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THERMAL CHARACTERIZATION OF BACTERIAL CELLULOSE–PHOSPHATE COMPOSITE MEMBRANES

H. S. Barud[1], *C. A. Ribeiro*[1*], *Marisa S. Crespi*[1], *M. A. U. Martines*[1], *J. Dexpert-Ghys*[2], *R. F. C. Marques*[2], *Y. Messaddeq*[1] *and S. J. L. Ribeiro*[1]

[1]Instituto de Quimica, UNESP, CP 355-Araraquara 14801-970, Brazil
[2]Centre d'Elaboration de Matériaux et d'Etudes Structurales, UPR N°8011, Université Toulouse III, B.P. 94347
29 rue Jeanne Marvig, 31055 Toulouse Cedex, France

Cellulose–phosphate composite membranes have been prepared from bacterial cellulose membranes (BC) and sodium polyphosphate solution. The structure and thermal behavior of the new composites were evaluated by X-ray diffraction (XRD), ^{31}P-nuclear magnetic resonance (NMR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetry (TG) and thermomechanical analysis (TMA). From XRD analyses the Iα and Iβ cellulose crystalline phases were identified together with crystalline sodium phosphate that covers the cellulose microfibrils as revealed by SEM. ^{31}P NMR spectra show peaks assigned to Q^0 and Q^1 phosphate structures to be compared to the Q^2 units that characterize the precursor polyphosphate. Glass transition temperature, T_g, obtained from TMA curves and thermal stability obtained from TG and DSC measurements, were observed to be dependent on the phosphate content.

Keywords: *bacterial cellulose, cellulose–phosphate composites, sodium polyphosphate*

Introduction

Cellulose, a linear β-1,4-linked glucose polymer is the most abundant natural biopolymer on the earth synthesized by plants and also some species of bacteria. Cellulose produced by *Acetobacter xylinum* is markedly different from cellulose obtained from trees and cotton. From the culture medium a pure cellulose network free of lignin and hemicellulose is obtained as a highly hydrated pellicle made up of a random assembly of ribbon shaped fibers less than 100 nm wide. These fibers themselves are composed of a bundle of much finer microfibrils of nanometric size [1, 2]. The unique properties provided by the nanometric structure have lead to a number of commercial products including tires, headphone membranes, special papers, and textiles [3], medical applications including temporary skin substitution [4]. Bacterial cellulose is also used as a source of dietary fiber (nata-de-coco) [5], as binding or thickening agents.

Interesting composite materials may also be obtained from cellulose. Princi *et al*. [6] studied the water uptake of cellulose-acrylic polymer composites. They concluded that the water uptake depends on the crystalline state of cellulose and the amount of grafted acrylic counterpart. Cellulose phosphate membranes were also studied concerning their biomedical applications. Phosphorylated cellulose seems to be interesting material for bone regeneration and osteointegration. In general, phosphorylation reactions are employed in order to obtain cellulose phosphates [7–9].

In this work, new composite membranes were prepared from bacterial cellulose membranes and sodium polyphosphate solution. Their characterization have been done using thermal analysis (DSC, TMA and TG), scanning electron microscopy, X-ray diffraction and ^{31}P NMR.

Experimental

8×6 cm bacterial cellulose membranes, 250–500 μm thick were soaked in aqueous sodium polyphosphate solutions at different molar ratios 1, 20, 40 and 80 mass/mass% for 48 h at ambient temperature. The composites obtained in this way were dried at 50°C for 12 h.

TG curves of the dried samples were recorded using TA SDT 2960 from TA Instruments Co. Samples were heated in open α-alumina pans from 40 to 500°C under nitrogen atmosphere (flow rate: 70 mL min^{-1}) at heating rate of 10°C min^{-1}. DSC curves were obtained from ambient to 400°C using a DSC Q600 from TA Instruments, heated in a sealed aluminum pan and under a flowing nitrogen atmosphere (70 mL min^{-1}) at heating rate of 10°C min^{-1}. The thermomechanical measurements were obtained in a TMA 2940 from TA Instruments at heating rate

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[*] Author for correspondence: ribeiroc@iq.unesp.br

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

of 10°C min^{-1} using contraction/expansion probe with static force of 0.05 N.

The X-ray diffraction patterns (XRD) were recorded in a Siemens Kristalloflex diffractometer using nickel filtered CuK_α radiation from 4 to 70° (2θ angle).

Scanning electron microscopy images were obtained in a Field Emission Scanning Electron Microscopy JEOL JMF-6700F model. Samples were put on copper support, cover with a 1 nm thick layer of gold for 60 s (3 kV and 9.5 μA).

^{31}P NMR measurements of a sodium polyphosphate 4 mol L^{-1} solution were obtained in a Bruker AC 2000 equipment at 81.02 MHz, 13.889 Hz spectral width, pulse of 11 μs, reference 85% H_3PO_4. The solid ^{31}P MAS (125.6166855 MHz) were obtained in a 300 MHz Varian Inova using TMS as internal standard. Relaxation time 110 s, rotation 6.0 KHz and pulse 90°.

Results and discussion

Figure 1 shows the XRD patterns obtained for the homogenous transparent composite membranes obtained for all compositions used. Diffraction peaks at 15 and 22.5° are assigned to the cellulose 1α and 1β phases ($100_{1\alpha}$, $110_{1\beta}$ and $010_{1\beta}$ planes at 15° and $110_{1\alpha}$ and $200_{1\beta}$ at 22.5°). Peaks at 31.6 and 28.6° are assigned to crystalline sodium phosphate [10–13]. It must be pointed that no phosphate leaching is observed by washing membranes with water at room temperature suggesting strong interactions between phosphate units and cellulose structure.

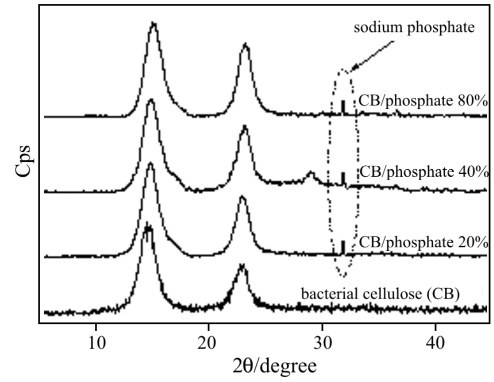

Fig. 1 XRD patterns of pure bacterial cellulose and bacterial cellulose containing 20, 40 and 80% of sodium polyphosphate

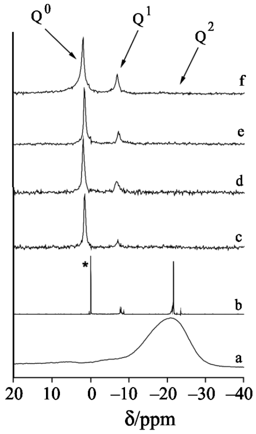

Fig. 2 ^{31}P NMR spectra for a – solid sodium polyphosphate, b – aqueous sodium polyphosphate 4 mol L^{-1}, c – BC–phosphate 1%, d – BC–phosphate 20%, e – BC–phosphate 60% and f – BC–phosphate 80%

Figure 2 shows ^{31}P NMR results obtained for the polyphosphate precursor and the composites. The metaphosphate structure of the polyphosphate precursor is mainly characterized by Q^2 and Q^1 peaks at –10 and –20 ppm, respectively [10]. From the relative intensities of the 2 peaks the polyphosphate chain is suggested to be composed of 25 phosphate units presenting 2 bridging oxygen in a metaphosphate structure. Figure 2 shows only Q^0 and Q^1 peaks for the composite membranes suggesting the hydrolysis of the polyphosphate original chains, leading to phosphate and pyrophosphate precipitation on the cellulose network.

Figure 3 shows a selected scanning electron microscopy image of the composite membrane in which the phosphate phase can be observed covering the cellulose fibrils.

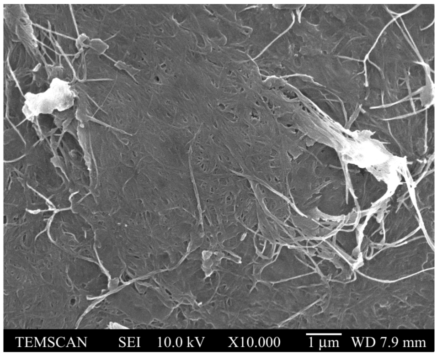

Fig. 3 SEM of BC–phosphate (60%) membrane

Figure 4 shows the TG curves. Two significant mass losses may be observed from room temperature to 200°C and from 200 to 400°C. The first mass loss, occurring from 30 to 300°C, is due to membrane dehydration. Physically adsorbed and hydrogen bond linked water molecules can be lost at that first stage. Increasing polyphosphate content leads to an increase in the amount of water.

The second mass loss is due to thermal degradation. Composites containing up to 20% polyphosphate presents thermal stability similar to pure cellulose, with the onset degradation temperature, T_{onset}, between 305–311°C. Above 20% polyphosphate the

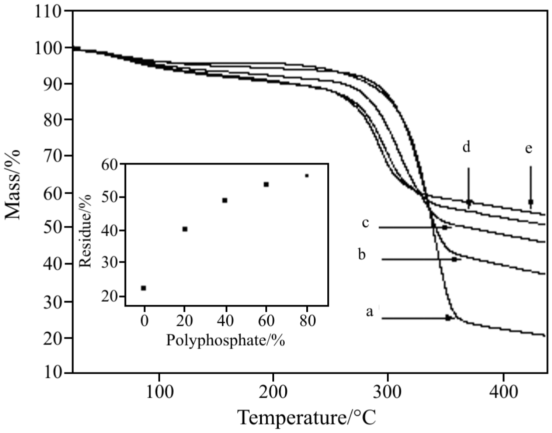

Fig. 4 TG curves of a – bacterial cellulose (BC), b – BC/sodium polyphosphate 20%, c – BC/sodium polyphosphate 40%, d – BC/sodium polyphosphate 60% and e – BC/sodium polyphosphate 80%

thermal decomposition starts at lower temperatures. The insert shows the residue (in %) at 400°C. A minor rate of mass loss regarding the pure cellulose may be due to some kind of thermal protection of the phosphate on the product of degradation of the cellulose giving more carbon than volatile products.

Figure 5 shows the DSC curves obtained from the BC membrane, sodium polyphosphate and the composites. An endothermic peak around 100°C is observed for pure BC (Fig. 5a) due to water loss. The broad exothermic peak around 330°C can be attributed to the partial pyrolysis due to fragmentation of carbonyl and carboxylic bonds from anhydrous glucoses units giving carbon or monoxide carbon.

Figure 5b shows the results obtained for sodium polyphosphate. At around 40°C a broad endothermic event is observed due to dehydration. Glass transition and crystallization are observed at 270 and 330°C, respectively.

Curves 5c and d show the results obtained for the composites containing 1 and 20% phosphate. In general the results are similar to the one obtained for BC. An endothermic event between 50 and 100°C is due to water loss. The exothermic event due to cellulose pyrolysis is observed at 330°C denoting a small downshift compared to pure BC.

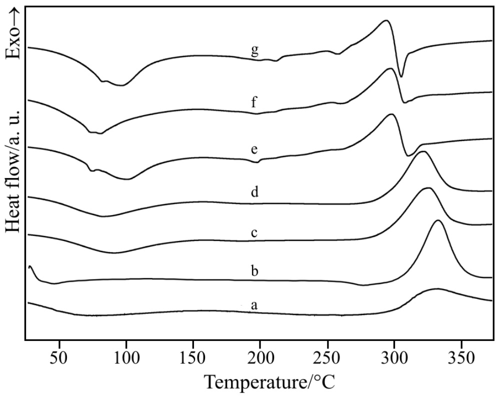

Fig. 5 DSC curves of a – bacterial cellulose (BC), b – sodium polyphosphate $(NaPO_3)_n$, c – BC–phosphate 1%, d – BC–phosphate 20%, e – BC–phosphate 40%, f – BC–phosphate 60%, g – BC–phosphate 80%

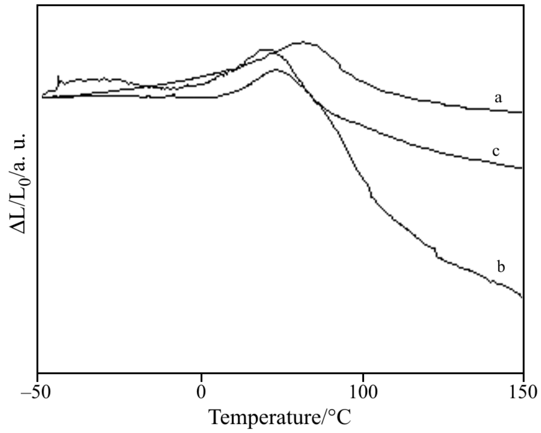

Fig. 6 TMA curves of a –bacterial cellulose (BC), b – BC–phosphate 1%, c – BC–phosphate 80%

Curves 5e–g show the results obtained for samples with higher polyphosphate content. The endothermic water loss is observed at around 100°C. A complex event occurs at higher temperatures for the 3 compositions. The peaks profiles suggest the contribution of an exothermic event followed by an endothermic one. Crystallization and/or phase transition of the phosphate counterpart could lead to the exothermic event followed the thermal degradation of the cellulose.

Figure 6 shows the TMA results. Glass transition can be readily determined from the temperature dependence of the expansion coefficient (α) and T_g value obtained for pure BC at around –16°C. Covering of the cellulose microfibrils by the phosphate phase leads to an increase in T_g values as it is shown in Table 2.

Table 1 Pyrolysis onset temperature, dehydration at 200°C (%), pyrolysis residue at 400°C (%)

	Sample				
	Bacterial cellulose	BC–phosphate 20%	BC–phosphate 40%	BC–phosphate 60%	BC–phosphate 80%
Onset temperature/°C	311	305	300	277	274
Dehydration of 200°C/%	4.1	6.4	7.5	8.9	9.3
Pyrolysis residue at 400°C/%	22.5	40.1	48.7	53.3	56.0

Table 2 Glass transition (T_g) values

Sample	T_g/°C
Bacterial cellulose (BC)	–16
BC/sodium phosphate 1%	–3.7
BC/sodium phosphate 80%	6.6

Conclusions

New bacterial cellulose phosphate composite membranes have been obtained by the interaction between hydrated cellulose membranes and a sodium polyphosphate aqueous solution. XRD and SEM results show clearly the covering of the cellulose fibril structure by a phosphate phase. Increasing the phosphate content markedly different thermal behavior is observed. An increase in T_g values together with a complex degradation event reflect the chemical interaction of the 2 components. Potential application of the composite membranes is under study.

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