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Highly Hydrophobic Biopolymers Prepared by the Surface Pentafluorobenzoylation of Cellulose Substrates

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New highly hydrophobic/lipophobic biopolymers were prepared by the controlled heterogeneous pentafluorobenzoylation of cellulose substrates, i.e., plant and bacterial cellulose fibers. The characterization of the modified fibers was performed by elemental analysis, FTIR spectroscopy, X-ray diffraction, thermogravimetry, and surface analysis (XPS, ToF-SIMS, and contact angle measurements). The degree of substitution of the ensuing pentafluorobenzoylated fibers ranged from 0.014 to 0.39. The hydrolytic stability of these perfluorinated cellulose derivatives was also evaluated and showed that they were quite water stable, although of course the fluorinated moieties could readily be removed by hydrolysis in an aqueous alkaline medium.

Introduction

Cellulose is the most abundant and widespread biopolymer on earth. It is biosynthesized not only by plants, but also by bacteria, algae, and fungi, although vegetal cellulose is still by far the most exploited macromolecule.[1] Bacterial cellulose is an extracellular polysaccharide produced by several microorganisms in a highly pure form, with DPs of 2000−8000.[1−3] It is generated as a three-dimensional network of highly crystalline nano- and microfibrils with 10−100 nm diameter, which possesses unique physical and mechanical properties, making it a very promising material for novel value-added applications.

Owing to its abundance, biodegradability, and specific properties, cellulose is a very important renewable resource for the development of environment friendly, biocompatible, and functional materials, quite apart from its traditional and massive use in papermaking and cotton textiles. Cellulose derivatives are currently used in a broad field of applications,[1,4] such as coatings, optical films, sorption media, controlled released systems, composites (with synthetic or biopolymeric matrixes), biodegradable plastics, and biomedical materials.

The controlled heterogeneous modification of cellulose fibers is a relatively recent research domain, which is gaining growing attention,[5] because reactions can be limited to the groups present in the accessible regions of the fibers, as opposed to homogeneous conditions, where the modification occurs indiscriminately along the cellulose macromolecules.

The functionalization of organic molecules with fluorine atoms or fluorinated moieties leads to substantial changes in their chemical and physical properties,[6] including (i) enhanced hydrophobicity/lipophobicity, (ii) low surface energy, (iii) high thermal and oxidative stability, (iv) chemical and biological inertness, and (v) remarkable gas-dissolving capacity. In this perspective, the chemical modification of cellulose with fluorine-containing moieties represents a potential strategy for the development of innovative functional biopolymeric materials for a multitude of applications. To date, only a few studies dealing with this topic have been published, namely, trifluoroacetylation (in both homogeneous and heterogeneous systems),[7−9] esterification with perfluorododecanoic acid chloride,[10] homogeneous modification with (trifluoroethoxy)- and (difluoroethoxy)acetic acid,[11,12] surface reaction with perfluorinated oligo(ethylene oxide),[13] and surface plasma treatment with carbon tetrafluoride[14] and fluorotrimethylsilane.[15]

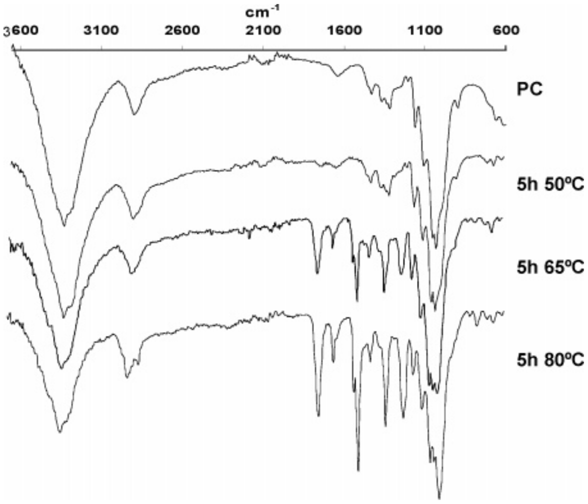

Figure 1. FTIR spectra of plant cellulose fibers before and after pentafluorobenzoylation at different reaction temperatures.

Pentafluorobenzoylation is a common derivatization procedure used for the chromatographic analysis of amines and alcohols,[16] because of its high rates and yields and the stability of the ensuing products.[16] This reaction has been applied to chitin,[17] but not, to the best of our knowledge, to cellulose. We report here, therefore, the surface modification of plant and bacterial cellulose fibers with pentafluorobenzoyl chloride in toluene, i.e., a nonswelling medium (Scheme 1), chosen to limit the modification to the fibers' surface.

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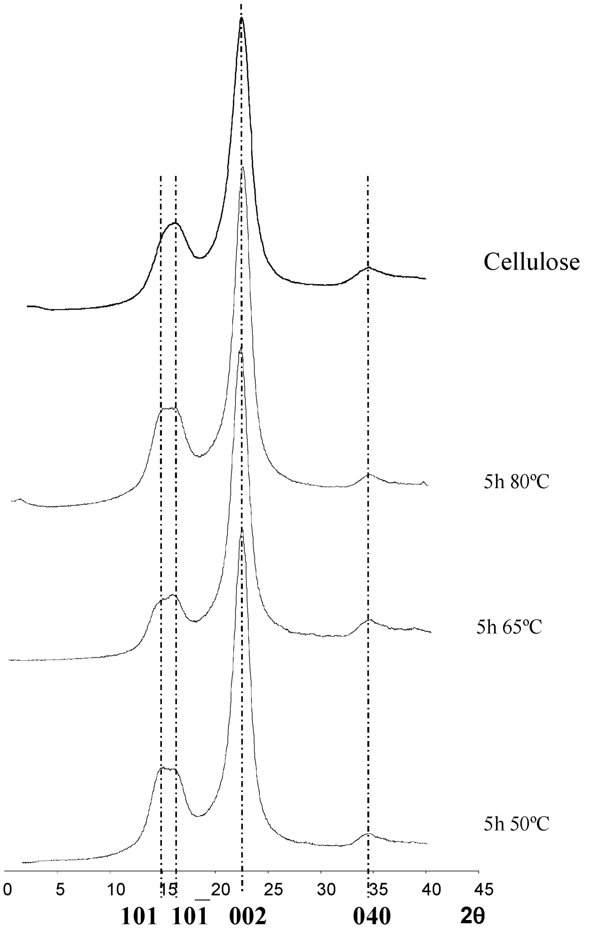


Figure 2. XRD patterns of plant cellulose before and after pentafluorobenzoylation at different reaction temperatures.

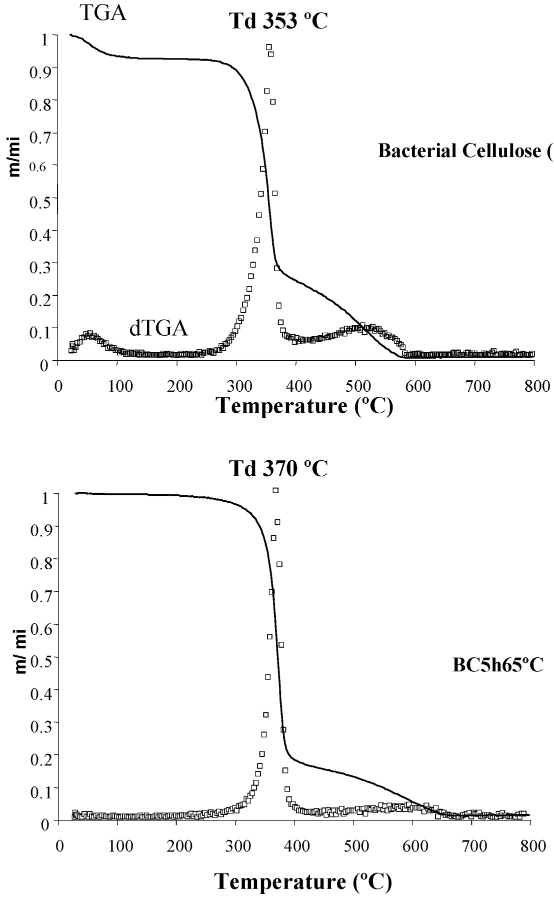


Figure 3. Thermograms of bacterial cellulose before and after pentafluorobenzoylation for 5 h at 65 °C.

Experimental Section

Materials. The cellulose substrates used in this study bore two distinct origins, namely, plant-derived fibers (PC) in the form of *Eucalyptus globulus* ECF (DEDED) industrial bleached kraft pulp and pure cellulose Schleicher & Schuell Microscience filter paper, the latter being used to provide flat surfaces for the measurements of contact angles and to compare the role of fiber assembly on the rate of hydrolysis of the modified materials, and bacterial cellulose (BC) produced by *Acetobacter xylum* in the form of a wet (~95% humidity) 3D network of ribbon-like nanofibril structures (50−100 nm width).

Plant fibers were vacuum-dried at 60 °C, whereas bacterial fibers were freeze-dried before use.

Pentafluorobenzoyl chloride was supplied by Sigma-Aldrich and used as received. Toluene was dried over sodium wire. Pyridine was purified and dried by distillation over sodium hydroxide.

Fiber Modification. One equivalent (relative to the total cellulose OH functions) of pentafluorobenzoyl chloride was placed in a 25 mL round-bottom flask, to which dry toluene (8 mL), pyridine (1 equiv), and finally cellulose (~200 mg) were added in a nitrogen atmosphere. Reactions were conducted under magnetic stirring at different temperatures (20, 50, 65, and 80 °C) and reaction times (1, 5, and 20 h). The esterified fibers were filtered and sequentially washed with toluene, CH_2Cl_2, and ethanol, before being submitted to a Soxhlet extraction with CH_2Cl_2 for 12 h and dried at 60 °C for 24 h.

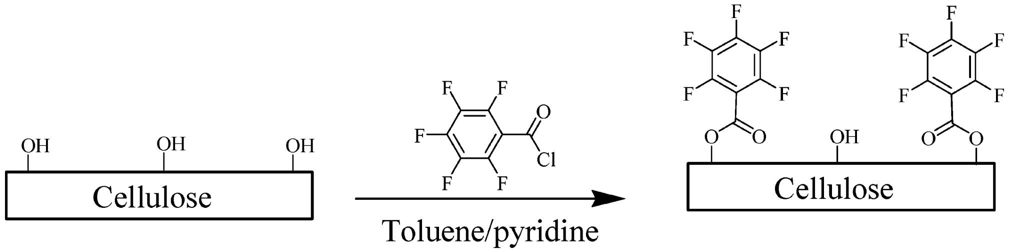
Hydrolytic Stability Evaluation. Aliquots (~50 mg) of the modified fibers (*E. globulus* fibers and filter paper) were placed in an Erlenmeyer flask containing 20 mL of water, and the ensuing suspension was stirred for different time periods (1−7 h). These experiments were also carried out without stirring and under acidic and alkaline conditions (pH 4 and 9, respectively) at room temperature. The progress of the hydrolysis was followed by FTIR spectroscopy and contact angle measurement.

Modified Fiber Characterization. The degree of substitution (DS) of the modified fibers, i.e., the number of pentafluorobenzoate groups per cellulose monosaccharide unit, was calculated from fluorine elemental analysis data ([F], %) (obtained in duplicate at the CNRS Service Central d'Analyse, Vernaison, France) using the following equation:

$$\mathrm{DS} = \frac{162[\mathrm{F}]}{9500 - 194[\mathrm{F}]}$$

The FTIR spectra were recorded with a Brücker IFS FTIR spectrometer equipped with a single horizontal Golden Gate ATR cell.

Scheme 1. Schematic View of Pentafluorbenzoylation of Cellulose Fibers



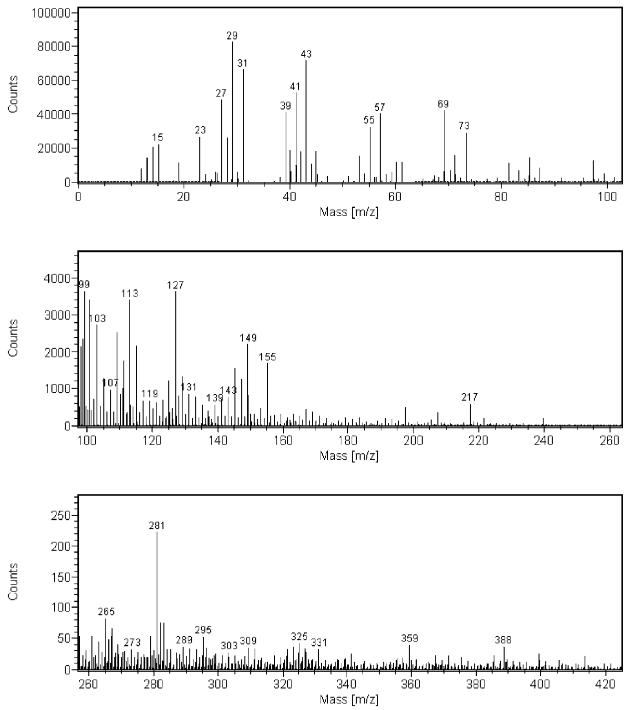


Figure 4. ToF-SIMS spectrum of BC.

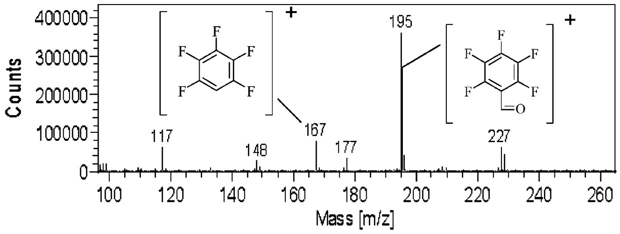


Figure 5. Partial positive ToF-SIMS mass spectrum of pentafluorobenzoylated BC (5 h at 65 °C).

For the X-ray diffraction (XRD) measurements, the fibers were gently pressed into small pellets using a laboratory press and analyzed with a Phillips X'pert MPD diffractometer using Cu Kα radiation.

The thermogravimetric assays were carried out with a Shimadzu TGA 50 analyzer equipped with a platinum cell. Samples were heated at a constant rate of 10 °C/min from around 22 to 800 °C, under a nitrogen flow of 20 mL/min. The thermal decomposition temperature was taken as the onset of significant ($\geq$0.5%) weight loss from the heated sample, after the moisture loss.

Contact angles with water, diiodomethane, formamide, and glycerol were measured with a "surface energy evaluation system" commercialized by Brno University (Czech Republic). Each θ value was the average of 5−10 determinations. These values were used to calculate the dispersive and polar contributions to the surface energy of the fibers, using Owens-Wendt's approach.[18]

X-ray photoelectron spectra of pulp hand sheet surfaces were obtained with a Physical Electronics PHI Quantum 2000 ESCA instrument equipped with a monochromatic Al Kα X-ray source and operated at 25 W with a combination of electron flood gun and ion bombardment for charge compensation. The takeoff angle was 45° in relation to the sample surface. The analyzed area was 100 × 100 μm^2. At least three different spots were analyzed on each sample. A Gaussian curve-fitting program was used to treat the C1s signal, and the following binding energies, relative to the C−C position at 285 eV, were employed for the relevant moieties: 1.7 ± 0.2 eV for C−O, 3.1 ± 0.3 eV for O−C−O or C=O, 4.6 ± 0.3 eV for O=C−O, and 2.7 ± 0.3 eV for C−F.

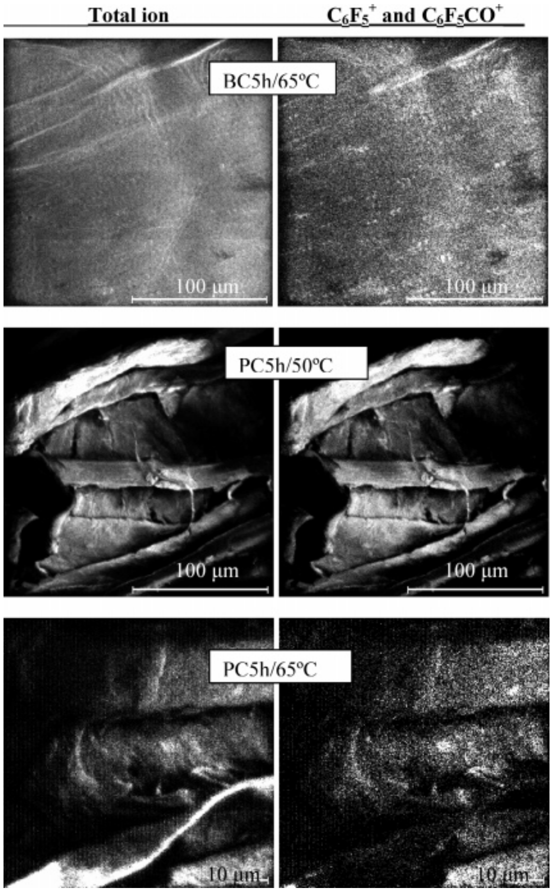


Figure 6. Total ion images and surface distribution of pentafluorobenzoyl moieties ($C_6F_5^+$ and $C_6F_5CO^+$) attached to the fibers' surface.

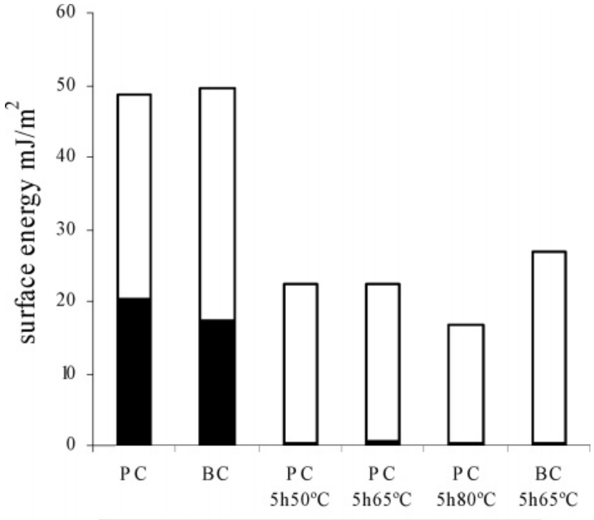


Figure 7. Variation of the surface energies of cellulose fibers after esterification.

Secondary ion mass spectra were recorded using a Physical Eletronics ToF-SIMS TRIFT II spectrometer. A primary ion beam of ^{69}Ga$^+$ liquid metal ion source (LIMS), with a 15 kV applied voltage, a 600 pA aperture current, and a bunched pulse width of 20 ns, was used in both positive and negative modes. A raster size of 200 × 200 μm^2 was scanned, and at least three different spots were analyzed. The surface distribution of the pentafluorobenzoyl moieties was obtained with the best spatial resolution using the ion gun operating at 25 kV, 600 pA aperture current, and an unbunched pulse width of 20 ns. The spectra

Table 1. XPS Results of Pristine and Modified PC and BC Fibers

		low-resolution XPS					high-resolution carbon				
sample	DS	[O]/%	[C]/%	[F]/%	O/C	F/C	[C1]/%	[C2]/%	[C3]/%	[C4]/%	[C−F]/%
PC		42.1	57.9		0.73		22.3	58.5	16.0	3.2	
BC		44.3	55.4		0.80		19.9	61.3	15.9	2.8	
PC, 5 h/50 °C	0.014	28.4	55.7	15.5	0.51	0.28	16.8	47.1	20.0	5.0	11.1
PC, 5 h/65 °C	0.23	22.9	53.4	21.7	0.4	0.41	7.8	45.4	24.3	8.9	13.6
PC, 5 h/80 °C	0.39	19.0	52.9	26.4	0.36	0.50	6.2	42.4	21.4	11.6	18.4
BC, 5 h/65 °C	0.16	34.1	48.7	12.5	0.70	0.26	10.1	54.7	18.5	4.6	12.1

Table 2. Contact Angles (θ, deg) for Different Liquids Placed on the Cellulose Substrates before and after Esterification

sample	DS	water	glycerol	formamide	diiodomethane
PC		56 ± 1	58[a]	33 ± 1	37 ± 2
BC		46 ± 0.1	63[a]	36 ± 0.1	40 ± 3
PC, 5 h/50 °C	0.014	120 ± 1	105 ± 2	96 ± 5	71 ± 6
PC, 5 h/65 °C	0.23	124 ± 2	108 ± 3	95 ± 6	73 ± 1
PC, 5 h/80 °C	0.39	128 ± 1	111 ± 6	107 ± 2	82 ± 2
BC, 5 h/65 °C	0.16	103 ± 2	90 ± 3	78 ± 4	64 ± 3

[a] These values are somewhat higher than those obtained with water, probably because of the high viscosity of glycerol.

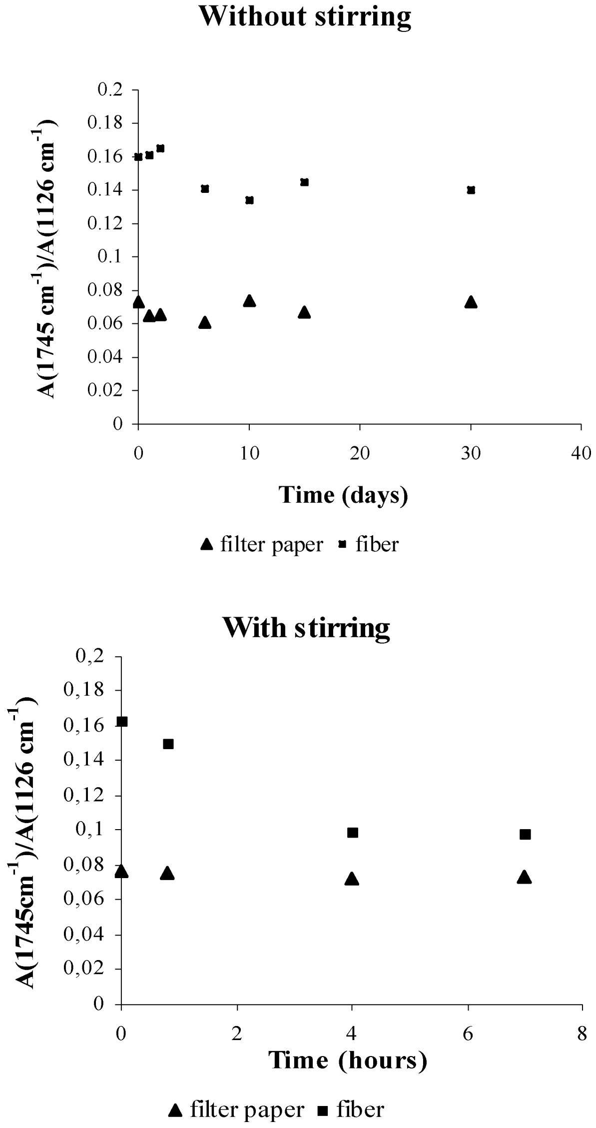
were acquired for 6 min with a fluency of $\sim$1012 ions/cm^2, ensuring static conditions. Charge compensation was achieved with an electron flood gun pulsed out of phase with respect to the ion gun.

Results and Discussion

In a first series of experiments, plant cellulose was esterified with pentafluorobenzoyl chloride at different reaction times and temperatures with the aim of studying the effect on the properties of the modified fibers. The success of the reactions, as well as their progress, was clearly confirmed by FTIR analysis, mainly on the basis of the appearance of a new carbonyl ester band at 1740 cm^{-1} (Figure 1). Additionally, the occurrence of new absorptions in the range 1000−1500 cm^{-1}, typical of C−F stretching modes and of the aromatic ring stretching vibrations,[19] gave further confirmation of the presence of fluorine-containing aromatic moieties.

These preliminary results showed that the reaction time had little effect on the extent of esterification, whereas temperature played a key role, particularly above 50 °C (Figure 1). For the characterization studies, three samples were chosen, namely, cellulose fibers treated for 5 h at 50, 65, and 80 °C, which gave DS values of 0.014, 0.23, and 0.39, respectively. Moreover, a sample of bacterial cellulose was reacted for 5 h at 65 °C (DS = 0.16). The somewhat lower DS value obtained with bacterial cellulose was attributed to a correspondingly lower accessibility of this substrate to the reagent, compared with that of the loose plant fibers, because of its more compact matlike morphology.

X-ray Diffraction. All pristine cellulose fibers displayed the typical XRD pattern of cellulose I, with the main diffraction signals at around $2\theta = 14.9°$, 16.3°, 22.5°, and 34.6°, assigned to the 101, 10$\bar{1}$, 002, and 040 diffraction planes, respectively. All the esterified fibers preserved this XRD pattern (Figure 2). In the case of the cellulose fibers esterified for 5 h at 80 °C, the reaction must have also involved hydroxyl groups of the amorphous regions of the inner layers, since the obtained DS values corresponded to more than 10% of the total hydroxyl groups borne by the fibers, whereas their surface counterparts represented less than 4%, as estimated from their average size.[20] It can be concluded that, with the more severe conditions, the esterification reaction proceeded beyond the fibers' surface through an in-depth attack of the amorphous cellulose chains.


Without stirring

With stirring

Figure 8. Variation of the extent of hydrolysis of the pentafluorobenzoyl groups as a function of time, stirring, and cellulose substrate.

Thermal Degradation. The thermal stability, as well as the TGA profile, of the modified fibers was, in general, very similar to that of the pristine substrates, as illustrated in Figure 3 for bacterial cellulose, showing the typical single weight loss feature, with a maximum decomposition temperature in the range of 340−370 °C, with the higher value for the modified fibers. Similar TGA tracings were obtained with plant fibers. The expected increase in thermal stability with fluorination was modest in the present context because of the correspondingly modest extent of fluorine incorporation.

The TGA results also indicated an increase in fiber hydrophobicity after modification, as shown by the absence of the

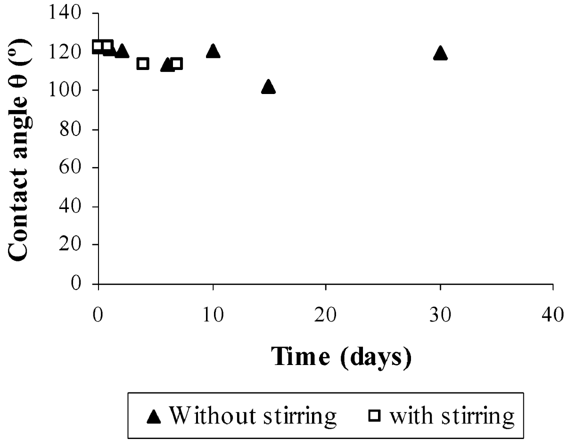


Figure 9. Variation of the contact angle with water as a function of hydrolysis time for cellulose fibers (filter paper) esterified for 5 h at 65 °C.

typical moisture loss around 100 °C, suggesting negligible water adsorption, compared with that of the pristine fibers (Figure 3).

Surface Characterization. *ToF-SIMS Analysis*. The ToF-SIMS spectra of all the untreated substrates showed the characteristic fragments at *m*/*z* 127 and 145, assigned to cellulose (Figure 4). In the case of the vegetable samples, secondary ions at *m*/*z* 115 and 133, typical of hemicelluloses, were also observed.

The spectra of the modified substrates clearly confirmed the presence of pentafluorobenzoyl moieties covalently bound to the fibers' surface, because of the dominance of secondary ions at *m*/*z* 167 $(C_6F_5)^+$ and 195 $(C_6F_5CO)^+$ (Figure 5), generated by the cleavage of the ester group. The absence of the quasimolecular ions $[C_6F_5COCl + H]^+$ at *m*/*z* 230, $[C_6F_5CO_2H + H]^+$ at *m*/*z* 213, and $[C_6F_5CO_2CH_2CH_3 + H]^+$ at *m*/*z* 213, indicated moreover that the removal of unbound pentafluorobenzoyl chloride, as well as the corresponding acid and ethyl ester, during the washing and extraction stages had been highly efficient.

ToF-SIMS imaging was used to study qualitatively the distribution (in terms of both homogeneity and extent of coverage) of the fluorinated moieties attached to the fibers' surface, by monitoring the $C_6F_5^+$ and $C_6F_5CO^+$ ions. Figure 6 clearly suggests that the distribution of the pentafluorobenzoyl moieties was, on the whole, quite heterogeneous and that an increase in the reaction temperature, particularly above 50 °C, gave rise to a dramatic increment in the extent of surface esterification, as already inferred from the IR analysis.

XPS Analysis. The surface chemical composition of the fibers before and after modification was also examined by XPS analysis, as summarized in Table 1. At low resolution, carbon and oxygen were the main elements detected in the unmodified cellulose samples (plant or bacterial), whereas the treated samples clearly showed the additional presence of fluorine, thus confirming the occurrence of the expected esterification reaction. In addition, the high-resolution deconvolution of the C1s peak revealed the increment of the contribution of C4 carbons (O−C═O) and the appearance of a new carbon environment, attributed to the C−F bonds (Table 1). The shakeup band of aromatic groups was also detected as a broad peak with low intensity at 295 eV.

The values of the C−F carbon contributions reflected the extent of surface coverage by the pentafluorobenzoyl groups. However, for cellulose fibers esterified at temperatures higher than 65 °C, the surface coverage increased only slightly with increasing DS, giving additional evidence in favor of in-depth esterification, following the consumption of the more accessible surface OH groups associated with the amorphous cellulose domains. These results are in good agreement with those obtained in our study of the esterification of cellulose fibers with fatty acid chlorides.[21,22]

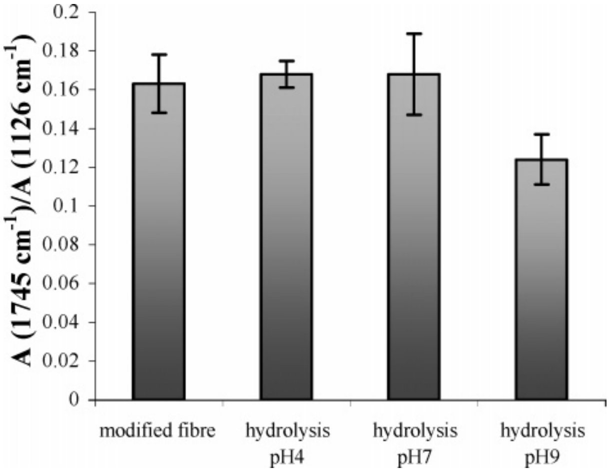


Figure 10. Hydrolysis of the pentafluorobenzoyl groups as a function of pH, as determined by FTIR, for cellulose fibers (PC) esterified for 5 h at 65 °C.

Contact Angles and Surface Energies. Table 2 gives the average contact angles measured with drops of liquids of different polarities deposited onto the pristine and modified substrates. The considerable increase in both the hydrophobicity and lipophobicity of the cellulose fibers, following the esterification with pentafluorobenzoyl chloride, was clearly demonstrated by the corresponding increase in contact angles with polar (water, glycerol, and formamide) and nonpolar (diiodomethane) liquids. This drastic change was expected on the basis of the well-known surface role of appended perfluoro moieties, but the fact that this biphobic character was already observed at low DS values suggested that a complete coverage of the fibers' surface with these moieties is not required for its manifestation. Indeed, further increases in the DS only produced minor increases in the values of the corresponding various contact angles, as shown in Table 2. This behavior had already been reported for cellulose fibers modified with trifluoroacetic anhydride.[7]

The value of the total surface energy of the modified fibers was ∼20 mJ/m^2, compared with ∼50 mJ/m^2 for the pristine substrates. This considerable decrease was induced mostly by the near elimination of the polar contribution brought about by the perfluorination of the fibers' surface, as shown unequivocally in Figure 7, although the dispersive contribution also decreased, albeit to a minor degree.

Hydrolytic Stability. It is well-known that perfluorinated esters, such as trifluoroacetates, are very sensitive to hydrolysis.[23] In the specific instance of cellulose derivatives, total hydrolysis with neutral water of highly substituted trifluoacetates, dissolved in DMF, only takes a few minutes.[8] In heterogeneous conditions, surface-trifluoroacetylated cellulose fibers (DS = 0.04) are completely hydrolyzed within 17 h.[7] It was therefore important to assess the hydrolytic stability of the materials prepared in this investigation.

The different pentafluorobenzoylated fibers were suspended in neutral water, at room temperature, and the extent of their hydrolysis was followed by FTIR through the decrease in the intensity of the carbonyl ester band at 1740 cm^{-1} and by measuring the contact angle formed with water.

The modified cellulose fibers were in general very stable toward hydrolysis when suspended in distilled water, with or without stirring. The pulp fibers were however moderately more sensitive to hydrolysis than the filter paper, particularly under vigorous stirring (Figure 8), where about 40% of the pentafluorobenzoyl groups were hydrolyzed within 4 days. This difference was attributed to a topochemical feature related to the lower accessibility of the hydrolyzable moieties in the case of the more compact morphology of the filter paper. Nevertheless, even in this case, the hydrophobic character of the fibers' surface was maintained, since the contact angles with water did not vary appreciably with time (Figure 9). The higher stability of these fluorinated cellulose derivatives, compared with their trifluoroacetylated counterparts,[7] is related to the fact that the fluorine atoms are not bound to the carbon atom directly linked to the carboxyl ester group.

Similar hydrolysis experiments (room temperature, 5 h, with stirring) were conducted in acidic (pH 4) and alkaline (pH 9) media. In the former conditions, no hydrolysis was detected, whereas in the alkaline conditions, ∼25% of the ester groups were removed (Figure 10), as indeed expected, at least qualitatively, with any ester. The total removal of the perfluoro moieties by base-catalyzed hydrolysis is therefore feasible, as previously reported for cellulose fatty acid esters.[24] These water-stable hydrophobic/lipophobic cellulose fibers can thus be readily recycled after their life cycle by regenerating their "normal" hydrophilic behavior through alkaline hydrolysis.

Conclusions

Both plant and bacterial cellulose fibers could readily be converted into highly hydrophobic and lipophobic materials by a simple esterification procedure involving a perfluorinated reagent. The resistance to hydrolysis of these modified cellulosic substrates is a key property in view of their potential applications in such major technologies as papermaking, packaging, and biomedical commodities. The fact that the perfluorinated moieties can be successfully removed in an aqueous alkaline medium constitutes an additional positive feature, since it ensures the straightforward repulping of these fibers. Work is in progress to enlarge our approach to this topic, through the use of a variety of novel perfluoro reagents.

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