

# Preparation and Characterization of Benzylated Sisal Fibers

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**ABSTRACT:** Sisal fibers were benzylated under different conditions and were characterized with infrared spectroscopy, X-ray diffraction, thermal analysis, and scanning electron microscopy. The benzylation reaction was monitored by the mass gain as a function of the reaction time. In the first stage, there was a mass loss associated with the loss of lignin and polyoses from the raw fiber, which was accompanied by an increase in mass due to benzyl incorporation. When fiber delignification was carried out before benzylation, the mass gain curves of the benzylation reaction presented no initial mass loss and a much higher mass gain. Benzylation promoted several morphological changes: (1)

the loss of the parenchyma cells, (2) the defibrillation of the technical fibers into ultimate fibers, (3) the microfibrillation of the ultimate fibers, and (4) benzyl incorporation. The crystallinity of the fibers decreased with benzylation, as observed by X-ray diffraction. The thermal stability of the fibers varied according to the treatment used. Other changes promoted in the fibers by chemical modification were examined. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2957–2965, 2003

**Key words:** natural fibers; sisal chemical modification

## INTRODUCTION

Until a few years ago, the worldwide applications of sisal fibers were basically in cordage, with baler twine being its main use.<sup>1</sup> The lack of research and development of new applications for this material could be demonstrated by the scarce and old literature usually available.<sup>1–3</sup> Lately, however, the plastic, automotive, and architectural industries<sup>4–8</sup> are renewing an interest in agrobased fibers, including sisal, as substitutes for conventional inorganic/mineral reinforcements, such as fiber glass, commonly used in polymer composites.

Among the many applications for which sisal fibers can satisfactorily be used to produce reinforced polymeric materials are those of the automotive industry,<sup>8</sup> including bumpers, parasols, instrument panels, roofs, door revetments, tool cases, and car seats. Some of these applications are already being used in the pro-

duction line on an industrial scale, whereas others are in different stages of development.

Several studies in the literature<sup>9–11</sup> report on the mechanical and dynamic properties, aging characteristics, and chemical modifications of vegetal fibers as reinforcing materials. These properties can usually be optimized as a function of the fiber–matrix adhesion and fiber characteristics such as loading, length, and orientation. The chemical modification of these fibers is a interesting way of changing the fiber characteristics to improve the composite performance.

In this sense, it is important to study the effects of different chemical modifications on the structure and morphology of vegetal fibers. In this work, we modified sisal fibers by benzylation with and without a previous delignification treatment. Fibers produced under different conditions were characterized with infrared spectroscopy, X-ray diffraction, thermal analysis, and scanning electron microscopy (SEM).

## EXPERIMENTAL

### Benzylation of the fibers

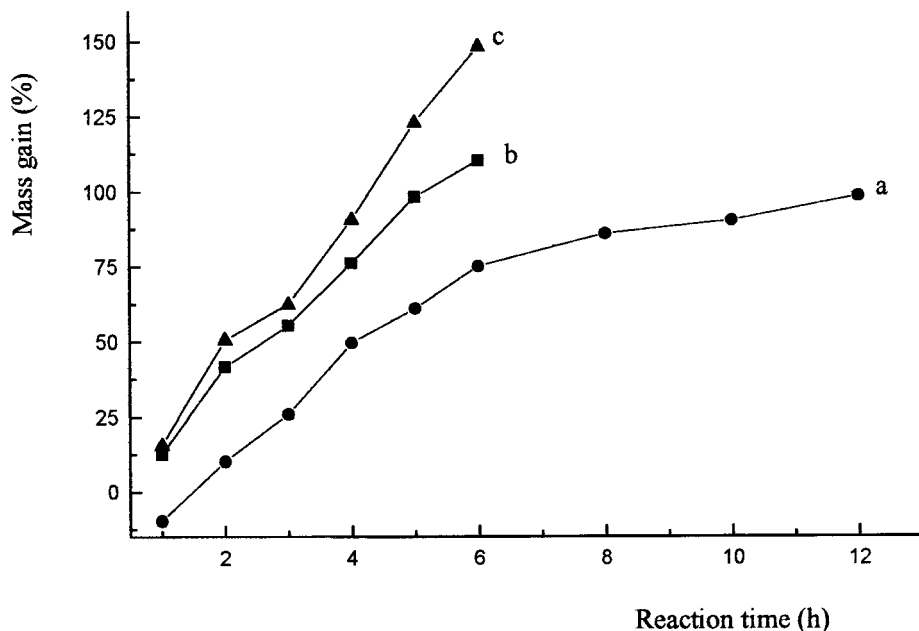
Sisal fibers (*Agave sisalana*) were supplied by Icomar S.A. (São Paulo, Brazil). The benzylation reactions were carried out on 1 g of dried sisal fibers mixed with 17.50 mL of 40% aqueous NaOH and 7.50 mL of benzyl chloride at 110°C. The reaction was monitored by the mass gain as a function of the reaction time. Benzylated sisal fibers were then extensively washed

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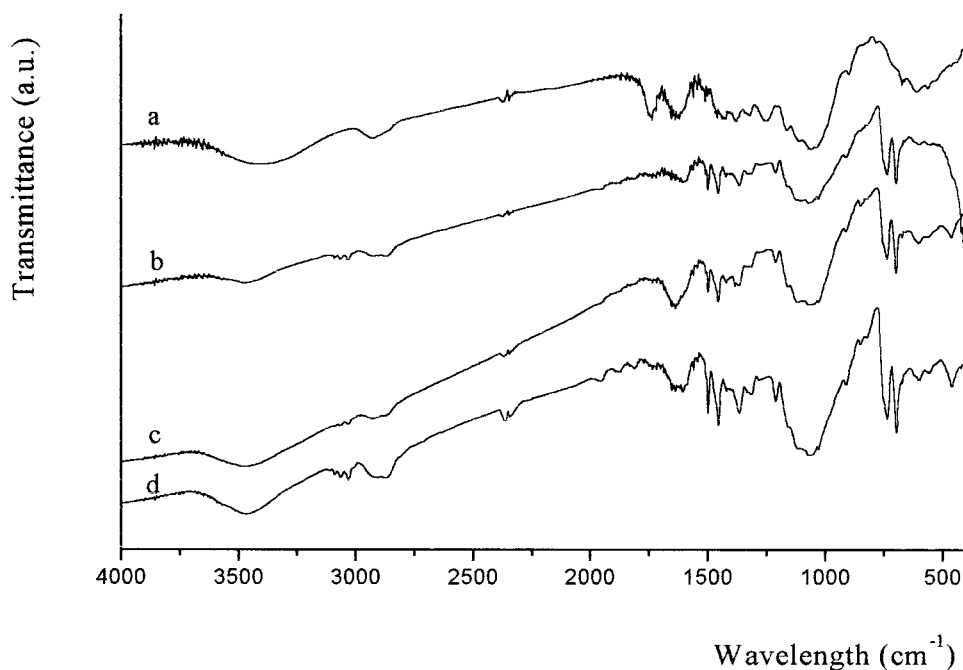


**Figure 1** Mass gain versus the reaction time for benzylation reactions carried out on (a) raw sisal fibers, (b) sisal fibers previously delignified for 1 h, and (c) sisal fibers previously delignified for 2 h.

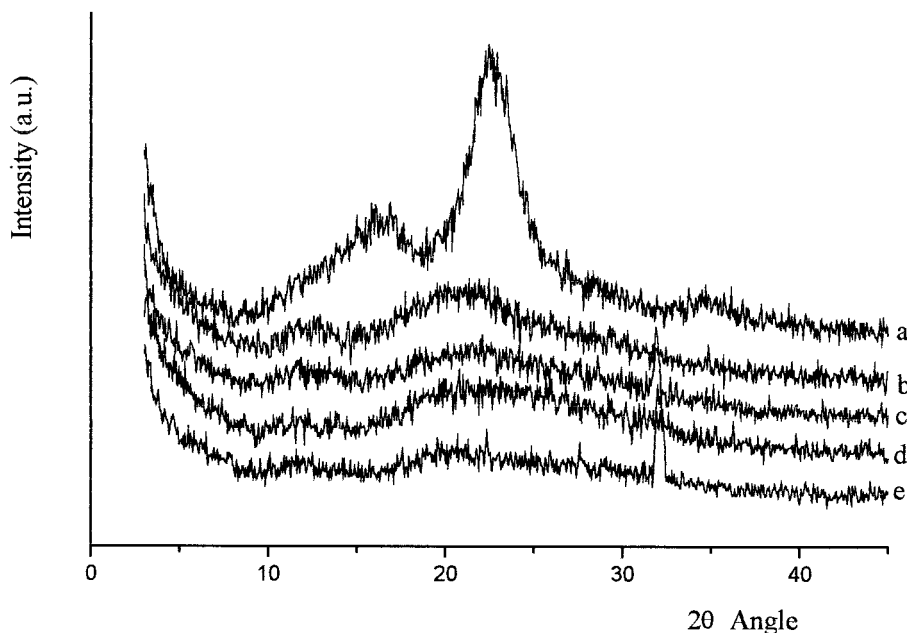
with ethanol and distilled water to eliminate any residues of benzyl chloride and salt. The delignification treatment was carried out with an organosolvent treatment with an acetone/water mixture (1:1 v/v) at 185°C for 1 or 2 h, after which the samples were washed extensively with acetone.

#### Fiber characterization

X-ray diffraction patterns were taken on a Rigaku RU-200B diffractometer (Tokyo, Japan) with Cu K $\alpha$  radiation and a nickel filter. Infrared spectroscopy was performed in KBr pellets with a Jasco IR 700 spectrom-



**Figure 2** Infrared spectra from sisal: (a) raw fibers, (b) raw fibers benzylated for 2 h, (c) delignified fibers (2 h) benzylated for 2 h, and (d) raw fibers benzylated for 6 h.

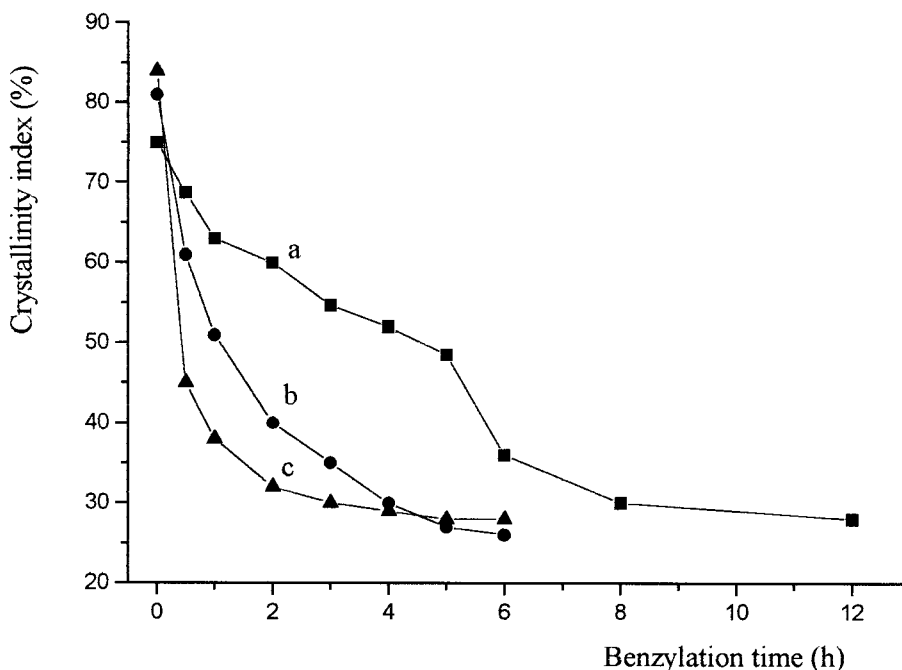


**Figure 3** X-ray diffraction patterns from sisal: (a) raw fibers, (b) raw fibers benzylated for 2 h, (c) raw fibers benzylated for 4 h, (d) delignified fibers (2 h) benzylated for 2 h, and (e) raw fibers benzylated for 6 h.

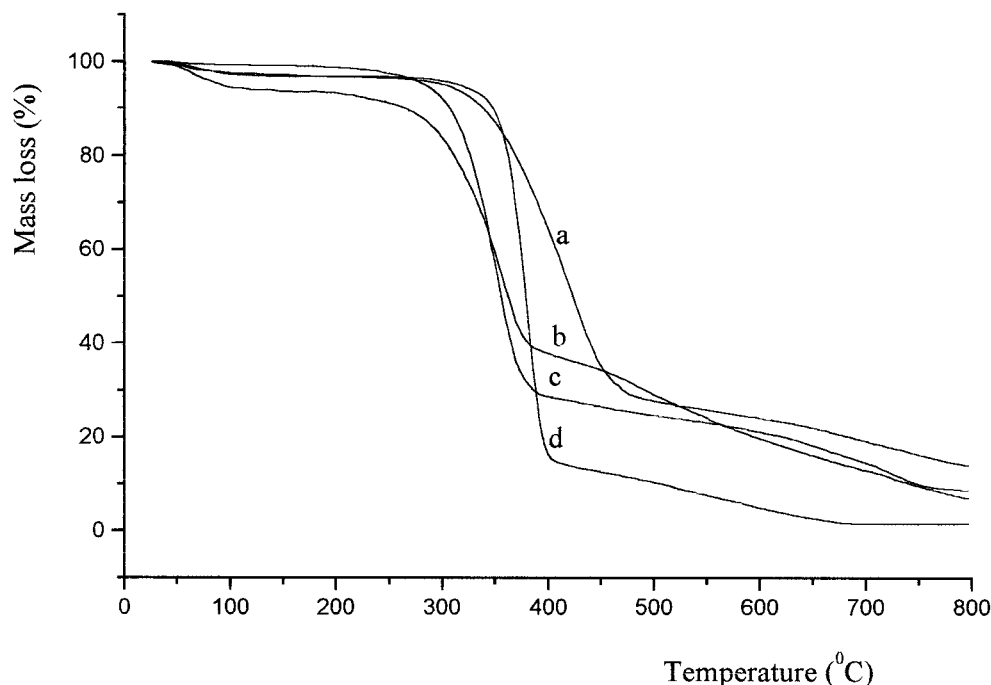
eter (Tokyo, Japan). Thermogravimetric analysis (TGA) was carried out with a Shimadzu TA-50 instrument (Tokyo, Japan) at a scanning rate of 10°C/min in a nitrogen atmosphere. SEM analysis was performed with a Zeiss DSM 960 computerized microscope (Jena, Germany) operated between 10 and 20 kV on samples containing a thin layer (ca. 15 nm) of sputter-coated gold.

## RESULTS AND DISCUSSION

Benzylation on raw sisal fibers, under the conditions studied in this work, can lead to a mass gain of up to approximately 100% after 12 h of reaction time, as shown in Figure 1(a). An initial mass loss ( $\approx 10\%$ ) was noted in the 1st hour of the benzylation treatment on raw sisal fibers [Fig. 1(a)] due to the swelling of the



**Figure 4** Crystallinity index versus the benzylation time of sisal: (a) raw fibers, (b) sisal fibers previously delignified for 1 h, and (c) sisal fibers previously delignified for 2 h.



**Figure 5** TGA thermograms of sisal: (a) fibers benzylated for 2 h, (b) raw fibers, (c) fibers benzylated for 6 h, and (d) fibers delignified for 2 h.

morphology and loss of extractives (lignin and polyoses). Moreover, the strong alkaline media used in the benzylation can also cause degradation of the fiber structure depending on the reaction time. The degree of substitution (DS) was calculated on the basis of the mass gain and NMR.<sup>12</sup> The DS values obtained after 6 h of benzylation from mass gain and NMR analyses were 2.25 and 2.73, respectively. The overall mass gain, plotted in Figure 1, was a result of two reactions: extractive elimination and benzyl incorporation. Therefore, because we could not subtract from the

mass gain the amount of extractives eliminated, lower DS values were obtained in this case than by RMN analysis, which considered only the benzyl incorporation.

However, when a previous delignification treatment was carried out on the fibers for 1 [Fig. 1(b)] or 2 h [Fig. 1(c)], a mass gain of up to approximately 110 or 150%, respectively, was observed after 6 h of benzylation time. The initial mass loss is not shown in Figure 1 for delignified sisal fibers because the process eliminated the extractives. Furthermore, delignifica-

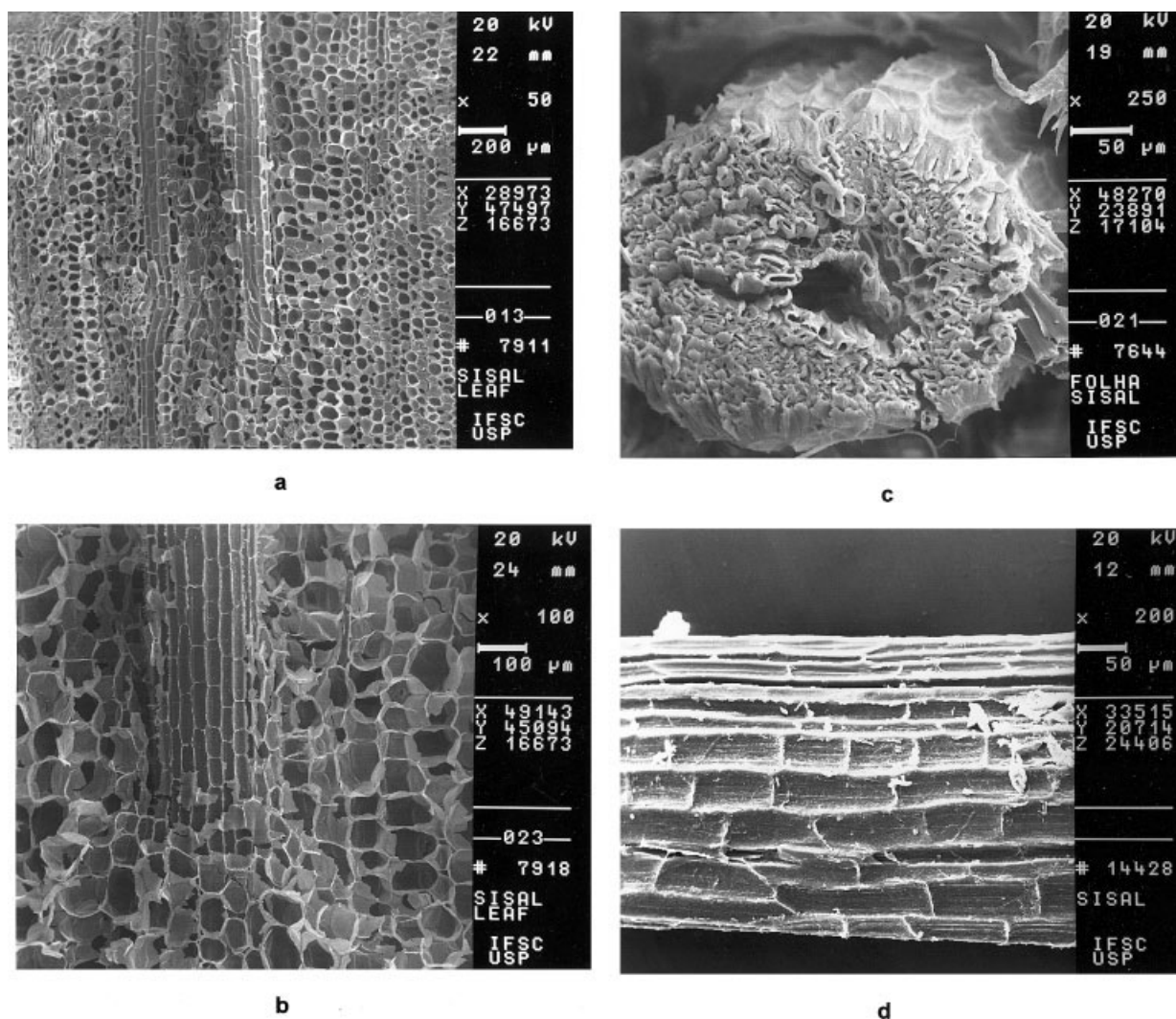
**TABLE I**  
Initial Decomposition Temperatures of Sisal Fibers as a Function of Benzylation Time as Determined by TGA

Benzylation time (h)	Initial decomposition temperatures <sup>a</sup> (°C)		
	Benzylated fibers <sup>b</sup>	Delignified (1 h) benzylated fibers <sup>c</sup>	Delignified (2 h) benzylated fibers <sup>b</sup>
0	180	250	280
1	220	240	240
2	260	235	220
3	250	235	225
4	240	235	230
5	235	250	240
6	230	250	240
8	230		
10	220		
12	220		

<sup>a</sup> The initial decomposition temperatures were obtained at the point at which the change in the slope of the TGA curve began.

<sup>b</sup> Benzylation was carried out on raw fibers.

<sup>c</sup> Fibers were delignified for 1 or 2 h, as indicated, prior to benzylation.



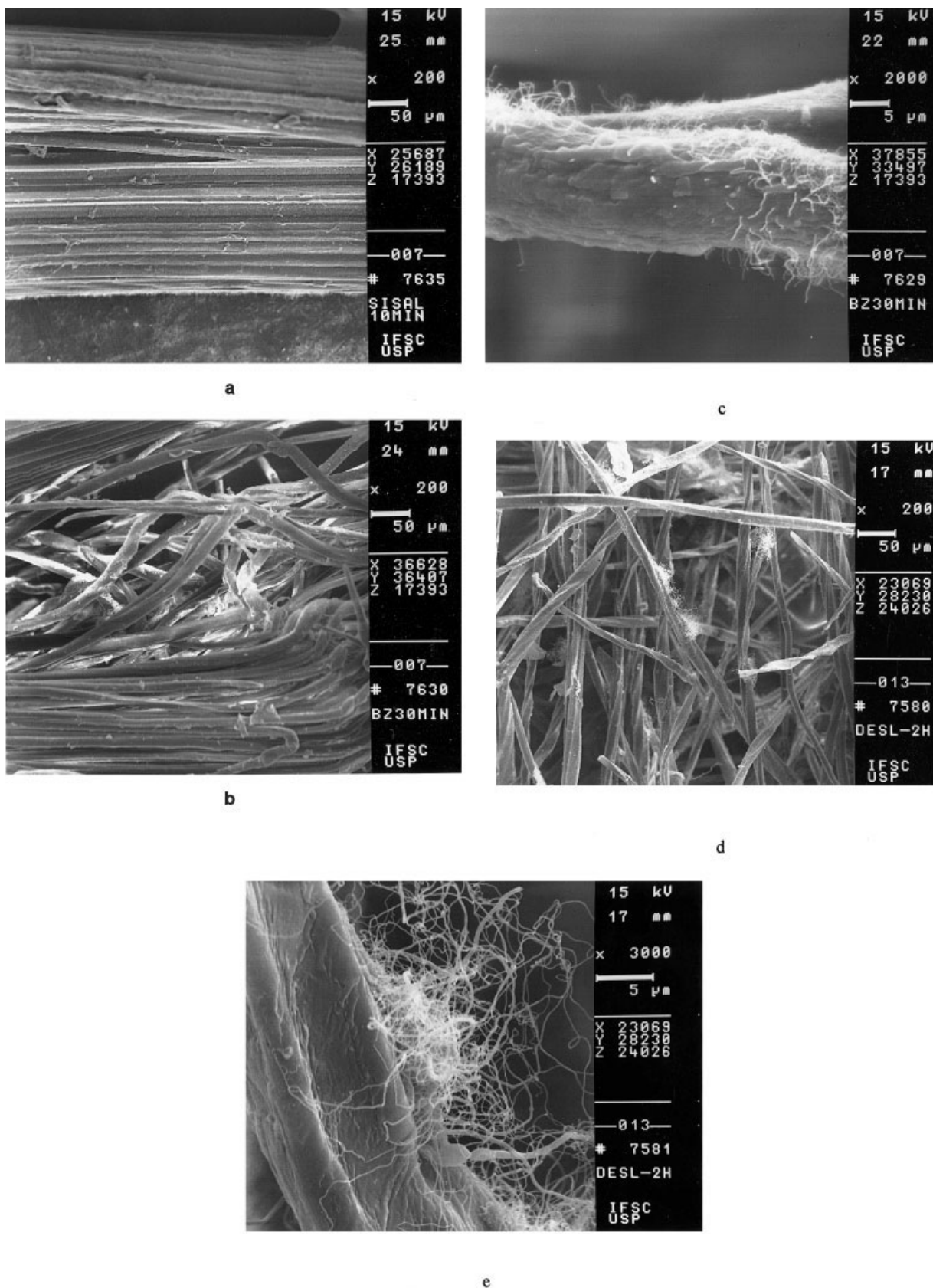
**Figure 6** SEM micrographs: (a) the longitudinal section of a sisal leaf showing a technical fiber surrounded by the parenchyma cells (original magnification, 50 $\times$ ), (b) the same section at a greater magnification (original magnification, 100 $\times$ ), (c) the transversal section of a sisal fiber (original magnification, 250 $\times$ ), and (d) the longitudinal section of a sisal fiber (original magnification, 200 $\times$ ).

tion favored further benzyl incorporation, which accounted for a greater extent of the benzylation reaction. This was attributed to an opening of the fiber morphology (as shown in this article), although other changes to other aspects, such as the molecular weight, could also occur. The greater the lignin extraction was (61 and 83% of the lignin was extracted after 1 and 2 h, respectively, of delignification),<sup>12</sup> the higher the benzyl incorporation was for a constant benzylation condition, as shown in Figure 1(b,c). The rate of the benzylation reaction also increased upon lignin extraction, as indicated by the slopes of the curves, which were greater for the more delignified samples.

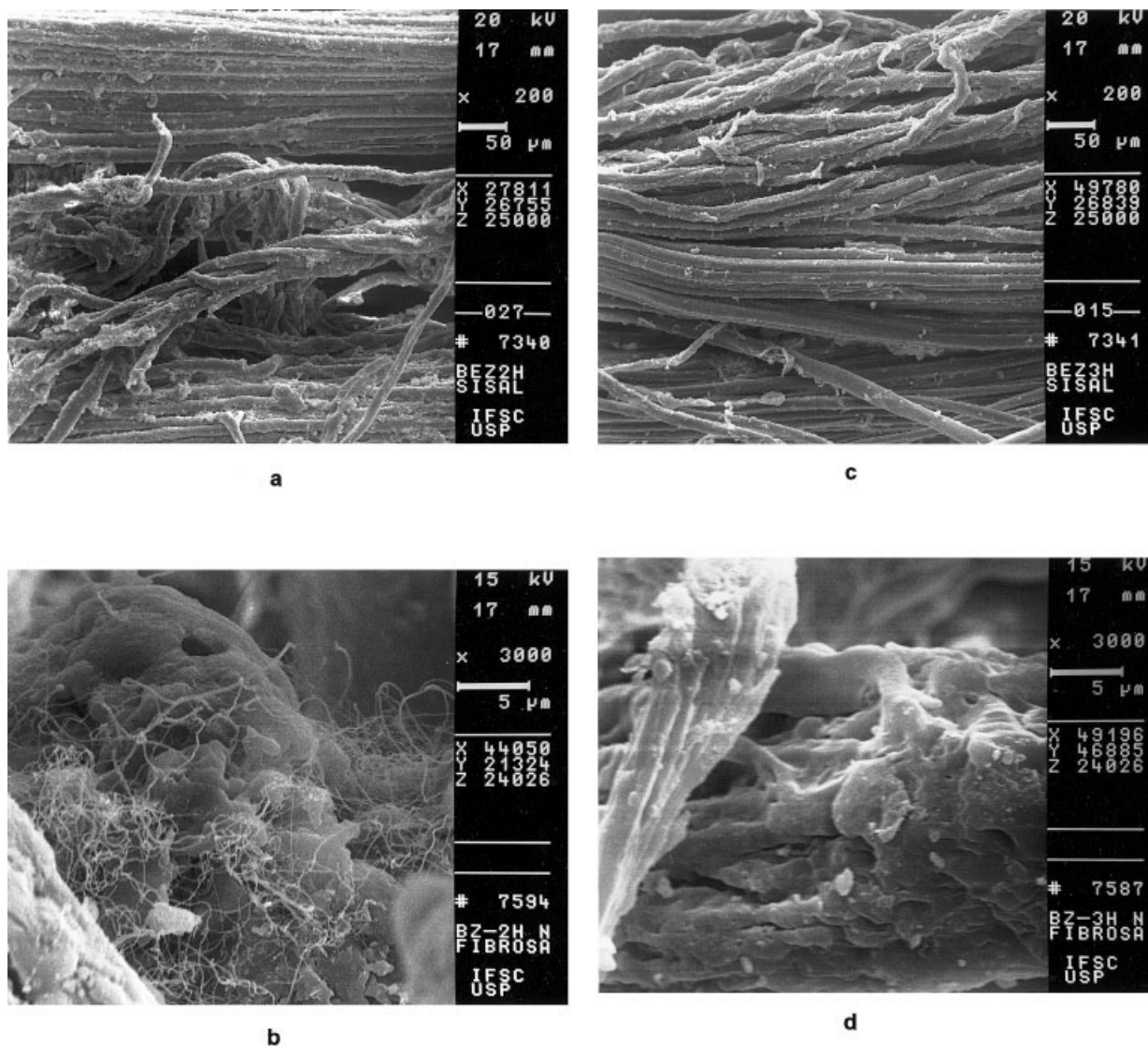
Fourier transform infrared analysis confirmed the changes in the chemical structure consistent with the benzylation of the fiber (Fig. 2). We can observe a decrease in the band at 3452  $\text{cm}^{-1}$  attributable to the axial deformation of the hydroxyl groups, which were

replaced with benzyl groups, in the benzylated fibers, as well as an increase in the bands at 1593–1610  $\text{cm}^{-1}$  and 738 and 690  $\text{cm}^{-1}$  assigned to aromatic C—C axial deformation and aromatic C—H angular out-of-plane deformation, respectively. Also, bands at 3028–3080  $\text{cm}^{-1}$  appeared in the benzylated samples that were associated with the presence of aromatic moieties due to aromatic C—H axial deformation. Furthermore, multiple peaks at 1950–1810 (weak triplet) and 700  $\text{cm}^{-1}$  (strong doublet), previously found in benzylated sugar cane bagasse,<sup>13</sup> were only seen for the benzylated fibers. The delignified/benzylated fibers presented similar infrared spectra behavior [Fig. 2(c)], but they were more prominent for shorter benzylation reaction times than the nondelignified benzylated fiber.

The X-ray diffraction analysis presented in Figure 3 shows the changes in the crystalline structure of the



**Figure 7** SEM micrographs from the surfaces of technical sisal fibers: (a) fibers benzylated for 10 min (original magnification, 200 $\times$ ), (b) fibers benzylated for 30 min (original magnification, 200 $\times$ ), (c) an ultimate sisal fiber benzylated for 30 min (original magnification, 2000 $\times$ ), (d) fibers delignified for 2 h (original magnification, 200 $\times$ ), and (e) an ultimate fiber delignified for 2 h (original magnification, 3000 $\times$ ).



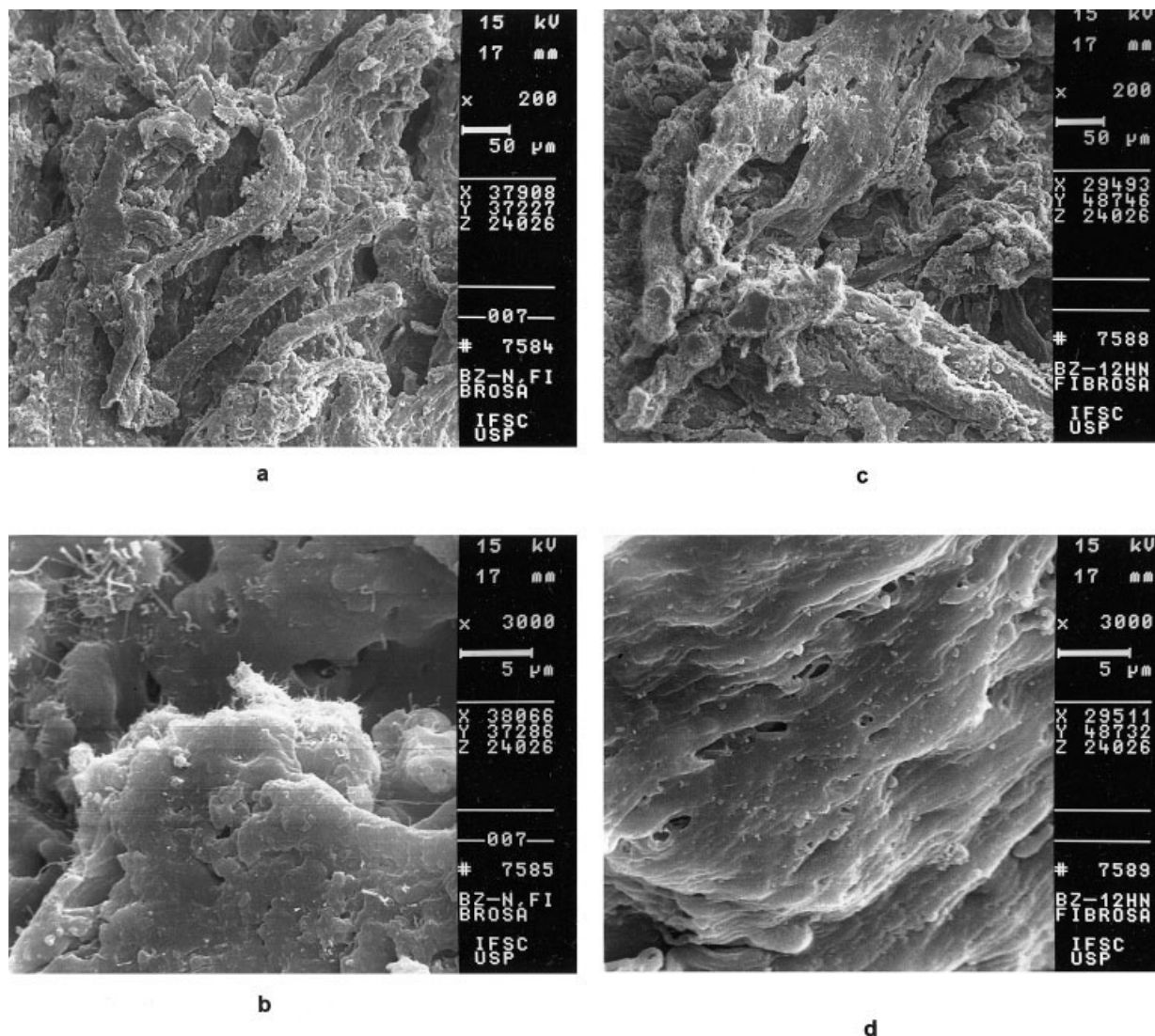
**Figure 8** SEM micrographs from sisal fibers benzylated for (a) 2 h (original magnification, 200 $\times$ ), (b) 2 h (original magnification, 3000 $\times$ ), (c) 3 h (original magnification, 200 $\times$ ), and (d) 3 h (original magnification, 3000 $\times$ ).

fiber upon benzylation. The raw sisal fiber presented an X-ray pattern characteristic of a cellulose I type of material, with a main diffraction peak at  $2\theta \approx 23^\circ$  associated with the diffraction of plane 002. Another minor peak at  $2\theta \approx 16^\circ$  can also be seen because of the diffraction of planes 101 and  $10\bar{1}$ . As can be seen in Figure 3(b–e) the peak corresponding to planes 101 and  $10\bar{1}$  disappeared for the benzylated fiber, and a smaller band at  $2\theta \approx 12^\circ$  emerged. The peak related to plane 002 was shifted to  $2\theta \approx 20^\circ$ , also being lower in intensity and broader in shape. These changes in the X-ray pattern upon benzylation could be attributed to the transformation from cellulose I to a corresponding more amorphous benzylated cellulose.<sup>14</sup> The estimation of the crystallinity index (CrI) was made according to the literature<sup>15</sup> with the following equation:

$$\text{CrI} = 100[(I_{002} - I_{\text{am}})/I_{002}]$$

where  $I_{002}$  is the intensity of the diffraction peak from plane 002 and  $I_{\text{am}}$  is the intensity of the diffraction from the background scattering minimum measured at  $2\theta = 15\text{--}18^\circ$ .

We can observe a decrease, for instance, from 75 to 5% [Fig. 4(a)] on going from the raw fiber to the fiber benzylated for 12 h. A similar behavior was observed for the delignified/benzylated samples [Fig. 4(b,c)], although in this case, the initial amount of cellulose was higher because of the extraction of the amorphous component (lignin) from the fiber; this also resulted in a higher initial degree of crystallinity. As mentioned before, the extraction of lignin promoted an opening of the fiber morphology that led to a greater and faster action of NaOH and, consequently, to a faster decrease of the cellulose I content, in comparison with the nondelignified fibers.



**Figure 9** SEM micrographs from sisal fibers benzylated for (a) 8 h (original magnification, 200 $\times$ ), (b) 8 h (original magnification, 3000 $\times$ ), (c) 12 h (original magnification, 200 $\times$ ), and (d) 12 h (original magnification, 3000 $\times$ ).

The thermal behavior of the fiber changed upon benzylation, as shown by TGA in Figure 5. The first mass loss, observed from 60 to 100 $^{\circ}$ C, was associated with water present in the fiber samples because of moisture uptake. Such moisture uptake decreased, for example, from approximately 5.0 to 1.0% for raw fibers and fibers benzylated for 6 h, respectively, because the hydroxyl content decreased upon benzylation. The thermal stability of sisal (presented in Table I) increased in the first stage of the benzylation reaction because of the elimination of easily degradable extractives (wax, polyoses, and lignins), after which it decreased because of the benzyl incorporation. However, delignification improved the thermal stability of the untreated sisal fiber, specially for the 2-h reaction, because of the elimination of extractives, after which it decreased upon benzylation. A similar behavior, although less intense, was also observed for the 1-h delignification treatment.

The SEM analysis of the sisal fibers revealed that the fibers were surrounded by the parenchyma cells within the leaf in the plant structure [Figs. 6(a,b)], the cell walls of which were stuck on the surfaces of the fibers. It is also clear from the cross-section micrograph [Fig. 6(c)] that the fibers were formed by a bundle of ultimate fibers. This fiber morphology persisted even after the technical fibers were extracted from the leaf by the decortication process [Fig. 6(d)] and, as we will see, affected the initial chemical modification that started on the fiber surface.

The effect of benzylation on the surface morphology of sisal fibers was demonstrated in the SEM analysis presented next. In the first stage of the benzylation reaction (up to ca. 30 min), the parenchyma cells, rounding the sisal fibers, were lost, and the ultimate fibers started to separate from one another [Figs. 7(a,b)] because of the action of the alkaline solution, which extracted the cementing component, mainly lig-



nin, and opened the fiber morphology. This observation is consistent with the initial mass loss detected in Figure 1, when benzylation was carried out without a previous delignification treatment. Also, some microdefibrillation started to occur on the fiber walls, as presented in Figure 7(c). Microfibrils with dimensions on the order of a few hundreds of nanometers are believed to be the finest morphology of cellulose in which macromolecules are closely packed. A similar opening of the fiber morphology and microdefibrillation effect [Fig. 7(d,e)] were seen during the lignin extraction by the delignification process.<sup>12</sup> Most of the sisal fibers benzylated in the initial stage (ca. 95%) still had the macroscopic visual aspect of a technical fiber, despite the loss of the parenchyma cells and the presence of some initial defibrillation in the ultimate fibers. Nevertheless, benzyl incorporation had already started to occur. As the reaction went for 2 h, the defibrillation of the fibers proceeded considerably, the ultimate fibers starting to swell because of the benzylation, as shown in Figure 8(a). As previously mentioned, this is consistent with the loss of lignin, the cementing agent, which caused the separation of the ultimate fibers. A great number of entangled microfibrils were also observed that were then benzylated and started to coalesce [Fig. 8(b)]. As the reaction proceeded for 3 h [Fig. 8(c,d)], the technical fibers were practically all separated into ultimate fibers, which were basically swollen because of the benzyl incorporation. The swelling effect increased for longer reaction times (8 and 12 h; Fig. 9), leading to the destruction and aggregation of the ultimate fiber structure, producing a pulp-like material that presented a remarkably benzylated morphology with a plastic-like feature. For the longest reaction time (12 h), no fiber could be observed anymore, the whole material being transformed into a material with a pulp-like aspect. For fibers previously delignified, a similar morphological transformation was observed but for shorter reaction times because the reaction kinetics increased in this case.

Ongoing atomic force microscopy studies are being carried out to investigate the effect of chemical modification by benzylation on the surface morphology of fibers at a greater resolution that might also allow the quantification of surface properties.

## CONCLUSIONS

The benzylation of sisal fibers was satisfactorily performed under the conditions described in this work, leading to a mass gain of up to 150% that depended on

the conditions used. A mass loss was observed in the first stage of benzylation that was associated with the loss of lignin and polyoses from the raw fiber, and it was accompanied by an increase in mass due to benzyl incorporation. When the delignification of the fiber was carried out before benzylation, the mass gain curves of the benzylation reaction presented no initial mass loss and a higher mass gain. Benzylation promoted several morphological changes: (1) the loss of the parenchyma cells, (2) the defibrillation of the technical fiber into ultimate fibers, (3) the microdefibrillation of the ultimate fibers, and (4) benzyl incorporation. Moreover, the crystallinity of the fiber decreased upon benzylation for all conditions studied, and the thermal stability of the fiber varied according to the treatment used.

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