematoporphyrin IX, which is strongly adhered on the Nb₂O₅ surface by the reaction of the porphyrin —CO₂H groups with Nb₂O₅ and forms the —COO—Nb chemical bond. In these cases the oxygen reduction was studied and showed that the system is potentially useful for developing a new oxygen sensor.⁴

Zirconium oxide was also incorporated into CA. In these cases the composite membranes were prepared from the hydrolysis of zirconium tetraisopropoxide. Phosphate retentions were 75 and 90% for the composite membranes in the permeation experiments with the advantage of low operational pressure being required to obtain high phosphate retention.⁵

Tetraethoxysilane (tetraethylorthosilicate, TEOS) was used as a precursor of the inorganic phase for preparing CA/TEOS hybrids. In these cases, CA was first functionalized to produce a CA that was chemically modified at two different levels of functional groups. The two grafted polymers had one grafted substituent per 10 CA repeat units and one grafted substituent per 27 CA repeat units. After the reaction with TEOS, crosslinked hybrid films were formed. All hybrid films showed phase separation on a molecular level with the inorganic TEOS domains surrounded by a CA matrix.²

Table I Volume of TEOS (V) Used to Prepare CA/TEOS Hybrid Films

CA/TEOS	V (mL)
100/0	0
80/20	0.40
60/40	1.08
40/60	2.42
20/80	6.45

The mass of the 5% (m/m) THF/CA solution was kept equal to 30 g.

The aim of the present work was to prepare and characterize CA/TEOS hybrids that could be useful as a new material because the sol–gel process allows the obtaining of hybrids with a large diversity of properties (e.g., permeability and selectivity properties) that are different from the pure CA. Also, we believe that the presence of the inorganic phase could cause an inhibition of fungus growth. The biofouling problem could also be minimized in membranes. On the other hand, if fungi growth is not inhibited, this new hybrid material with unique properties is also very interesting in regard to waste prevention and minimization.

EXPERIMENTAL

Materials

The CA (number-average molecular weight = ca. 30,000 g/mol, 39.8 wt % acetyl content, Aldrich) and TEOS (Aldrich) were used without previous purification. Tetrahydrofuran (THF, Merck) was distilled using sodium as a secant agent.

Hybrid Film Preparation

According to Table I, different volumes of TEOS were carefully added to a 5 wt % THF/CA solution under stirring at 50°C. A 0.15 mol/L HCl aqueous solution was added to keep the 2:1 molar water/TEOS stoichiometric proportion. The solution (ca. 30 g) was stirred for another 8 h at 50°C and transferred to a closed Petri dish with a 10-cm diameter. The reaction was allowed to continue for 16 h. The dish was opened, the solvent was evaporated at 50°C, and the films were dried under vacuum for 1 week.

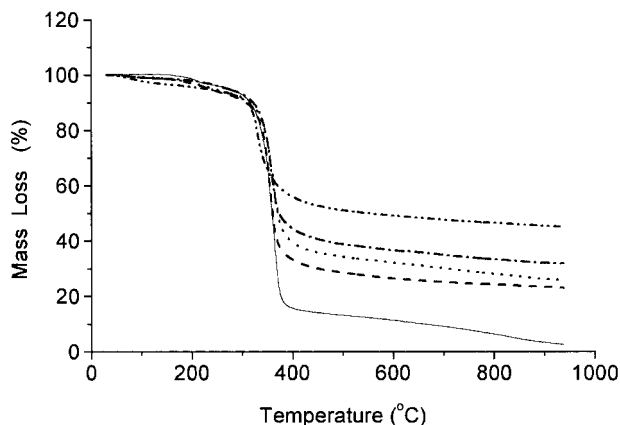


Figure 1 Thermogravimetric curves of (—) pure CA and CA/TEOS hybrids with compositions of (---) 80/20, (···) 60/40, (-·-) 40/60, and (-··-) 20/80.

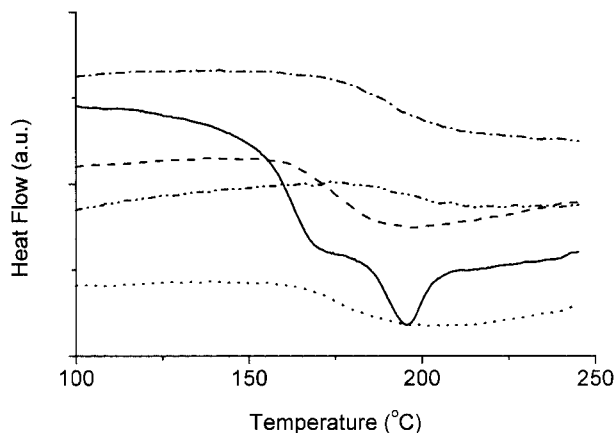


Figure 2 Differential scanning calorimetry of (—) pure CA and CA/TEOS hybrids with compositions of (---) 80/20, (···) 60/40, (-·-) 40/60, and (-··-) 20/80.

Composite Membrane Preparation

The initial preparation was similar to that described above. After the stirring period (8 h at 50°C), the solutions containing different CA/TEOS ratios were scattered on a poly(vinylidene fluoride) (PVDF) porous support. The supports were kept under air to evaporate the excess of the solvent. They were further dried at 80°C for 2 h.

Electron Microscopy and EDS Analysis

Samples were fractured in liquid nitrogen and sputter coated with gold. Images were obtained in a Jeol JSM-6340F field emission scanning electron microscope at 3.0-kV accelerating voltage, which allows a better morphological resolution. Samples were also analyzed in a Jeol T-300 scanning electron microscope operating at 15 kV. This microscope was equipped with an energy disper-

sive spectrometer, which allowed the chemical analysis of different regions in the sample.

Thermal and Mechanical Analysis

Thermogravimetric analysis was performed in a Du Pont 2000 thermal analyzer in the range from 25 to 950°C at 10°C/min under argon.

Differential scanning calorimetry was performed in a TA Instruments 2910 MDSC thermal analyzer. About 10 mg of sample were heated at 10°C/min under nitrogen from 25 to 250°C.

Dynamic mechanical analysis was performed with a TA Instruments DMA 983 thermal analyzer from 25 to 280°C at 5°C/min using a frequency of 1 Hz and an amplitude of 0.20 mm.

Biodegradation Tests

Thricoderma harzianum fungus was used in the biodegradation tests because it is a typical microorganism found in soils and it easily biodegrades materials derived from cellulose. CA/TEOS hybrid films of different compositions and dimensions of approximately 1 × 1 cm were immersed in a 93 wt % ethanol (Merck) aqueous solution for 15 min. Samples were washed with distilled water and inoculated in Petri dishes containing solid agar and malt extract. The culture medium pH was 7. All the materials and culture medium that were used were sterilized in an autoclave at 200°C. The *T. harzianum* fungus was inoculated onto the culture medium. The Petri dishes were incubated at 28°C for 30 days. Petri dishes containing CA homopolymer films and the culture medium without fungus inoculation were used as

Table II Percentage of Residue at 900°C (R) Obtained from Thermogravimetry, Glass-Transition Temperature (T_g), and Glass-Transition Width (ΔL) Obtained by Differential-Scanning-Calorimetry for Pure CA and CA/TEOS Hybrids with Different Compositions

CA/TEOS	R (%)	T_g (°C)	ΔL (°C)
100/0	3.3	164	31
80/20	22.5	179	38
60/40	26.7	183	41
40/60	30.8	196	38
20/80	43.3	207	38

controls. After the incubation period the samples were washed with the ethanol solution and a 1 wt % NaClO_2 aqueous solution, dried, and observed in a CBA-K optical microscope.

Permeation Tests

The permeation tests were performed using the CA/TEOS composite membranes as a filter layer. The membrane permeability was considered equal to the permeate flux across the membrane by the unity of area, pressure, and time. The permeability was calculated using eq. (1)⁶:

$$p = J/(A \times t \times P) \quad (1)$$

where p is the permeability, t is the time, J is the effluent flux, P is the pressure, and A is the membrane surface area.

In order to determine the permeability, a 65-mm diameter and 150-mm height cell was used. The permeability cell was filled with distilled water. The pressure used in all determinations was equal to 5 kgf/cm^2 , and the stirring rate was 600 rpm.

The membrane cutoff was determined using an aqueous solution containing 0.1 wt % of each poly(ethylene glycol) (PEG) at 600, 1,500, 4,000, 8,000, 10,000, and 40,000 g/mol. The permeability cell was filled with 300 mL of the solution containing PEG. After the flux stabilization, which occurred after the permeation of about 30 mL of the solution, samples of both the permeate and retained phases were analyzed by gel permeation chromatography in a Knauer HPLC Pump 64 analyzer using an UltrahydrogelTM 250 poly(methyl methacrylate) column with $7.8 \times 300 \text{ mm}$ dimensions. The retention of the different PEGs was calculated using eq. (2):

$$R = \{1 - (C_p/C_r)\} \times 100\% \quad (2)$$

where R is the retention, C_p is the concentration of the permeate solution, and C_r is the concentration of the retained solution.

In these cases, the C_p and C_r were obtained by considering the intensities of the peaks on the chromatograms.

RESULTS AND DISCUSSION

Thermal and Mechanical Properties

Figure 1 shows thermogravimetric curves for pure CA and CA/TEOS hybrid films. Independent

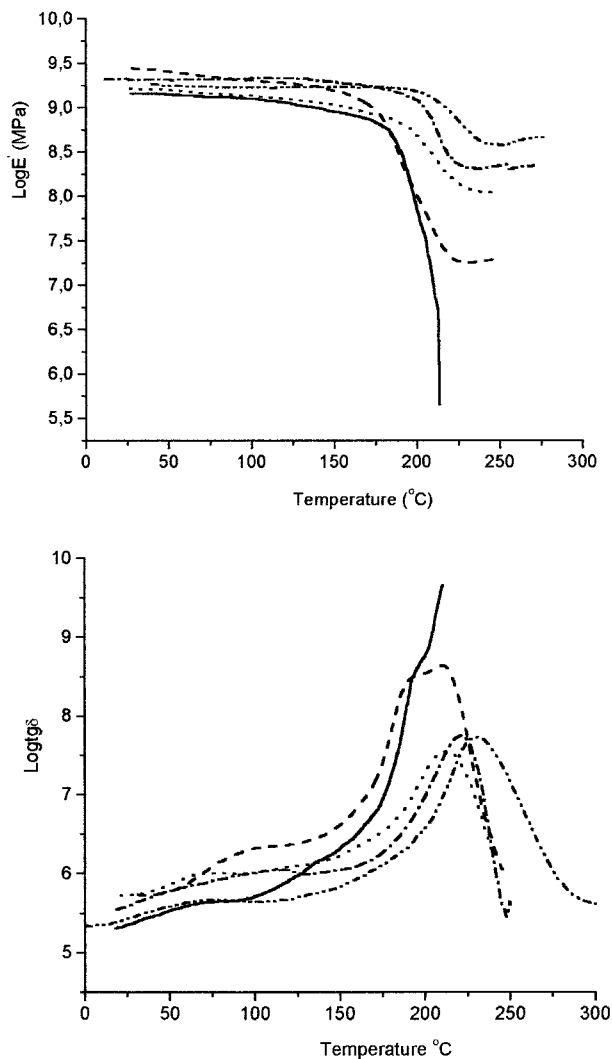


Figure 3 Dynamic mechanical analysis for (—) pure CA and CA/TEOS hybrids with compositions of (---) 80/20, (···) 60/40, (-·-·) 40/60, and (-·-·-) 20/80.

of the composition, the thermal stability of the hybrids was similar to that observed for pure CA. In all cases, one main stage of mass loss was observed, which started near 300°C . This mass loss process is assigned to the cellulose polymer degradation. In the case of CA, the first reaction is loss of acetyl groups, followed by the acetic acid catalyzed decomposition of cellulose. It is important to keep in mind that the source of the CA can impact its decomposition because commercial CA can have sulfonic acid residues from the original esterification reaction and the amount of these residues can also have a significant impact on the thermal decomposition pathways.

Furthermore, an increase of the residue amount was verified at 900°C when the inorganic

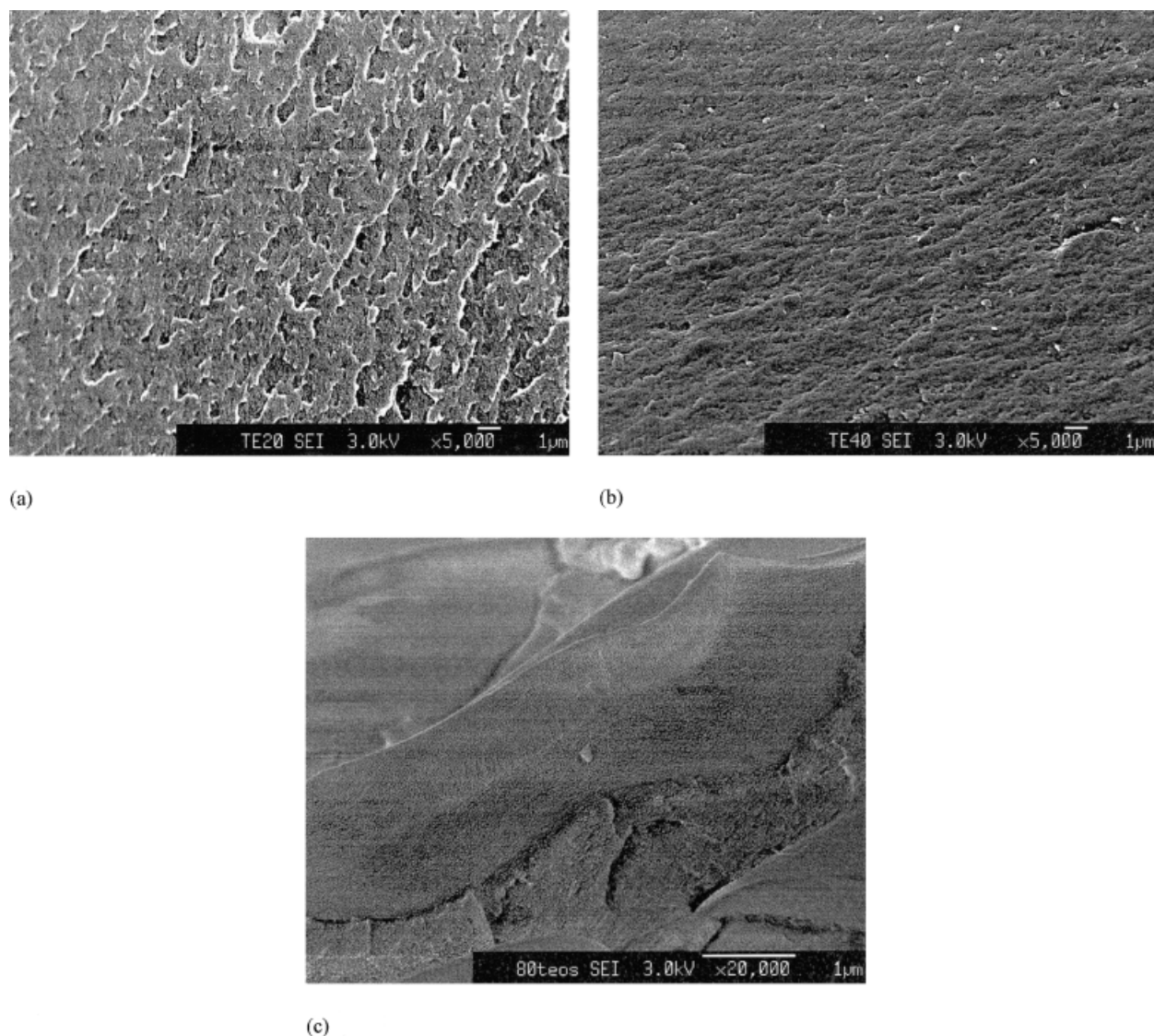


Figure 4 Field emission scanning electron microscopy of the surface fracture of CA/TEOS hybrids with compositions of (a) 80/20, (b) 60/40, and (c) 20/80.

phase content increased, as expected. Table II shows the residue percentage at 900°C as a function of the hybrid composition.

Figure 2 shows differential scanning calorimetry curves for CA/TEOS with different compositions. For pure CA one can observe a transition at 164°C, which is assigned to the glass-transition temperature (T_g) of the polymer, and an endothermic peak at 198°C, which is due to the fusion of the crystalline fraction of the CA. These values are lower than those reported in the literature,^{7,8} probably because in the present case CA films were prepared by casting of the polymer solution.

For hybrid films the fusion process was not observed. In these cases the presence of the inorganic phase can inhibit the polymer crystallization as was verified in a previous work for poly(ethylene oxide-*b*-amide-6)/TEOS systems.⁹ With respect to the T_g , as shown in Table II, there is a T_g increase when the TEOS content is increased, which is evidence that the inorganic phase is acting as a reinforcement filler. In the glass-transition width (ΔL), which is defined as the distance between the beginning and the end of the transition process, a slight increase was observed with the TEOS addition into the polymer. The ΔL is

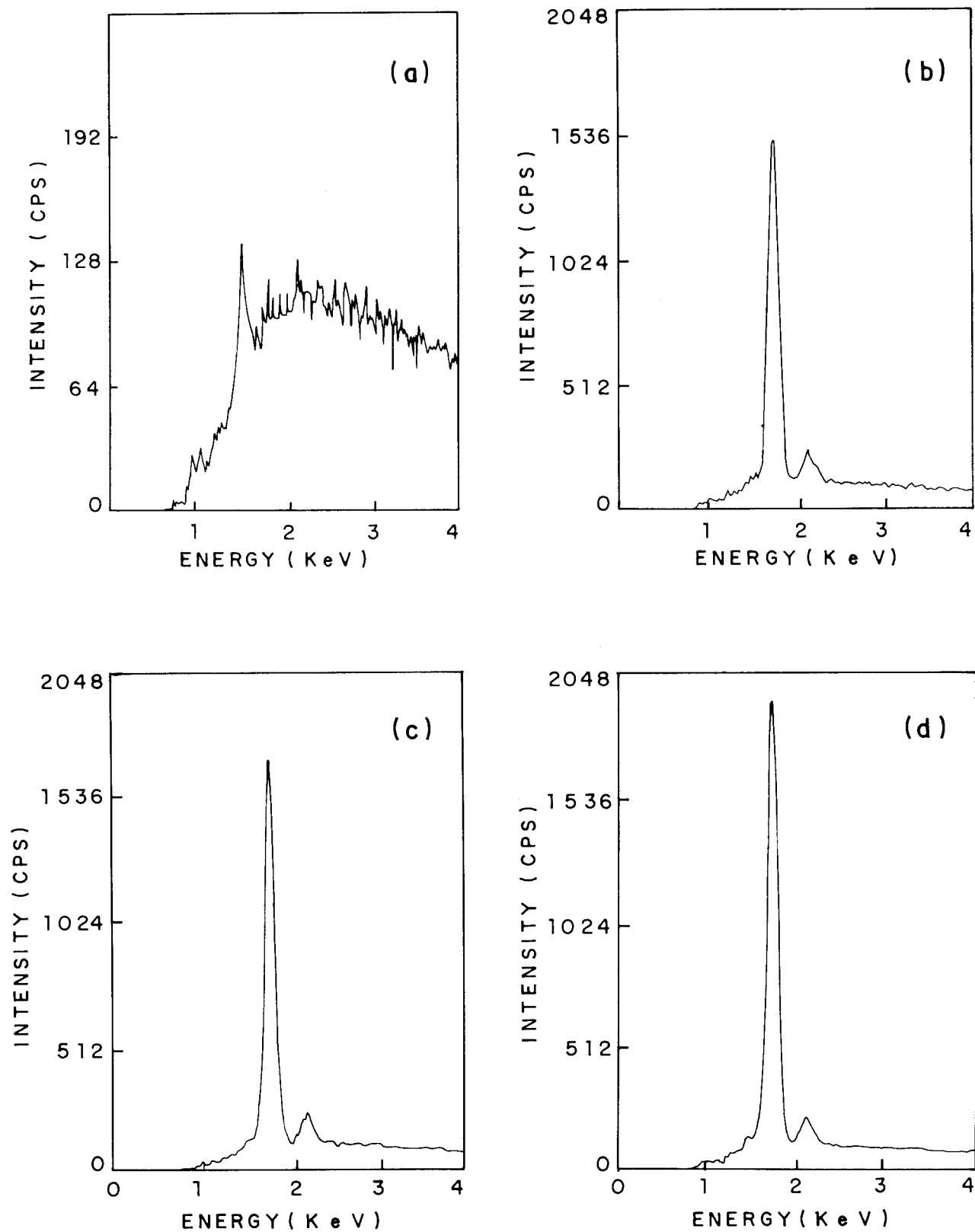


Figure 5 EDS analysis of CA/TEOS hybrid films with compositions of (a) 100/0, (b) 80/20, (c) 60/40, and (d) 40/60.

associated with the presence of microheterogeneities in the system, which are caused by differences in the interaction density between the components or the presence of an infinite number of environments with different compositions. The ΔL also reflects the number of relaxations during the glass transition. The relaxation in different microenvironments takes place in different amounts of time, causing the broadening of the glass transition. There are two possible types of phase separation that can occur in these systems. The first type is solid–liquid phase separation of the polymer that can occur during the film formation. This type of phase separation was extensively studied for a CA/acetone/water system.¹⁰ Because there is water added to the hybrid system and water generated during the hydrolysis and condensation reactions of TEOS, it is logical to consider that solid–liquid phase separation of the CA film can take place during the casting and drying steps. This phase separation is attributable to the relatively rapid evaporation of the good solvent that results in an increase in the relative concentration of the nonsolvent. Eventually the concentration of the nonsolvent rises to the point where phase separation can occur. However, all prepared films were completely transparent, so the possibility of the occurrence of this type of phase separation was discarded. The second type of phase separation would be that of the CA and TEOS condensation product. There is a great deal of work on these types of polymer/TEOS and polymer/titanium alkoxides,¹¹ which describes the formation of a second phase originating from the inorganic reagent. Even when the film is clear, which is consistent with a very small inorganic phase that does not scatter light, the existence of a second phase is not rejected. Thus, considering these aspects, the ΔL increase can be evidence of microheterogeneity in the hybrid films.

Figure 3 shows the dynamic mechanical properties for pure CA and CA/TEOS hybrids. These results are similar to those verified in particulate filled polymers.¹² Rigid fillers have a larger effect in raising the modulus (E') above the T_g than below it. The main reason for this is the larger modulus ratio ($E_{\text{filler}}/E_{\text{polymer}}$) of the components when the polymer is in the rubbery state compared to the rigid glassy state. Less important factors contributing to this effect are the larger Poisson's ratio above the T_g and the presence of induced thermal stresses below the T_g .

Fillers also shift the break in the modulus curves to higher temperatures. At high filler concentrations the slope of the modulus curves decreases in the transition region.

The most pronounced effect of the fillers is the broadening of the transition region by high concentrations of fillers. Fillers often decrease the damping as expressed by G''/G' , in which case the damping can be generally approximated by eq. (3)¹²:

$$G''/G' = (G''_1/G'_1)\phi_1 + (G''_2/G'_2)\phi_2 \quad (3)$$

where G'' is the imaginary part of the modulus, G' is the real part of the modulus, and ϕ is the molar fraction. The indices 1 and 2 represent the number of components in the system, for instance, one organic polymeric matrix (component 1) and one mineral filler (component 2) such as silica. The symbols used without indices refer to the mixed system that contains the two components.

The damping of most rigid fillers is very low compared to that of the polymer, so (G''_2/G'_2) is nearly zero and can be neglected. However, there are numerous cases where fillers increase the damping, probably by the introduction of new damping mechanisms that are not present in the pure polymer. These new damping mechanisms include particle–particle friction where particles touch one another as in weak agglomerates, particle–polymer friction where there is essentially no adhesion at the interface, and excess damping in the polymer near the interface because of induced thermal stresses or changes in the polymer conformation or morphology. In the CA/TEOS hybrid films a damping decrease was observed when the TEOS content was higher than 20 wt %; for TEOS content in the range of 40–80 wt %, however, the damping practically did not change.

The presence of fillers can or cannot shift the T_g . When a shift occurs, the damping peak and T_g are observed at higher temperatures. The shift in the T_g should be proportional to the surface area of the filler. Thus, the effect should increase with the concentration and as the size of the particles decrease because the effect should be due to changes in the polymer that becomes adsorbed onto the filler. Adsorption of polymer onto a surface restricts molecular motion, changes the density of packing of polymer chains, and modifies the conformation and orientation of chain segments in the neighborhood of the surface. Although rigid fillers may either increase or de-

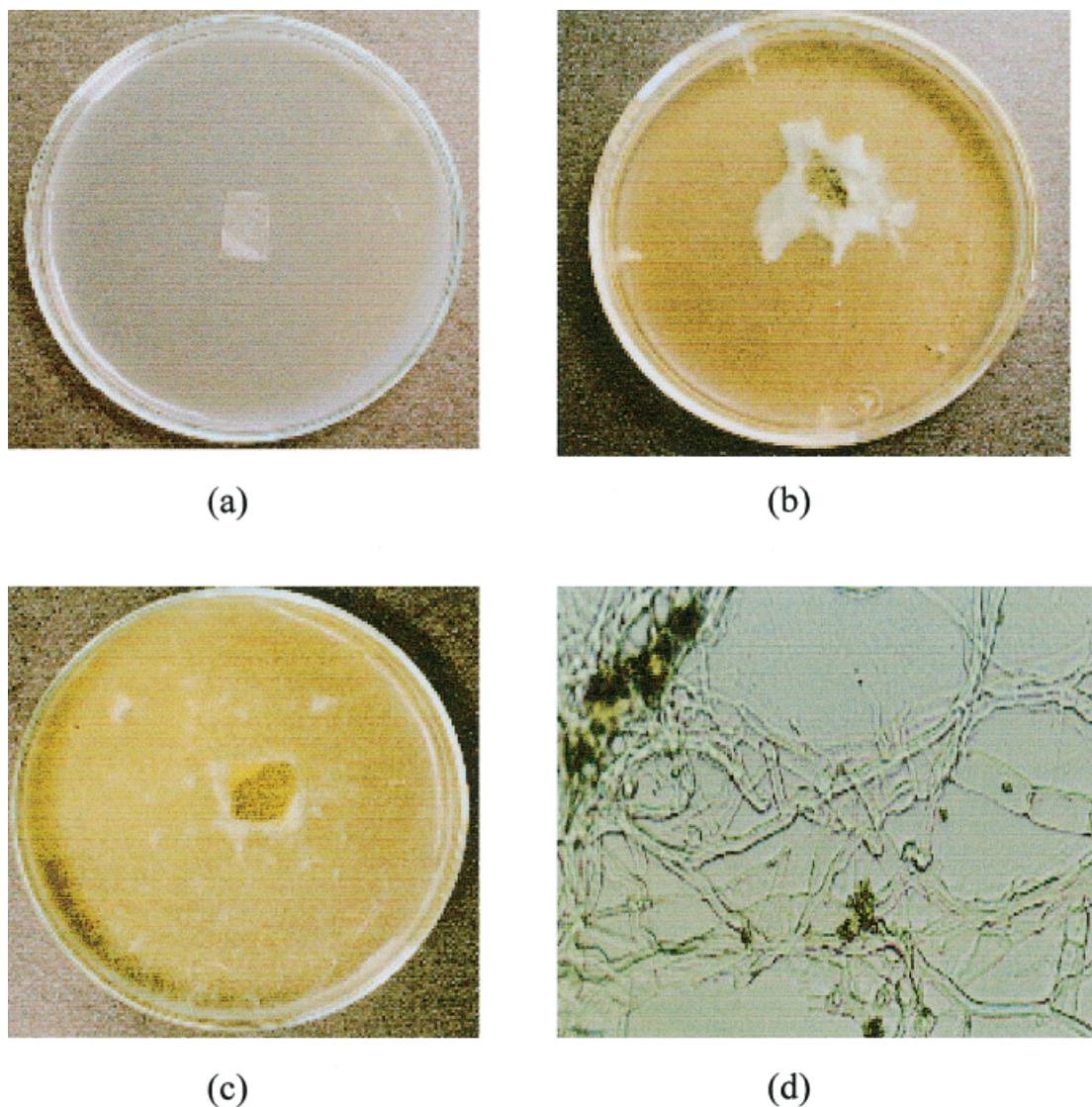


Figure 6 (a,b) Pure CA and (c) 40/60 CA/TEOS hybrid films in the culture medium after 30 days of incubation: (a) the Petri dish control in which CA homopolymer film was incubated without the fungus inoculation, (b,c) Petri dishes in which the fungus inoculation was carried out, and (d) light microscopy of the cleaned surface of the 40/60 CA/TEOS hybrid after 30 days of inoculation and incubation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

crease the damping as measured by G''/G' , such fillers nearly always increase the G'' . This is because the increase in the G' more than compensates for any decrease in the G''/G' in the equation $G'' = (G''/G')G'$.¹² For CA/TEOS hybrids the T_g increased when the TEOS content increased. These results are in accordance with those obtained by differential scanning calorimetry.

Morphology and EDS Analysis

Figure 4 shows field emission scanning electron micrographs of the fracture surface of CA/TEOS

hybrid films with different compositions. The morphology of pure CA films obtained by casting of the polymer solution in THF was very similar to that shown in Figure 4(a) for the 80/20 CA/TEOS hybrid. The surface fracture of the films became more dense and smooth as the TEOS content increased, and phase separation was not clear. With EDS coupled with scanning electron microscopy, the presence of Si in the hybrid films was confirmed (Fig. 5). An increase of the Si peak intensity when the TEOS content increased was verified. Comparing the Si peak intensities of the

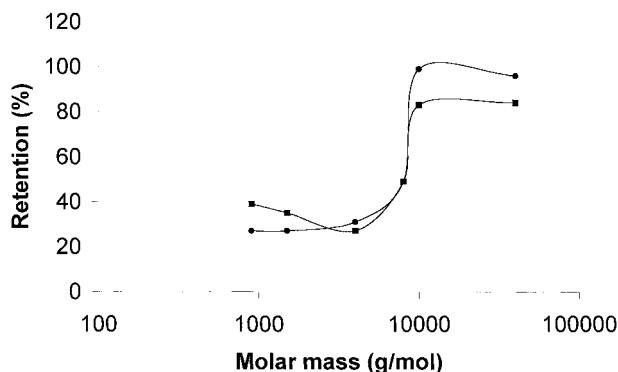


Figure 7 The retention as a function of the PEG molar mass: (■) pure CA and (●) 60/40 CA/TEOS hybrid composite membranes.

80/20 CA/TEOS composition samples with the 60/40 ones, and the 60/40 with the 40/60, the increase of the peak intensity was 10 and 12%, respectively. Because the peak intensity increase remained practically constant, we considered the Si distribution to be homogeneous in these cellulose matrices. The analysis was performed in different regions of the fracture surfaces, and no preferential accumulation of Si was detected.

Biodegradation Properties

Figure 6 shows photographs of pure CA and CA/TEOS hybrid films submitted to the biodegradation tests. The control refers to CA films that were incubated but not inoculated with the *T. harzianum* fungus. Independent of the hybrid composition, after 30 days of inoculation and incubation, a large amount of spores was observed on the surface of the samples. Samples also became yellow, indicating that a degradation process promoted by the fungus was started. Similar results were observed for CA homopolymer films. It is interesting to note that the CA control after the same period of incubation did not show color alteration or fungus growth.

As described in the Experimental section, these samples were cleaned and analyzed by optical microscopy. The presence of hyphae and spores was observed for samples that were inoculated with the *T. harzianum* fungus, even after the cleaning [Fig. 6(d)]. Hyphae have a filament shape and they constitute the fungus structure and spores are the fungus reproductive part. Their presence on the material surface indicates that the fungus is using the polymeric matrix as a carbon source for its growth. Nonbiodegradable materials do not show this kind of behavior.

Permeation and Retention Properties

Preliminary permeation tests were carried out using hybrid composite membranes. Tests were performed with three different specimens of each sample. Reproductive results were obtained only for composite membranes in which the filter layer was constituted of CA homopolymer or 60/40 CA/TEOS hybrid. For other compositions the deviation was as high as the permeability values, probably because of inefficient coating of the PVDF support surface. The presence of defects in the CA membrane surface strongly contributes to the decrease in the reproducibility of the permeation results.

The water permeability was 1.82 ± 0.06 and 0.3 ± 0.1 L/h/m²/bar for the CA homopolymer and 60/40 CA/TEOS hybrid composite membranes, respectively. As described previously, the incorporation of an inorganic phase into the polymeric matrix originated more rigid materials with a more dense morphology. Thus, the water permeability decrease is in accordance with the fact that hybrid composite membranes have a more rigid and dense filter layer. In addition, the alkoxy groups may not be completely eliminated in the resulting materials. Therefore, the organic groups attached to Si atoms can also affect the permeation property of water molecules because of the hydrophobic character of the organic group. These characteristics also affected the retention of solutes with different molar masses. Figure 7 shows the retention as a function of the PEG molar mass. For both CA homopolymer and 60/40 CA/TEOS composite membranes, the retention step occurred near 10,000 g/mol. The membrane cutoff is defined as the minimum value of the molar mass in which the membrane retention is equal to or higher than 90%. The cutoff of the PVDF support is higher than 100,000 g/mol.¹³ According to Figure 7, the cutoff for the 60/40 CA/TEOS membrane was about 9000 g/mol. For the CA homopolymer membrane the retention became constant before reaching the 90% value, so the exact determination of the membrane cutoff was not possible.

CONCLUSIONS

The preparation of hybrid organic–inorganic films using the sol–gel process was described. CA was used as an organic matrix and silicon oxide was prepared by hydrolysis and polycondensation of

TEOS. As expected, more rigid films were obtained with the inorganic phase content increase. The thermal stability of the hybrid films was similar to that shown by the pure CA. Composite membranes were prepared by casting of CA/TEOS mixtures onto a PVDF porous support. The water permeation flux was decreased with the incorporation of the inorganic phase into the CA matrix. The cutoff for 60/40 CA/TEOS composite membranes was nearly 9000 g/mol. Hybrid films were also submitted to biodegradation tests in the presence of the *T. harzianum* fungus. The presence of the inorganic phase did not substantially inhibit the fungus growth.

The authors thank FAPESP for financial support.

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