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# Facile grafting of bioactive cellulose derivatives onto PVC surfaces

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Bioactive methyl cellulose and hydroxyethyl cellulose were successfully grafted onto PVC films using a two-step pathway. PVC surface was first modified with isothiocyanate in DMSO/water medium. Then, unmodified polysaccharides were directly grafted onto the thiocyanated surface in acetonitrile/DMSO mixture, in presence of DBTL as catalyst. The polysaccharide grafting onto the PVC surface was evidenced by contact angle measurements, AFM and XPS.

## 1. Introduction

Biofilm formation and infection is a problem of major concern covering several applications fields, especially the Biomaterials one. In order to prevent this phenomenon, several strategies were developed in the past such as: antibiotic impregnation, surface coating by some metals like copper and silver or by some specific polymers like hydrogels. However, these techniques exhibited some disadvantages such as antibiotic exhaustion, appearance of bacteria resistance phenomena, physical instability and lost of the biological activity in the long term.

During the last decades, a promising strategy consisting in surface modification was developed. This strategy employed either physical treatment such as plasma, or direct chemical treatment such as grafting of specific species and functionalities. In this context, the wet-chemical process has been found to be the best pathway to control the surface chemical and physical properties, in particular when active polymers are grafted onto the surface. Indeed, comparing to small molecules, polymer grafting offers numerous advantages such as surface stability and longevity, high surface coating and high bioactivity.

Polyvinyl chloride (PVC) is one of the most important polymers thanks to its versatile physico-chemical and biological properties. PVC is employed in various applications such as construction, packaging and medical devices. Many medical articles are based on PVC such as: blood bags, indwelling catheters, urinary catheters etc.

Polysaccharides represent a major natural, renewable and available resource in the polymer field. Their applications vary from textile [1,2] to medical systems [3–15]. They are non-toxic, biocompatible, often biodegradable and water soluble. Such properties make them suitable for many uses in the biomedical field, health care, or drug delivery systems [3]. As example, heparin and chitosan, are used to improve biocompatibility and/or to prevent attachment of bacteria, blood platelets or proteins onto biomaterial surfaces [4–15]. Recently, cellulose derivatives, especially methyl celluloses, have been described as potent bacteria repellents when they are grafted onto a silicone surface [12].

Nevertheless, in the literature only few examples describe the grafting of polysaccharides onto PVC surfaces. Mao et al. [13] grafted *O*-butyrylchitosan (OBSC) onto PVC surface in order to improve blood compatibility. OBSC was first bound to 4-azidobenzoic acid, coated on the PVC film surface and then, it was covalently immobilized by ultraviolet irradiations. In order to prevent bacteria attachment, Asadinezhad et al. [14] functionalized PVC surface by a multistep procedure. In a first step, the surface was activated by discharge plasma in air. Then, acrylic acid was polymerized from the surface via a radical graft copolymerization and in a final step chitosan layers were grafted onto the surface by amidification. With the aim of mimicking the nonthrombogenic properties of the endothelial cell, Zhou et al. [15] reported the development of a new generation of NO release polymeric coatings that employ NO release chemistry in combination with surface immobilized active heparin. Heparin was grafted onto aminated PVC after modification of the polysaccharide chains with *N*-hydroxysuccinimide, using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide as coupling agent. All these examples support the need of alternative procedures to graft polysaccharides onto PVC.

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Herein, we describe a simple and an alternative procedure for the grafting of polysaccharides onto PVC surfaces. First, isothiocyanate groups (NCS) were introduced onto PVC surfaces using potassium thiocyanate in a water/DMSO mixture. These groups are analogue to isocyanate (NCO) groups, and are commonly present in fluorescent probes for protein labelling. Then, cellulose derivatives exhibiting bacteria repellent properties [12] were directly grafted onto PVC-NCS surfaces in presence of a catalyst. The grafting efficiency was assessed by mean of contact angle measurements, XPS and AFM analysis.

## 2. Experimental

### 2.1. Materials

Commercial bulk polymerized PVC was obtained from Sigma-Aldrich, Lyon, France. The average molecular weights determined by SEC were  $\bar{M}_n = 47000$  g/mol and  $\bar{M}_w = 80000$  g/mol. Methyl cellulose (DS = 1.5–1.9), hydroxyethyl cellulose (DS = 1.6) and tetrabutylammonium hydroxide (TBAH, 40 wt% in water) were purchased from Sigma-Aldrich. Potassium thiocyanate was purchased from Merck.

### 2.2. Characterizations

NMR spectra were recorded on a Bruker Avance (300 MHz) Spectrometer.

IR spectra were recorded on a FTIR (Perkin-Elmer) equipped with a diamond ATR device (attenuated total reflection).

XPS measurements were carried out at room temperature. An Axis Nova instrument from Kratos Analytical spectrometer with Al K $\alpha$  line (1486.6 eV) as excitation source has been used. The core level spectra were acquired with an energy step of 0.1 eV and using a constant pass energy mode of 20 eV, to obtain data in a reasonable experimental time (energy resolution of 0.4 eV). The pressure in the analysis chamber was maintained lower than  $10^{-7}$  Pa. The background spectra were considered as Shirley type and curve fitting was achieved with a mixture of Gaussian-Lorentzian functions [16]. The error in defining the position of peaks was estimated at about 0.1 eV. No surface cleaning, using Ar sputtering for example was made. We know from experience that carbonaceous atmospheric contamination on material usually occurs, but in our case, ion sputtering can be suspected of changing chemical composition and inducing structural damage.

Surface energy of the materials were evaluated using Digidrop Goniometer (GBX, France), by static contact angle ( $\theta_i$ ) measurements on the sample surfaces with 3 liquids: water, diiodomethane and glycerol. The static contact angles were measured at the equilibrium time. At least, five measurements on different surfaces were performed to calculate the mean contact angle and its standard deviation. According to the Owens-Wendt relationship (1) the dispersive  $\gamma_s^d$  and polar  $\gamma_s^p$  components of the surface energies ( $\gamma_s = \gamma_s^d + \gamma_s^p$ ) of the samples were determined.

$$\frac{(1 + \cos \theta_i)\gamma_i}{2\sqrt{\gamma_i^d}} = \sqrt{\gamma_s^p} \times \sqrt{\frac{\gamma_i^p}{\gamma_i^d}} + \sqrt{\gamma_s^d} \quad (1)$$

where  $\gamma_i$ ,  $\gamma_i^d$ ,  $\gamma_i^p$  are the solvent superficial tension parameters.

Surface polarities (P) of the materials are calculated using Eq. (2):

$$P = \frac{\gamma_s^p}{\gamma_s} \times 100 \quad (2)$$

An AFM microscope (JPK instruments, NanoWizard, Berlin, Germany) was used for imaging and roughness measurements.

AFM images were obtained by using the intermittent contact mode AFM in air. Classical silicon cantilevers were used (NanoWorld Pointprobe® NCHR). The average force constant and resonance were approximately 42 N/m and 320 kHz, respectively. Topographic images were taken at different locations on the surface, in order to account for any heterogeneity in the coverage of the polysaccharides. AFM data were analyzed by the software SPM Image Processing v.3 from JPK Instruments, to extract the surface roughness (calculated on a  $10 \mu\text{m}^2$  area).

### 2.3. Preparation of PVC films

About 1 g of PVC powder was dissolved in 40 mL of dichloromethane and poured into a Teflon mould. PVC films were then obtained by slow solvent evaporation under nitrogen atmosphere.

### 2.4. Preparation of PVC-isothiocyanate surfaces (PVC-NCS)

In a round bottom flask, KSCN ( $9.0 \times 10^{-2}$  mol) and TBAH ( $4.5 \times 10^{-2}$  mol) were dissolved in a 60 mL of DMSO/water (4/1) mixture. PVC sheets (1 cm  $\times$  1 cm) were immersed and the medium was heated at 60 °C for 17 h under slow-stirring. Then, the PVC sheets were thoroughly washed with water, rinsed with diethyl ether and dried at 60 °C. The same reaction mixture could be recycled 4–5 times.

FTIR:  $\nu_{\text{max}}/\text{cm}^{-1}$  . . . 2150 (S–CN), 2051 (N=C=S), 1600 (C=C).

### 2.5. Grafting of polysaccharides onto PVC-NCS surfaces

In a round bottom flask equipped with a magnetic stirrer, 12 mg of polysaccharide were dissolved in 2 mL of DMSO at room temperature. Then, 4–12 mL (Table 1) of acetonitrile were added and the mixture was heated to 60 °C. Then, 0.05 equivalent of DBTL with regards to the polysaccharide hydroxyl groups were added. After, PVC sheets were immersed in this solution under gentle stirring for 24 h. The treated PVC films were washed several times with water and then put in water bath under ultra sound (30 min), rinsed with diethyl ether and dried at 60 °C.

## 3. Results and discussion

### 3.1. Preparation of grafted and ungrafted PVC-NCS surfaces

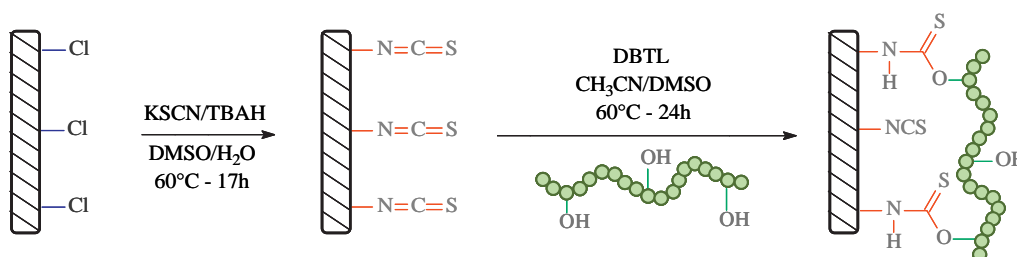
The common strategy to directly graft a polysaccharide onto polymer surfaces consists in esterification reaction between the polysaccharide hydroxyl groups and surface carboxyl groups, in presence of coupling agents such as *N,N*-dicyclohexylcarbodiimide (DCC) or *N,N'*-carboimidazole (CDI). In this study, an original procedure involving isothiocyanate groups was developed since these groups are easier to introduce onto the PVC chains compared to carboxyl groups. The chemical grafting of polysaccharides onto PVC surfaces was achieved in two steps (Scheme 1).

In a first step, isothiocyanate groups were introduced onto PVC surfaces. Actually, the reaction of thiocyanates with an alkyl halide is a nucleophilic substitution (SN2) that results in the formation of the corresponding alkyl isothiocyanate. The reaction proceeds in homogenous or heterogeneous conditions and may be applied to polymers as well. Thus, it has been shown [17] that thiocyanation of PVC surfaces can be achieved in a solid/liquid two phase system in the presence of a phase transfer catalyst in aqueous media. A similar heterogeneous procedure was used herein to apply the reaction to the PVC surface. Chloride groups were substituted by isothiocyanate groups (–NCS) using KSCN, in the presence of TBAH as phase transfer catalyst in a DMSO/water (4/1) mixture.

**Table 1**  
Experimental conditions and static contact angle data relative to PVC surfaces.

Entry	Surface	$M_w$ (g/mol)	DBTL (equiv./OH)	CH <sub>3</sub> CN/DMSO (v/v)	Static $\theta_{\text{water}}$ (°) <sup>a</sup>	$\gamma^d$ (mN/m) <sup>a</sup>	$\gamma^p$ (mN/m) <sup>a</sup>	Polarity (%)
1	PVC	/	/	/	89 ± 5	42.2 ± 0.2	1.0 ± 0.8	2.3 ± 1.8
2	PVC-NCS	/	/	0/0; 2/1; 4/1; 6/1	44 ± 2	38.9 ± 1.3	18.9 ± 0.1	32.7 ± 0.7
3	PVC-MeC 1	41,000	0.00	6/1	47 ± 2	36.9 ± 0.7	18.1 ± 0.1	32.9 ± 0.3
4	PVC-MeC 1	41,000	0.02	6/1	45 ± 1	38.6 ± 3.2	19.9 ± 0.3	34.0 ± 2.1
5	PVC-MeC 1	41,000	0.05	6/1	59 ± 2	39.0 ± 1.6	11.9 ± 0.2	23.4 ± 0.9
6	PVC-MeC 2	88,000	0.00	2/1	48 ± 2	38.7 ± 0.4	17.6 ± 0.6	31.3 ± 0.6
7	PVC-MeC 2	88,000	0.05	2/1	60 ± 4	37.4 ± 0.5	11.0 ± 1.4	22.7 ± 2.4
8	PVC-HEC 1	720,000	0.00	2/1	43 ± 2	38.3 ± 0.4	19.4 ± 0.3	33.6 ± 0.2
9	PVC-HEC 1	720,000	0.02	2/1	45 ± 1	37.4 ± 0.3	19.2 ± 0.2	33.9 ± 0.1
10	PVC-HEC 1	720,000	0.05	2/1	65 ± 2	41.4 ± 0.4	7.1 ± 0.9	14.6 ± 0.9
11	PVC-HEC 2	250,000	0.00	4/1	41 ± 3	40.2 ± 0.8	18.7 ± 0.5	31.7 ± 0.7
12	PVC-HEC 2	250,000	0.05	4/1	55 ± 1	37.8 ± 0.8	13.6 ± 0.4	26.5 ± 1.4

<sup>a</sup>  $\theta_{\text{water}}$ : contact angle with water;  $\gamma^d$ : dispersive component of the surface energy;  $\gamma^p$ : polar component of the surface energy.



**Scheme 1.** The chemical pathway used to graft polysaccharides onto PVC surface.

In a second step, methylcellulose and hydroxyethylcellulose with different molecular weights were dissolved at a concentration of 1 mg/mL in appropriate acetonitrile/DMSO mixtures in which the PVC films was not dissolved or damaged (Table 1). Then, an optimal amount of a catalyst, i.e., dibutyltin dilaurate (DBTL), was added (Table 1). After, the PVC-NCS samples were immersed in the polysaccharide solution during 24 h at 60 °C, to allow the chemical grafting. The obtained PVC grafted polysaccharide surfaces were thoroughly cleaned before characterizations.

### 3.2. Surface characterisations

#### 3.2.1. Contact angle measurements

The contact angle measurement was a quick, simple and efficient method to control the chemical grafting of polysaccharides onto the PVC-NCS surface and to optimize the experimental conditions.

Static contact angles with water as well as surface energies and polarities of the modified and unmodified PVC surfaces are reported in Table 1.

Comparing to PVC surface, the PVC-NCS surface showed a significant decrease of the static contact angle with water, i.e., from 89° to 44°, indicating that thiocyanation increased considerably the hydrophilicity of the PVC surface. In addition, the polar component of the surface energy increased from 1 to 19 mN/m and the surface polarity increased from 2.3% to 32.7% (Table 1, entries 1 and 2).

Static contact angles with water of PVC-NCS surfaces that were in contact with polysaccharides were dependent on the amount of DBTL with regards to polysaccharide hydroxyl groups. For 0 and 0.02 equiv. of DBTL/OH (Table 1, entries 3, 4, 6, 8, 9 and 11), one can observe that the contact angle as well as surface energy and polarity were very close to those of the PVC-NCS surface (Table 1, entry 2), which suggest that chemical grafting did not happen in these conditions. For 0.05 equiv. of DBTL/OH (Table 1, entries 5, 7, 10 and 12), the surface properties changed significantly, suggesting that the chemical grafting of polysaccharide onto the PVC-NCS surfaces were successful. Actually, the two methylcellulose surfaces

exhibited similar properties, i.e., contact angles with water around 60° and polarities around 23%. However, hydroxyethyl cellulose surfaces were different; the PVC-HEC1 surface exhibited higher contact angle (65° against 55°) and lower polarity (14.6% against 26.5%) comparing to PVC-HEC 2. Overall, the grafted surfaces were less -but still- hydrophilic and less polar than the ungrafted PVC-NCS surface. These grafted surfaces were then characterized by FTIR, XPS and AFM.

Dynamic contact angle with water was also performed to assess the surface wettability (Table 2). The AA is characteristic of the wettability of the low-energy or hydrophobic part of the surface whereas the RA is more characteristic of the high-energy or hydrophilic part.

Native PVC surface exhibited AA around 90° and RA around 43°. After thiocyanation, the AA and RA decreased dramatically and the balance between the two parts was also reduced as suggested by the decrease of hysteresis value from 48° to 33° (Table 2, entries 1 and 2).

PVC-NCS surfaces grafted with polysaccharides exhibited AA very close to static angle, whereas RA was in the range of 15–20° (Table 2, entries 3–6). Thus, hysteresis values ranged from 35° to 47° and were consequently higher than the PVC-NCS hysteresis (33°). This behaviour is likely to be associated with the hydrophobic backbone of the polymer chains that increase the

**Table 2**

Dynamic contact angle data relative to PVC-NCS surfaces grafted with polysaccharide in presence of 0.05 equiv. of DBTL.

Entry	Surface	Dynamic $\theta_{\text{water}}$ (°)		
		AA	RA	Hyst
1	PVC (control 1)	90 ± 3	43 ± 5	48 ± 2
2	PVC-NCS (control 2)	46 ± 2	13 ± 2	33 ± 3
3	PVC-MeC 1	60 ± 1	15 ± 1	44 ± 1
4	PVC-MeC 2	60 ± 1	16 ± 1	45 ± 1
5	PVC-HEC 1	66 ± 1	19 ± 1	46 ± 1
6	PVC-HEC 2	53 ± 1	20 ± 1	33 ± 2

AA: advancing angle; RA: receding angle; Hyst: hysteresis.

**Table 3**  
XPS data of the prepared surfaces: elemental analysis; peak assignment and contribution.

Chemical state	Binding energy (eV)	PVC	PVC-NCS	PVC-MeCell 1	PVC-MeCell 2	PVC-HEC 1	PVC-HEC 2
% C	-	66.6	81.7	66.7	67.3	70.9	63.8
C-(C,H), C=C	284-285	52.9	64.5	61.9	65.6	59.2	68.4
C-S, C-O, C-N, C-Cl, C-C ring	286.4	47.1	17.2	25.5	23.0	26.8	21.1
O-C-O	287.7	/	/	6.0	5.4	6.3	5.0
(C=O)-O-, (C=O)-NH, NH-(C=S)-O	288.9	/	/	6.6	5.9	6.9	5.5
% O	-	0	<1*	16.3	16.4	13.9	15.8
-(C=O)-NH, (C=O)-O-	531.6	/	/	32.3	27.5	28.2	32.8
C-O-C, C-O-H	532.2	/	100	35.3	45.0	46.4	34.5
-(C=O)-O	533.4	/	/	32.3	27.5	28.2	32.8
% N	-	0	1.5	1.7	1.5	1.5	1.6
SCN <sup>-</sup>	394.8	/	5.6	6.3	5.3	0.0	0.0
-N=C=S, (C=O)NH-S-C≡N, (C=S)NH	399.9	/	74.2	69.6	63.0	61.5	74.5
C-N <sup>+</sup>	401.5	/	20.2	24.6	31.7	38.5	25.5
% S	-	0	1.3	1.4	1.6	1.2	1.6
C-S-CN, SCN <sup>-</sup>	136.8	/	52.7	40.9	48.7	45.1	31.5
>C=S	168.1	/	47.3	59.1	51.3	54.9	68.5
% Cl	-	33.4	15.5	12.0	10.4	10.3	15.9

hydrophilic-hydrophobic balance of the surface. Besides, hysteresis can also be explained by surface heterogeneity, texture and roughness.

### 3.2.2. Spectroscopic analysis

The thiocyanation of PVC surface was followed by ATR-FTIR. The appearance of a new band at  $\sim 2050\text{ cm}^{-1}$  attributed to isothiocyanate groups, according to literature [18], indicated once again that the reaction was successful. The detection of this band by this technique showed that the NCS groups were grafted on a PVC surface zone of  $3\ \mu\text{m}$  of depth at least. This probably resulted from surface swelling in the DMSO/acetonitrile medium, which allowed the penetration of the thiocyanate ions. However, because of their big hydrodynamic volume, polysaccharides were only grafted on the extreme surface and were therefore not detected by this technique.

The elemental compositions of the grafted surfaces and their controls (PVC and PVC-NCS), were determined by XPS analysis. Results are shown in Table 3.

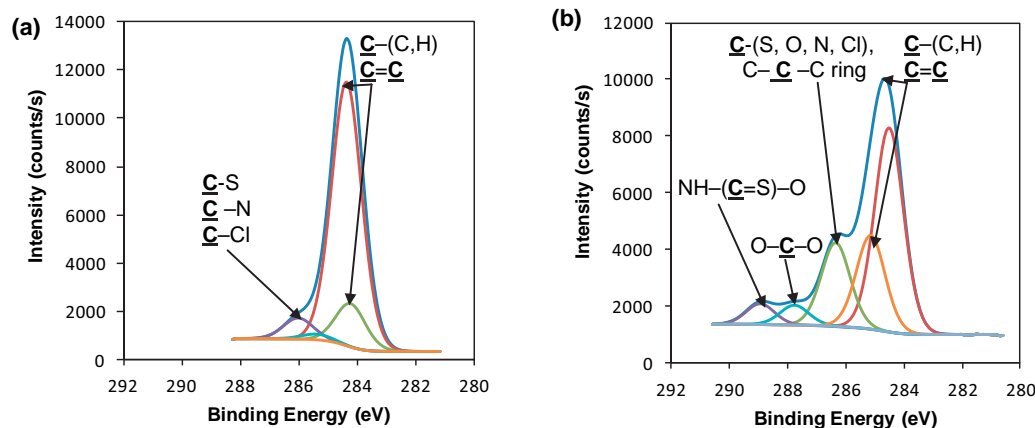
As expected, XPS survey scans obtained from the PVC surface gave two signals corresponding to C and Cl with contributions of 66.6% and 33.4%, respectively. The elemental analysis of the PVC-NCS surface confirmed the presence of N (1.5%) and S (1.3%) coming from the isothiocyanate groups. However, the percentage of Cl decreased (15.5%) suggesting an elimination of HCl (PVC dechlorination), which was not observed by FTIR. Kameda et al. [18] also observed this side reaction and have shown that the presence of phase transfer agents, such as TBAH, largely favoured the

substitution reaction over the elimination one. The elemental analysis of the grafted surfaces showed the presence of O with abundance around 15%, suggesting the presence of polysaccharides.

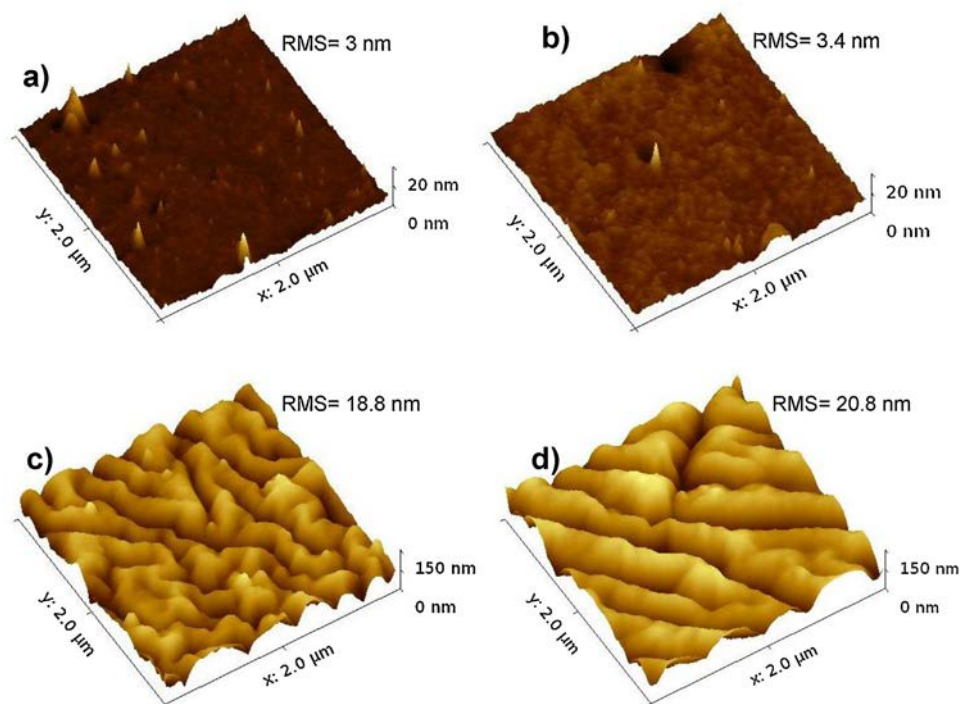
The XPS survey scans for the main components were analyzed to assign the peaks  $C_{1s}$ ,  $N_{1s}$  and  $S_{2p}$  to chemical functions (Table 3). Typical examples of  $C_{1s}$  high resolution XPS spectra are presented in Fig. 1.

For PVC-NCS surface, the  $C_{1s}$  peak was decomposed into four peaks. The peaks ranging from 284 to 285 eV are ascribed to C of saturated and unsaturated hydrocarbon chains. The peak at 286.4 eV is attributed to C making single bonds with N, S or Cl. The contribution of this peak is weak (15.5%) confirming the elimination of Cl during chemical treatment. The high resolution XPS spectra of the  $N_{1s}$  region revealed three peaks. The peak at 394.8 eV is owing to residual thiocyanate ions adsorbed onto the surface. The peak at 399.9 eV is ascribed to grafted isothiocyanate groups. The peak at 401.5 eV is due to ammonium groups of residual TBAH, which exhibited also a very weak signal at 532.2 eV, undetectable in the survey spectra (<1%). The high resolution XPS spectra of the  $S_{2p}$  region revealed two peaks; each peak corresponds to two spin-orbit transitions. The main spin-orbit transition 3/2 was used for quantification. The peak at 163.8 eV is ascribed to the S in thiocyanate groups and residual thiocyanate ions. The peak at 168.1 eV is ascribed to the S in isothiocyanate groups.

The PVC-NCS surfaces grafted with polysaccharides exhibited a  $C_{1s}$  peak at 286.4 eV with increased intensity because of the supplemental contribution of carbons of C-O and C-C bonds from polysaccharides rings. This peak contribution varied from 21% to



**Fig. 1.** XPS high resolution spectra of the  $C_{1s}$  region: (a) PVC-NCS and (b) PVC-MeC 2.



**Fig. 2.** IC-AFM height images ( $10\ \mu\text{m} \times 10\ \mu\text{m}$ ) of (a) PVC, (b) PVC-NCS and (c) PVC-HEC 1, (d) PVC-Mec 1.

27% where about 17% was due to the surface control (PVC-NCS). In addition, two supplemental peaks were observed in the  $C_{1s}$  region, the peak at 287.7 eV was ascribed to C in acetal or hemiacetal functions in polysaccharides. The peak at 288.9 eV was attributed to C in the thiocarbamate links ( $\text{NH}-(\text{C}=\text{S})-\text{O}$ ). The XPS high resolution spectra of the  $N_{1s}$  and  $S_{2p}$  regions were similar to those of the PVC-NCS surface but with variable peak contributions.

### 3.2.3. AFM analysis

AFM images of PVC and PVC-NCS surfaces as well as typical examples of grafted surfaces are shown in Fig. 2.

One can observe that the surface treatment with NCS led to changes in surface morphology without significant variation in the surface roughness, which was around 3 nm.

In contrast, polysaccharide grafting onto the PVC-NCS surface changed dramatically the surface topography, and the surface roughness increased to around 20 nm.

Furthermore, according to the literature [19,20], the surface being homogeneous and roughness values being lower than 100–500 nm, the hysteresis measured by dynamic contact angle with water would be exclusively due to the hydrophilic–hydrophobic balance.

## 4. Conclusions

In this work we have grafted bioactive cellulose derivatives onto PVC surfaces using a straightforward pathway. First, PVC-NCS surfaces were prepared by a heterogeneous thiocyanation of the PVC surface in a DMSO/water mixture. Then, the selected polysaccharides were directly grafted onto the PVC-NCS surfaces in a DMSO/actonitrile media, in presence of DBTL as catalyst. The impact of DBTL amount on polysaccharide grafting onto the surface was monitored by contact angle measurements. 0.05 equiv. of DBTL by polysaccharide hydroxyl group seemed to be an optimal ration. In these conditions, the grafting reaction was effective and the resulted surfaces exhibited modulated properties comparing to the ungrafted surfaces.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apsusc.2013.06.123>.

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