Functionalization of Poly(ethylene terephthalate) Fibers by Photografting of a Carbohydrate Derivatized with a Phenyl Azide Group

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Grafting of a new carbohydrate UV-reactive molecule, an azidophenyl lactamine (AzPhLac), was achieved on fibers of three different diameters: 12, 18, and 32 μm. Adsorption of AzPhLac on fibers was obtained by using the dip-coating method in solution. The effect of the solution concentration on surface density and yield of grafted AzPhLac was investigated. Surface densities in the range 3−67 nmol/cm^2 were obtained without marked difference related to the diameter of the fiber. Quantitative grafting was obtained with a surface of fiber of 1 cm^2 and the lowest concentration (0.5 mM) of AzPhLac solution. The surface density and grafting yield decreased with the available surface of the fibers. This phenomenon could be attributed to a masking core−shell effect with outer fibers in the shell preventing the UV grafting of the fibers located in the core of the fibers' bundles. Scanning electron (SEM) and atomic force (AFM) microscopic observations suggested that homogeneous grafting might be obtained.

Introduction

Fiber-forming polymers are from either natural or synthetic origins. The most widely used synthetic polymer fibers are based on polyamides, polyesters, acrylics, polyolefins, polyurethanes, and certain vinyl derivatives. The chemical structures of these polymers give the necessary mechanical properties of a common polymer fiber, which are strength, stiffness, and low extensibility.[1]

The modification of polymer fibers to create new bioactive materials could be beneficial for a wide range of applications. For example, the current worldwide crisis in microbial infection and health care of wounds suggests that more research is necessary to understand practical and effective ways of creating safe bioactive textiles. The future development of biomedical and protective textiles with selective properties that benefit the consumer will be based on applying scientific and clinical advances in wound healing, antimicrobial, and enzyme-based fabrics.[2] The same kind of thinking can be applied to safety in the case of blood filtration, where white blood cells are removed to reduce the risk of infection. The appropriate modification of the blood filter could eventually solve the problem of future eventual blood infection. Polymer fibers have been used for a long time as blood filters.[3] The first polymer used was cotton. Usually, the kind of polymer and the design of the blood filters were chosen empirically. It was shown only recently that PET and polyimide fibers exhibit the highest leukocyte adhesion in a blood filter among other polymer fibers [polypropylene, poly(vinyl alcohol), and cellulose].[4] The efficiency of PET fibers as blood filter could be explained by the hydrophobic interaction between PET and integrin, a membrane protein of the white blood cell (WBC).[5] To improve the retention of WBC we have decided to modify PET fibers by incorporating a sialyl-Lewis^x oligosaccharide as it is known to interact specifically with L-selectin, another membrane protein of the WBC.[6]

On addition, the use of PET fibers presents other major advantages. PET fibers are often used in the biomedical field, for example, as implants, as vascular grafts for synthetic vessel replacement, or as cardiac heart valves.[7] Second, among all synthetic fibers, PET fibers have become the most dominant.[8] It now challenges cotton as the most common textile fiber. This is due to numerous advantages, including the cheapness and availability of the raw materials, the possibility to recycle PET fibers, the melt spinning process used for the production of PET fibers, which is clean and economical, the relatively high-temperature resistance, etc.

Last but not least, PET fibers are also good candidates for surface modification due to their geometrical and chemical structure. The possible modifications include chemical modifications[9] and modification by plasma discharge[10] or radiation.[11] The grafting method we used consists of the UV irradiation of a molecule containing a photoreactive aryl azide group coated on a polymer surface. Harmer[12] used simple molecules containing a heterocyclic azide group (for example, 3-azidopyridine), and Sugawara and Matsuda[13] used a polymer partially derivatized with a phenylazido group in its side chain. This method was also used to bind covalently carbohydrates[14] or polysaccharide[4] to polymer surfaces. In the case of organic azides (upon photolysis with ultraviolet light), a nitrene radical is generated. The nitrene radical formed is extremely reactive and can undergo a multitude of reactions, for example, insertion into C−H, N−H, and O−H bonds, addition to olefins, proton abstraction reactions to give the corresponding amine, and in the case of aryl azides a number of ring expansion reactions have been observed.[15] Although the precise mechanism of surface modification is not fully understood, this method has been demonstrated to be very effective for a wide range of surfaces (glass, polymer, tin oxide,

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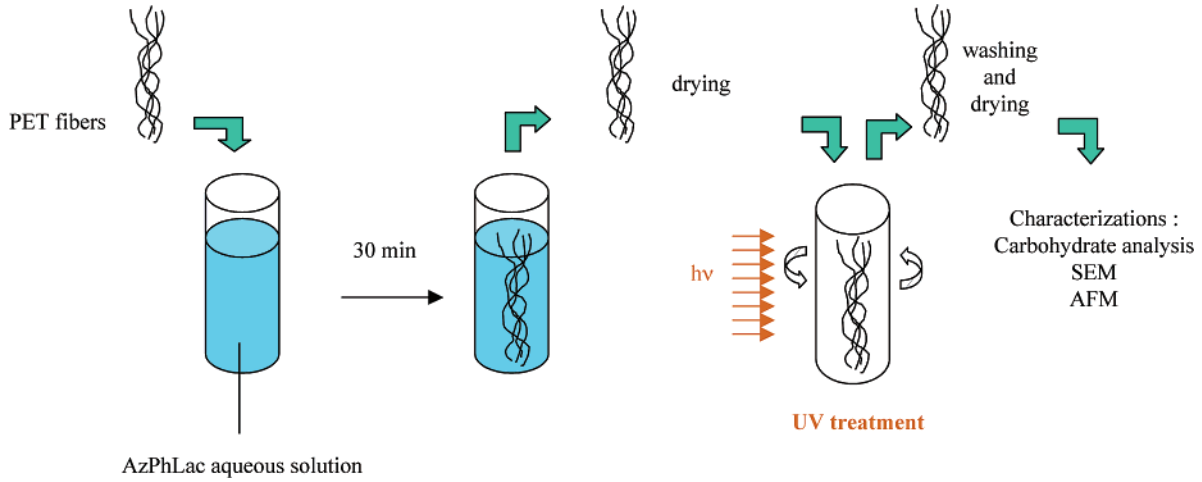
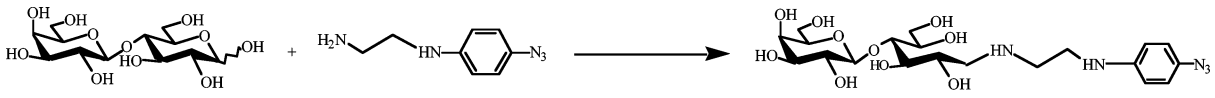


Figure 1. Procedure for grafting AzPhLac **1** on PET fibers.

Scheme 1. Synthesis of AzPhLac **1** by Reductive Amination of Lactose **2** by *N*-(*p*-Azidophenyl)-1,2-diaminoethane **3**



2 **3** **1**

silicon, and aluminum) with film thickness that can be varied from the region of monolayer to multilayer.[12]

In this work we have first synthetised the new UV-reactive carbohydrate molecule, the β-D-galactopyranosyl-(1−4)-1-*N*-[2-(4-azidophenylamino)ethylamino]-1-deoxy-D-glucitol (AzPhLac) compound **1**, by introducing the phenylazido group on lactose **2** by reductive amination of lactose with an aminated phenyl azide molecule **3** (Scheme 1).

Then we have found out optimal conditions to graft our model carbohydrate molecule on PET fibers. After an evaluation of the grafting efficiency by carbohydrate analysis, a study of the surface morphology has been undertaken by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Materials and Methods

Synthesis: (A) General Remarks. All moisture-sensitive reactions were performed under argon in oven-dried glassware. Anhydrous solvents were dried over standard drying reagents and freshly distilled prior to use. Reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 F_{254} or poly(ethylenimine) (PEI)−cellulose F. Detection was performed with UV light and/or 5% sulfuric acid in ethanol or 2% orcinol in ethanol or 10% phosphomolybdic acid in ethanol, followed by heating. Flash column chromatography was performed on silica gel 6−35 μm. ^{1}H and ^{13}C NMR spectra were recorded at room temperature unless otherwise specified. Chemical shifts are reported in parts per million, ppm (δ) versus Me_4Si when recorded in $CDCl_3$ or versus acetone when recorded in D_2O.

Compound **3** was synthesized according to Godovikova et al.[16]

(B) β-D-Galactopyranosyl-(1−4)-1-*N*-[2-(4-azidophenylamino)-ethylamino]-1-deoxy-D-glucitol (AzPhLac 1). Lactose (2 g, 5.64 mmol) and compound **3** (0.5 g, 2.82 mmol) were dissolved in 10:10:1 MeOH−H_2O−AcOH (21 mL). After 1 h, $NaBH_3CN$ (0.355 g, 5.64 mmol) was added and the mixture was heated at 40 °C in the dark. After 24 h, the solvent was evaporated to dryness under reduced pressure. Flash chromatography on silica gel (3:1:0.5 AcOEt−AcOH−H_2O) gave **1** (1.56 g, 2.5 mmol, 88% yield) as a brownish-orange solid. Compound **1** is obtained in its protonated form with acetate as counterion. R_f = 0.3 (3:1:1 AcOEt−AcOH−H_2O). ^{1}H NMR (250 MHz, D_2O) δ 1.9 (6H, acetate), δ 4.43 (d, H-1 gal, $J_{1,2}$ = 8 Hz), 6.70 (d, 2H-arom, J = 9 Hz), 6.84 (d, 2H-arom, J = 9 Hz). ^{13}C NMR (62.5 MHz, D_2O) 22.9 (CH_3 acetate), 40.0 (CH_2 amine), 46.6 (CH_2 amine), 49.8 (C-1 glc), 61.4 (C-6 gal), 62.1 (C-6 glc), 67.9 (C-2 glc), 68.9 (C-4 gal), 70.7 (C-3 glc), 71.2 (C-2 gal and C-5 glc), 72.6 (C-3 gal), 75.5 (C-5 gal), 78.5 (C-4 glc), 103.0 (C-1 gal), 115.3 (2C-arom), 120.3 (2C-arom), 130.2 (2C-arom), 144.8 (2C-arom), 180.5 (C=O acetate). IR (KBr pellet) 3369 and 2849 cm^{-1} (NH_2); 2114 cm^{-1} (N_3). ES$^+$ MS m/z = 504.2 (M + H$^+$), 526.2 (M + Na$^+$)

Materials: (A) PET Fibers. PET fibers were kindly provided by Tergal Fibers (Gauchy, France). Fibers with different diameters were used: 12, 18, and 32 μm. The Tex values, which represent the mass in grams of 1 km of PET fiber, are respectively 0.145, 0.33, and 1.1 g. The lengths of the 12, 18, and 32 μm fibers are 60, 55, and 80 mm, respectively. Fibers were Soxhlet-extracted in dichloromethane (CH_2Cl_2) for at least 16 h and dried in a desiccator before grafting.

(B) UV Grafting Procedure. A high-pressure mercury lamp (Heraeus TQ-150) with a broad emission spectrum (λ = 200−600 nm with a total radiation flux φ = 47 W and a radiation flux φ = 1.4 W at λ = 265 nm) was used at a distance of 15 cm from the polymer surface during an irradiation time of 10 min. The conditions were the same as those used previously by Knaus et al.[14b]

A known mass of fibers was soaked in a volume of 1 mL of aqueous solution of AzPhLac of different concentrations for 2 h. Fibers were then removed from the solution, dried overnight in air, and introduced into a quartz tube, which was itself fixed in a homemade setup to allow the slow rotation of the tube around its own axis to get more homogeneous irradiation of the fibers (Figure 1).

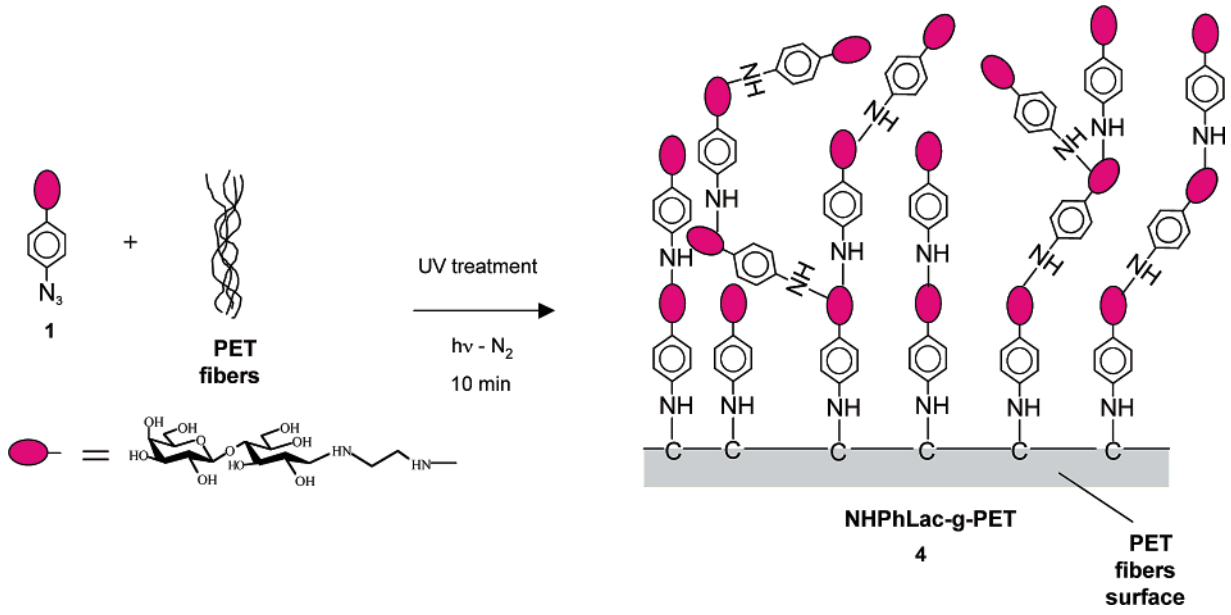
Methods: (A) Determination of Grafting Amount. After UV grafting, materials were washed in water (2 × 100 mL) to eliminate the nongrafted AzPhLac.

The amount of grafting was quantitatively obtained by cleaving using acidic conditions the remaining *O*-galactosyl linkage of the grafted AzPhLac molecule. Grafted materials were dipped in 3 mL of 2 M trifluoroacetic acid (TFA) for 2 h at 120 °C.

The free galactose was revealed by the phenol−sulfuric acid method[17] at a wavelength of 490 nm and by using galactose as standard.

For the grafting yield calculations, the quantity of adsorbed AzPhLac after dip-coating has been generally obtained by weighing. For S = 1 cm^2, owing to the lack of accuracy of the weighing method, the quantity of adsorbed AzPhLac after dip-coating was determined after the fibers were dipped in water, which resulted in the desorption of AzPhLac molecules, the amount of which was then characterized by the same carbohydrate analysis reported above.

Scheme 2. Surface Modification of PET Fibers after Grafting of AzPhLac



For the surface density determination, the fibers surface (S) was calculated from the surface of a cylinder $\pi \times D \times L$, where D is the fiber diameter and L is the total length of the fibers, which was obtained from the knowledge of the linear density (Tex value) after weighing the fiber mass (grams).

(B) Scanning Electron Microscopy. PET materials were glued on one face of a double-face carbon-coated cylindar piece of 3 mm in diameter and were then coated for 30 s by use of a carbon coater (Cressington). SEM was performed in a LEO 260 microscope equipped with a field emission gun.

(C) Atomic Force Microscopy. AFM observations were carried out in air at atmospheric pressure with a microscope PICO LE (Molecular Imaging, Tempe, AZ). AFM images were acquired exclusively in the tapping mode, with a silicon cantilever. For the analysis, one fiber is fixed on a mica support by gluing each extremity of the fiber with double-coated tape.

For a line containing N data points, the root-mean-squared (rms) roughness is given by the average deviation of the data, determined by the standard definition:

$$\mathrm{rms} = \sqrt{\frac{\sum_{i=1}^{N} (z_i - \bar{z})^2}{N - 1}}$$

where $\bar{z}$ = mean z height. The rms has been calculated on the total image sample after a second-order flatness treatment of the raw data to take into account the curvature of the fiber surface. Images have been recorded on different zones in order to be representative of the total sample surface state.

Results

(A) Comments on AzPhLac Synthesis and UV Reactivity. AzPhLac is obtained in high yield (88%) by reductive amination of lactose[18] with the UV-reactive phenyl azide molecule **2** (Scheme 1). The functionalization is carried out on the anomeric position of a rather simple carbohydrate. This model reaction will serve to modify complex oligosaccharides at their reducing end.

AzPhLac is characterized by an optimum absorption at 267 nm in aqueous solutions. This value is of the same order as compared with previous works using similar compounds.[19,20] The value of the molar extinction coefficient, measured in the concentration range 0.01−0.05 mM at a wavelength of 267 nm, is $\epsilon = 23\,000\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$. Figure 2 shows the corresponding absorption spectra in the range 200−600 nm of an AzPhLac solution ($C = 0.5$ mM) before and after UV irradiation for 10 min.

(B) Comments on the Grafting Procedure. As compared to a previous grafting procedure for carbohydrate phenyl azide molecules on polyolefin film,[14] our compound AzPhLac is only functionalized at its reducing end and not statistically distributed on all the hydroxy groups. That should enable us to introduce a complex oligosaccharide at one end by following the scheme illustrated in Scheme 2.

The carbohydrate molecule derivatized with a photoreactive phenylazido group is adsorbed by dip-coating on the fiber surface. To exclude reaction of water with the highly reactive nitrene, the solvent is evaporated.[21] UV light is then irradiated on the coated surface for chemical fixation of the lactamine moiety via conversion of the phenylazido group to the highly reactive phenylnitrene, which spontaneously forms covalent bonds with the neighboring hydrocarbon of the PET surface. The complete surface modification is still not fully understood; the proposed mechanism shown in Scheme 2 led to the formation of secondary amine **4**. The highly reactive phenylnitrene can form covalent bonds not only with the hydrocarbon of the PET surface but also with linkages of AzPhLac molecules in its immediate surroundings, leading to the formation of a polymeric multilayer (Scheme 2). In those conditions it is possible that the nitrene inserts onto the −OH groups. It is also obvious that the nitrene and ketenimime intermediates can lead to the formation of molecules[15,22] like amines, nitro, or nitroso not attached to the surface. However these free molecules must be removed by washing.

In fact the chemical structure of the grafted inner multilayer must be very complicated. But in our case, the preservation of the chemical structure of the carbohydrate moiety should be obtained, at least at the extreme surface of the grafted multilayer. That is the main point and interest of our grafting procedure. This seems not trivial in an energetic point of view. However, Kou et al.[10] gave some arguments to support this point of view. In a work where they performed the grafting of allyl-glucose (AG) on polypropylene hollow fibers, they showed that the static angle of pure water on the membrane decreased from 120° to

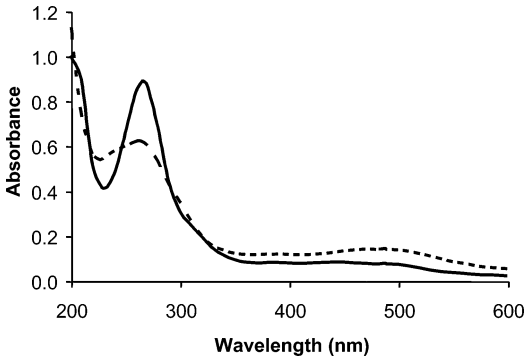


Figure 2. UV spectra of AzPhLac **1** solution (C = 0.05 mM) before (—) and after (---) a UV irradiation time of 10 min.

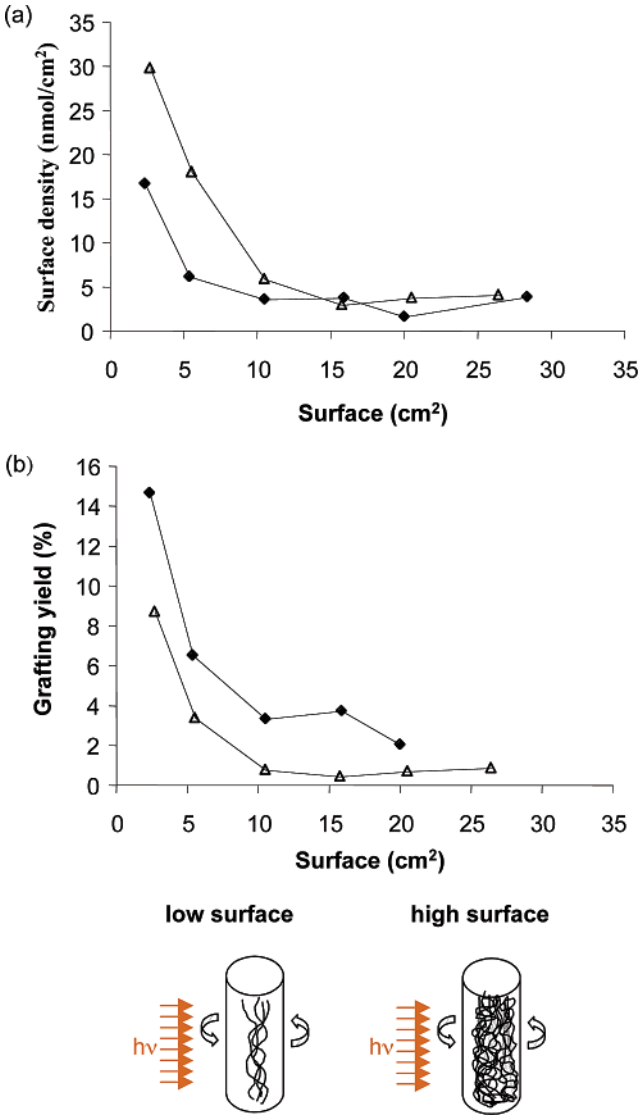
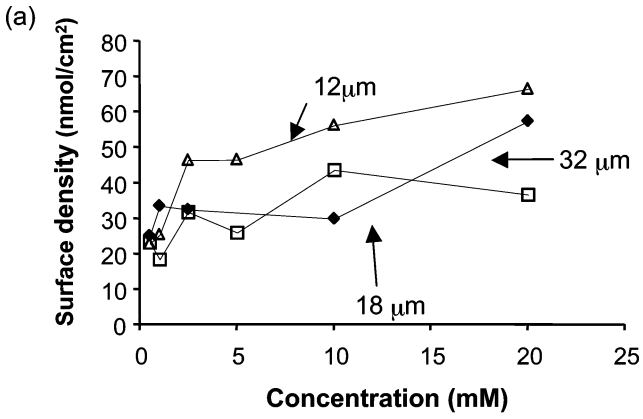


Figure 3. Surface density (a) and yield (b) of grafted AzPhLac on 12 μm PET fibers as a function of the surface of the fiber for different concentrations C of AzPhLac solutions: 5 mM (◆) and 30 mM (△). At the bottom: illustration of bundles of fibers for low and high surfaces.

36° with the increase of the AG grafting degree from 0 to 3.46 wt %. Most importantly, the contact-angle measurements also revealed that the hydrophilicity was permanent.

(C) Grafting Amount by Carbohydrate Analysis: *Surface Optimization.* Figure 3a shows the grafting surface density versus the accessible surfaces (S) of the 12 μm PET fibers for



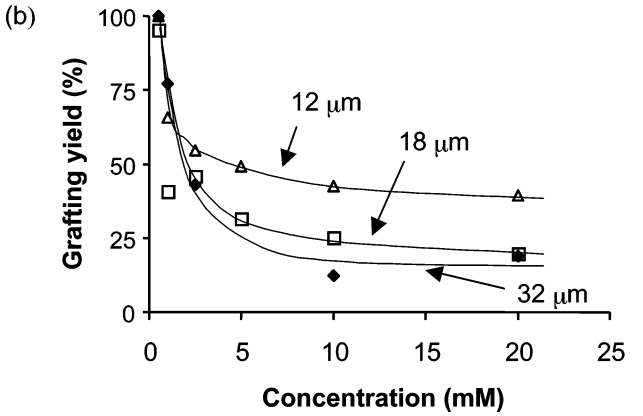


Figure 4. Surface density (a) and yield (b) of AzPhLac on PET fibers of different diameters, 12 (△), 18 (□), and 32 μm (◆), as a function of the concentration of AzPhLac solution for a fixed surface (S = 1 cm²).

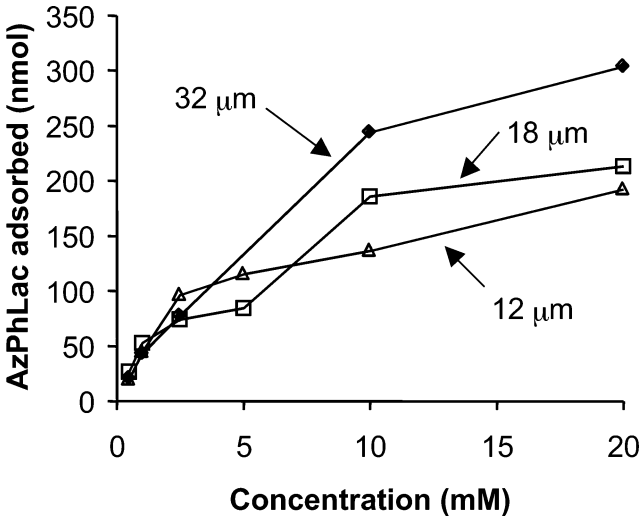


Figure 5. Adsorption of AzPhLac at the surface (1 cm²) of PET fibers of different diameters, 12 (△), 18 (□), and 32 μm (◆), as a function of AzPhLac concentration in solution.

two different concentrations (5 and 30 mM) of AzPhLac solution used for dipping the fibers. A clear dependence on C is observed for surface areas below 10 cm² : higher surface densities are obtained as C increases from 5 to 30 mM. The highest density value of 30 nmol/cm² is obtained for C = 30 mM and S = 2.5 cm². For S > 10 cm², surface density levels off down to 3−6 nmol/cm².

Grafting density values are in the range 3−30 nmol/cm². This is much higher than the grafting density calculated in the theoretical case of monolayer grafting. In that case, a surface

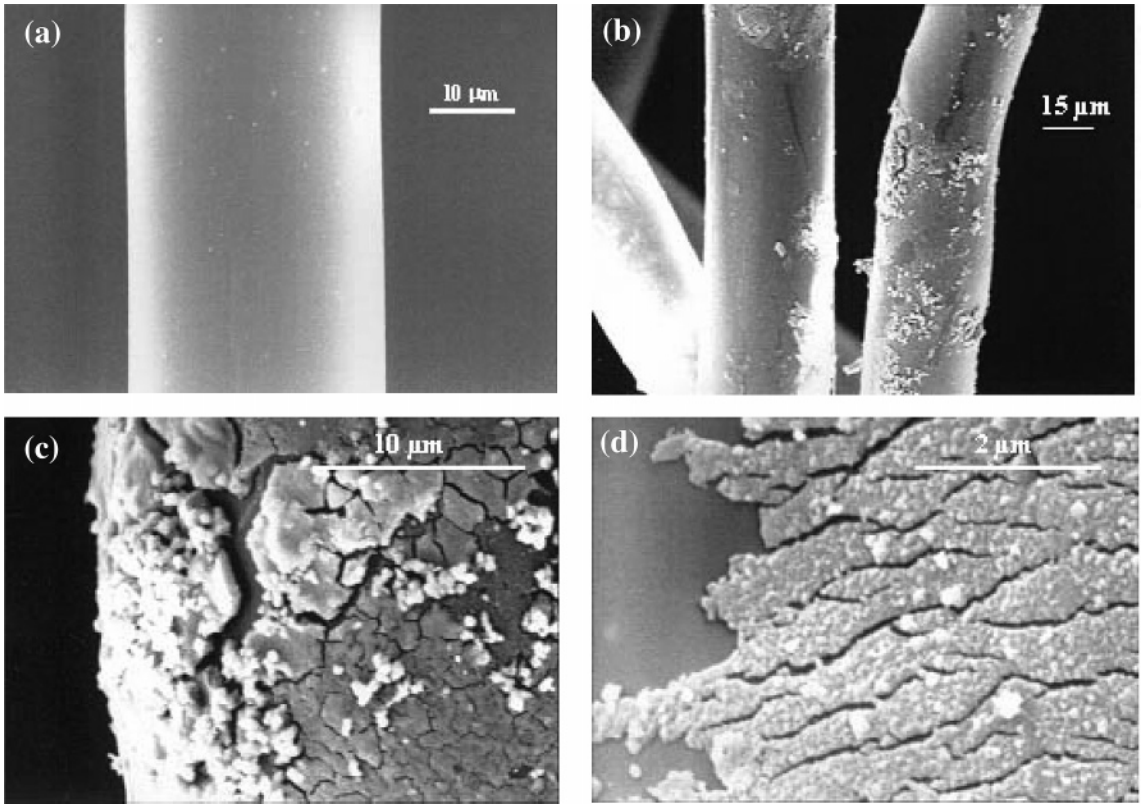


Figure 6. SEM images of 32 μm PET fibers: (a) virgin and (b−d) UV-treated with a grafting density of 35 nmol/cm^2 and then scraped on the sample holder to reveal the grafted layer.

density value in the range 0.2−0.8 nmol/cm^2 is expected depending on the position of the grafted AzPhLac molecule, lying flat on the surface or perpendicular to the surface. The higher experimental grafting density values confirm the polymeric nature of the grafted layer.

Under the investigated concentration conditions the grafting yield is very low, from 8−14% at 2.5 cm^2 down to nearly zero (Figure 3b). This could be attributed to a masking core−shell effect owing to the entanglement of PET fibers (see illustration, bottom of Figure 3). In this case, outer fibers in the shell prevent the UV grafting of the fibers located in the core by the very strong screening effect of PET for the far UV (<300 nm). This phenomenon seems to be even more pronounced as the surface of PET fibers increases.

The conclusion of this surface dependence study is that the lower the surface, the higher the density and the grafting yield. Therefore we decided to investigate the influence of the concentration of the AzPhLac solution on the grafting yield and surface density for a surface area of 1 cm^2 in the case of fibers of different diameters.

Concentration Optimization. To get a constant surface S = 1 cm^2, three corresponding masses of fiber were used, respectively 0.4, 0.6, and 1.1 mg for 12, 18, and 32 μm fibers.

In Figure 4a, it can be seen that the density increases steadily from 20 up to 50−65 nmol/cm^2 as the concentration increases from 0.5 up to 20 mM. The highest density value of 65 nmol/cm^2 is obtained for the 12 μm fiber. For concentrations higher than 1 mM, the highest density value is systematically obtained for the fiber with the smallest diameter (12 μm).

Considering now the grafting yield, it can be seen on Figure 4b that for a surface of 1 cm^2, the values are markedly improved with quantitative grafting for C = 0.5 mM. Then as C increases to 10−20 mM, grafting yield values decrease sharply down to 20% for 18 and 32 μm fibers and to a lower extent of 40% for the 12 μm fiber.

The main result of this study dealing with the concentration influence is that we have succeeded in finding optimal conditions to graft 100% of the adsorbed AzPhLac molecules. This is obtained for the lowest concentration, 0.5 mM, of the AzPhLac dipping solutions and a fiber surface of 1 cm^2 whatever the diameter of the fiber. This will be particularly important for grafting more complex carbohydrates of low availability.

Then we tried to explain the influence of the diameter of the fiber on the grafting characteristics (surface density and yield). Therefore, we investigated the quantity of adsorbed AzPhLac versus the concentration of AzPhLac dipping solution for the three different fibers (Figure 5). It can be seen that if there is no marked difference in the low concentration range up to 2.5 mM, at higher concentrations of 5, 10, and 20 mM the 32 μm fibers adsorb higher quantities of AzPhLac molecules than the two others. A higher quantity of matter implies a higher thickness of the adsorbed AzPhLac layer and a decrease of the efficiency of UV treatment. That is effectively what is observed in Figure 4b.

This behavior could be explained roughly on the basis of UV-depth penetration. When the layer made of the AzPhLac molecules adsorbed on the fibers is too thick compared with the maximum penetration depth of the UV radiation, the yield is low (high concentration range), and as the thickness of the layer decreases, the grafting increases (low concentration range).

In fact, the thickness of the deposit layer e_p is proportional to the mass uptake:

$$e_p = (D - D_0)/2 = V/S = m/(\rho S)$$

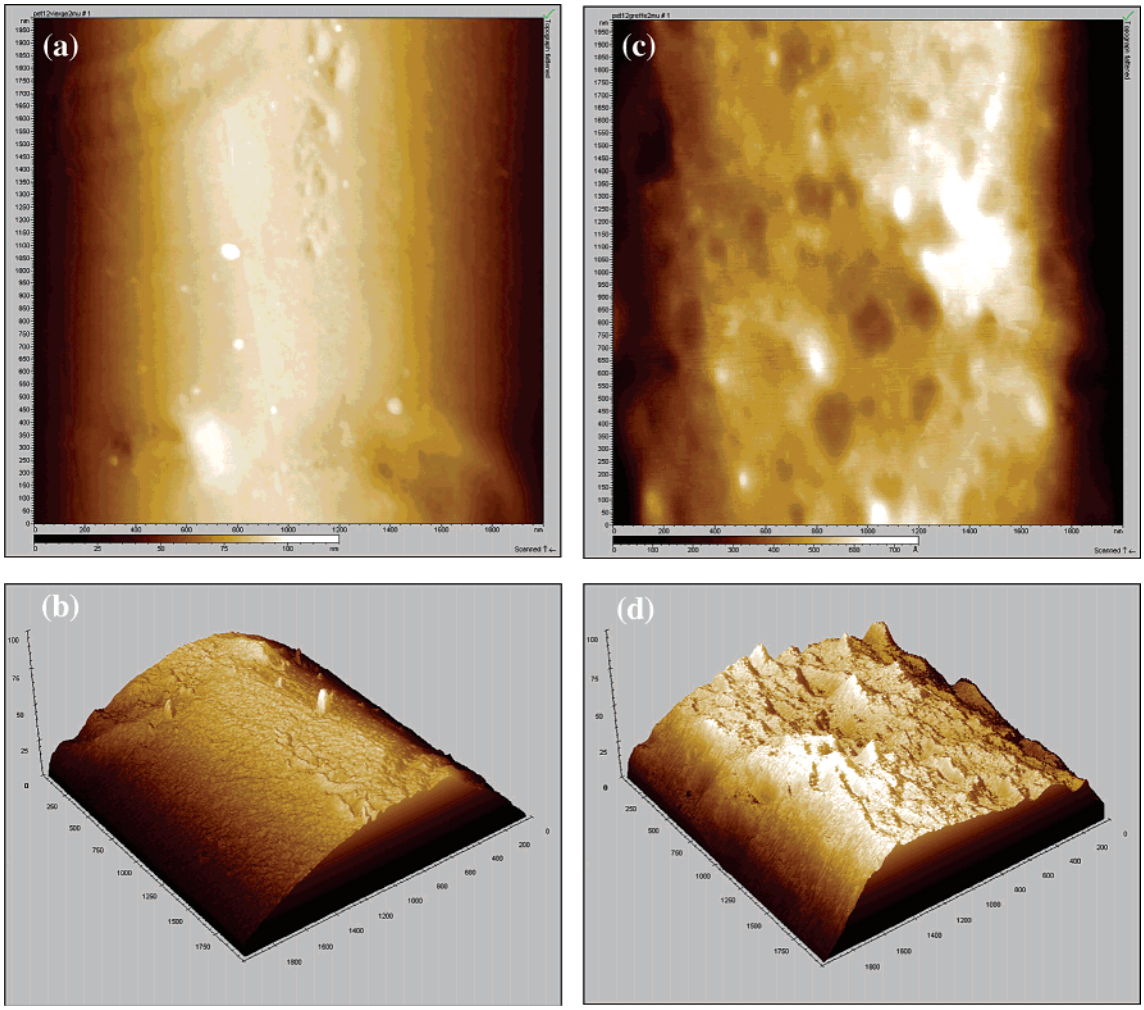


Figure 7. AFM images of 12 μm PET fibers: (a,b) virgin and (c,d) UV-treated with a grafting density of 67 nmol/cm^2.

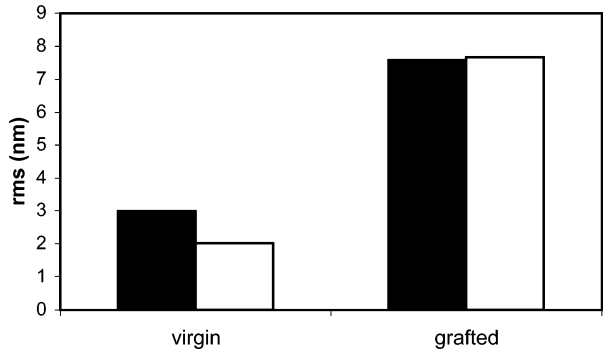


Figure 8. AFM rms of virgin and grafted 12 μm (■) and 32 μm (□) PET fibers.

where D_0 is the diameter of a virgin fiber; D is the diameter of the fiber after dip-coating, washing, and drying; m is the mass uptake; ρ is the density of AzPhLac; and S is the surface of the fiber.

For a density of 1.5 for AzPhLac and a surface $S \sim 1$ cm^2, it is possible to roughly estimate a value of the thickness of the dry deposit layer. For example, for the 12 μm fiber, the values of e_p are 80, 180, 400, 480, 570, and 800 nm for concentrations of the AzPhLac dipping solution of 0.5, 1, 2.5, 5, 10, and 20 mM, respectively.

Then it is possible to calculate the maximum penetration length of the UV treatment (e_p) by use of the Beer−Lambert law. Considering that the treatment is ineffective for a transmission of the initial UV radiation below 1% (corresponding to an absorbance $d_0 = 2$), taking a concentration calculated with a density value of 1.5, $c = 2.4$ mol/dm^3, and a molar absorption coefficient $\epsilon = 23\,000$ L·mol^{-1}·cm^{-1}, e_p reaches a value of 360 nm.

These values agree with the high grafting yield experimentally determined in the case of the lowest AzPhLac concentration. But if this model is simply applied, no grafting for a thickness of the deposit layer higher than 360 nm is expected, which is, however, not the case. Indeed, the grafting yield is higher than 50% for a calculated deposit layer of 400 nm. This result could be explained by a photobleaching phenomenon already observed during a photopolymerization process.[23] In fact, the above calculation of the theoretical grafted thickness was realized at 267 nm with the absorption coefficient $\epsilon = 23\,000$ L·mol^{-1}·cm^{-1} of the molecule before irradiation. This wavelength should mainly correspond to the aromatic group absorption but also to the azide group absorption. During the UV treatment, the disappearance of the azide groups leads to a decrease in absorbance (a decrease of 20% in optical density is observed in Figure 2 in the case of the UV irradiation of an AzPhLac aqueous solution), allowing an increase of UV light intensity crossing the AzPhLac layer and then of the photografted layer thickness.

(D) SEM Observations. Figure 6 shows the SEM images of 32 μm PET fibers. No differences are observed between washed virgin PET fibers (Figure 6a) and UV-grafted fibers with a grafting density of 35 nmol/cm^2. Statistically, no increase in fiber diameter is observed, and the surface seems not to be

affected by the grafting. Due to the polydispersity in size it was not possible to characterize an increment in size after grafting by this technique. But grafting can be further evidenced on damaged fibers obtained by just scraping the fibers glued on the sample holder. In these conditions heterogeneous surfaces are observed with both smooth areas and other areas coated by a crackled surface (Figure 6b−d). From Figure 6c, the depth between the top of the crackled layer and the smooth surface could be roughly estimated to be 300 nm. This value corresponds to the expected increase in diameter, which can be calculated from the mass uptake.

(E) AFM Experiments. Grafting was further evidenced by tapping-mode AFM experiments. Whereas a relatively flat surface is observed on the $2 \times 2\ \mu m^2$ AFM images of 12 μm virgin PET fibers (Figure 7a,b), a heterogeneous and rough surface is observed on a UV-treated 12 μm PET fiber with a grafting surface density of 67 nmol/cm^2 (Figure 7c,d). The same kind of observation has been obtained in the case of 32 μm PET fibers (AFM images not shown). Figure 8 shows that rms rugosity values of the two virgin fibers are in the range 2−3 nm with a slightly higher rugosity for the 12 μm fiber than for the 32 μm fiber. After grafting, rms value increases to the same value of 7.6−7.7 nm. On this basis, we can conclude that the two surfaces are similar after grafting and not influenced by the initial fiber diameter.

Conclusion

Grafting of a new carbohydrate UV-reactive molecule has been achieved on fibers of different nominal diameters by using the dip-coating approach. The effect of the solution concentration on surface density and yield of grafted AzPhLac led to the conclusion that a masking effect occurred during the UV treatment of the coated PET fiber. However, in optimized grafting conditions, SEM and AFM observations suggested that homogeneous grafting could be obtained. The best conditions were obtained by treating the lowest surface of PET fibers. Work in progress in our lab aims at optimizing the grafting conditions in order to obtain functionalized polymer surfaces on a larger scale. These studies involve either the use of other chemical and physical treatments and/or polymers with different chemical structures.

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