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# Click grafting of seaweed polysaccharides onto PVC surfaces using an ionic liquid as solvent and catalyst

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ABSTRACT

Seaweed antibacterial polysaccharides were grafted onto poly(vinylchloride) (PVC) surfaces using an original click chemistry pathway. PVC isothiocyanate surfaces (PVC–NCS) were first prepared by nucleophilic substitution of the chloride groups by isothiocyanate groups in DMSO/water medium. Then, unmodified Ulvan, Fucan, Laminarin or Zosterin was directly grafted onto the PVC–NCS surface using 1-ethyl-3-methyl imidazolium phosphate, an ionic liquid, as solvent and catalyst. To attest the grafting effectiveness, the new PVC surfaces were well characterized by AFM, XPS and contact angle measurements.



## 1. Introduction

In the context of sustainable chemistry the development of new straightforward pathways using natural resources is of major interest.

Polysaccharides are the most abundant natural biopolymers in the world. Mainly located in plants and vegetables they represent a major renewable source in the polymer field.

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 for instance. As example, heparin and chitosan were used to improve biocompatibility and/or to prevent attachment of bacteria, blood platelets or proteins onto biomaterial surfaces (Goddard & Hotchkiss, 2007). Hyaluronan hydrogels have been recently envisaged also in the fields of tissue engineering and regenerative medicine (Demange et al., 2012). Seaweed polysaccharides such as alginates, carrageenan, agarose and fucans (Bohn & BeMiller, 1995; Costa et al., 2010; Leung, Liu, Koon, & Fung, 2006; Rinaudo, 2008; Wijesekara, Pangestuti, & Kim, 2011) exhibit biological properties in correlation with their chemical structures. Especially, sulfated polysaccharides from algae possess important pharmacological activities such as anticoagulant, antioxidant, antiproliferative, antitumoral, anticomplementary, anti-inflammatory, antiviral, antiseptic and antiadhesive activities (Azevedo et al., 2009; Costa et al., 2010; Cumashi et al., 2007; Damonte, Matulewicz, & Cerezo, 2004).

However, because of their water soluble properties, chemical reactions on polysaccharides are restricted to few solvents. Furthermore, the grafting of polysaccharides onto hydrophobic polymers and vice versa often involves uncontrolled surface physical treatments or multi-step chemical modifications of the surface and/or of the polymer (Goddard & Hotchkiss, 2007).

PVC is a hydrophobic polymer derived from fossil fuels but which could be produced from sugarcane and salt according to Solvay Indupa company. Widely used as biomaterial, it represents 25% of the plastics used in medical applications (Tickner, Schettler, Guidotti, McCally, & Rossi, 2001). Nevertheless, in the literature only few examples describe the grafting of polysaccharides onto PVC surfaces. With the aim to improve blood compatibility, Mao, Zhao, Zhu, Shen, and Lin (2004) grafted *O*-butyrylchitosan (OBCS) onto PVC surface. 4-Azidobenzoic acid was first grafted to OBCS, and the resulting polymer was then coated on the PVC film surface and covalently linked by ultraviolet irradiations. In order to prevent bacteria attachment, Asadinezhad et al. (2010) functionalized PVC surface by a multistep procedure. A surface activation by plasma in air was performed in a first step. Then, acrylic acid was copolymerized from the activated surface. Finally, chitosan/pectin multilayer was grafted onto the functionalized surfaces by amidification using a coupling agent. By mimicking the nonthrombogenic properties of

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the endothelial cell, Zhou and Meyerhoff (2005) reported the development of a new generation of NO release polymeric coatings that combined NO release chemistry 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. Thus, all these examples support the need of alternative procedures to graft polysaccharides onto PVC.

During the last decade, room temperature ionic liquids (ILs) have known a great development as media and/or catalysts for organic reactions and polymerizations (Lozinskaya, Shaplov, & Vygodskii, 2004; Mallakpour & Rafiee, 2007; Natrajan & Wen, 2011; Vijayaraghavan, Pringle, & MacFarlane, 2008; Wang & Wang, 2003; Wang et al., 2009; Wilpiszewska & Spychaj, 2011). Indeed, their recyclability and their catalytic activities make them a green alternative to organic solvents. Moreover, ILs display many others advantages like chemical and thermal stabilities, and ability to solvate a broad range of organic and inorganic compounds.

Recent studies have reported the dissolution and chemical modification of polysaccharides, especially cellulose, in ionic liquids (ILs) such as *N*,*N*′-diimidazolium chloride salts (Swatloski, Spear, Holbrey, & Rogers, 2002), *N*,*N*′-diimidazolium formate, phosphate or phosphonate (Fukaya, Hayashi, Wada, & Ohno, 2008; Fukaya, Sugimoto, & Ohno, 2006) and 1-butyl-3-methylimidazolium chloride or acetate (Ding et al., 2012; Heinze, Schwikal, & Barthel, 2005; Gao, Luo, & Luo, 2012). Indeed, because of a high number of intra-molecular hydrogen bonds, cellulose is difficult to dissolve in common organic solvents. In contrast, appropriate ILs are able to cleave these intra-molecular hydrogen bonds by their ionic interactions and thus dissolve cellulose (Pinkert, Marsh, & Pang, 2010).

In this work, we have developed 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 isothiocyanate in a water/DMSO mixture. These groups are analogue to isocyanate (NCO) groups, and are commonly present in fluorescent probes for protein labeling. Then, unmodified polysaccharides were directly grafted onto PVC–NCS surfaces using [C2mim][(MeO)(H)$PO_2$], an 1-ethyl-3-methyl-imidazolium phosphate, as ionic liquid. The selected IL is of major interest since it should play a concomitant role of solvent and catalyst. Bioactive seaweed polysaccharides as well as methylcellulose, a strong bacteria and protein repellent polymer (Mussard, Kebir, Kriegel, Estève, & Semetey, 2011), were selected. Their effective grafting on PVC surfaces 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 GPC ($CH_2Cl_2$, 1 mL/min, 2 mixed-C columns, polystyrene standards) were $\overline{M_n} = 88,000$ g/mol and $\overline{M_n} = 47,000$ g/mol. Seaweed polysaccharides were provided from the CEVA (www.ceva.fr), Paimpol, France. Their characteristics are depicted in Table 1. These polysaccharides contain a small amount of nitrogen owing to the presence of residual proteins coming from their natural media.

Methylcellulose ($\overline{M_n} = 88,000$ g/mol, degree of methylation (DM) = 1.5–1.9), tetrabutylammonium hydroxide (TBAH) (40 wt% in water) and *N*-ethylimidazole (≥95%) were purchased from Sigma–Aldrich. Potassium thiocyanate (KSCN) was purchased from Merck, and dimethylphosphite (98%) from Alfa Aesar.

### 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 Kα 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 (Berresheim, Mattern-Klosson, & Fresenius, 1991). 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 was evaluated using Digidrop Goniometer (GBX, France), by static contact angle ($\theta_i$) measurements on the sample surfaces with three 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.

**Table 1**
Some characteristics of the used seaweed polysaccharides.

| Polysaccharide | Seaweed | Mw (g/mol)[a] | S (%)[b] | N (%)[b] | Conditions of dissolution in IL (*C* = 1 mg/mL) |
|---|---|---|---|---|---|
| Methylcellulose | – | 80,000 | ND | ND | 60 °C (15 min) |
| Laminarin 822 | *L. saccharina* parmeat | 6,990 | ND | ND | 60 °C (15 min) |
| Ulvan 901 | *U. clathrata* | 360,000 | 2.2 | 1.6 | 80 °C (15 min) |
| Ulvan 815 | *U. rotundata* | 620,300 | 3.14 | 1.2 | 80 °C (15 min) |
| Ulvan 816 | *U. compressa* | 876,250 | 2.6 | 1.9 | 80 °C (15 min) |
| Fucan 812 | Fucus/Ascophyllum | 438,600 | ND | ND | 80 °C (15 min) |
| Zosterin 900 | Zosteraceae | 340,200 | ND | ND | 95 °C (30 min under sonication) |

ND: stands for not determined.

[a] Data supplied by the CEVA: $\overline{M_n}$ values were determined by High performance size exclusion chromatography (HP-SEC) using Pullulan calibration curve ranged from 5800 to 1,600,000 g/mol.

[b] Data supplied by the CEVA: N (%) was determined by the Kjeldhal technique; S (%) was determined by an internal method (turbidimetry after mineralization).

Surface polarities ($P$) of the materials are calculated using equation (2):

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

Dynamic contact angle measurements with water were also performed to get the advancing angle (AA) and the receding angle (RA) as well as the surface hysteresis (Hys = AA − RA).

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$^{-1}$ and 320 kHz, respectively. Topographic images were taken at different zones of 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 μm$^2$ 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 tetrabutylammonium hydroxide (TBAH) ($4.5 \times 10^{-2}$ mol) were dissolved in a 60 mL of DMSO/water (4/1) mixture. PVC sheets ($1 \times 1$ cm$^2$) 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 to 5 times.

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

### 2.5. Synthesis of 1-ethyl-3-methyl-imidazolium phosphate ([C2mim][(MeO)(H)PO$_2$])

The ionic liquid (IL), i.e. 1-ethyl-3-methyl-imidazolium phosphate, was prepared as described by Fukaya et al., 2008. Briefly, in a round bottom flask containing 225 mL of THF, *N*-ethylimidazole (622 mmol) and dimethyl phosphite (622 mmol) were added dropwise under nitrogen atmosphere at room temperature. Then, the mixture was stirred at 90 °C for 2 days. Then, a biphasic system was obtained. The lower phase containing the IL was separated from the upper phase (THF) and washed with diethyl ether. The obtained IL was dissolved in dichloromethane, purified on neutral activated alumina and then dried under vacuum. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm) 1.58 (t, 3H, $J$ = 7.4 Hz, $NCH_2CH_3$), 3.44 (d, 3H, $J$ = 11.8 Hz, $POCH_3$), 4.01 (s, 3H, $NCH_3$), 4.32 (q, 2H, $J$ = 7.4 Hz, $NCH_2CH_3$), 6.96 (d, 1H, $J$ = 5.41 Hz, P*H*), 7.32 (d, 2H, $J$ = 11.4 Hz, NC*HCH*N), 10.40 (s, 1H, NC*H*N). $^{13}$C NMR (75 MHz, $CDCl_3$, $\delta$ ppm) 15.8, 36.7, 45.5, 50.7, 121.7, 123.6, 139.3.

### 2.6. Grafting of polysaccharides onto PVC–NCS surfaces

Each polysaccharide was dissolved in the IL (C = 1 mg/mL) under appropriate conditions (Table 1). Then, the PVC–NCS sheets were added to these solutions at 60 °C. After stirring for 24 h, the PVC sheets were thoroughly washed with water, rinsed with diethyl ether and dried at 60 °C. The IL was recycled by dialysis in water. The polysaccharides were retained in the dialysis tube and the IL migrated outside the tube. Then, the IL was dried under vacuum.

## 3. Results and discussion

The common strategy to graft directly a polysaccharide onto polymer surfaces consists in esterification reaction between the polysaccharide hydroxyl groups and surface carboxyl groups, in the presence of coupling agents such as *N*,*N*-dicyclohexylcarbodiimide (DCC) or *N*,*N*′-carboimidazole (CDI). In this study, another 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 performed in two steps (Scheme 1).

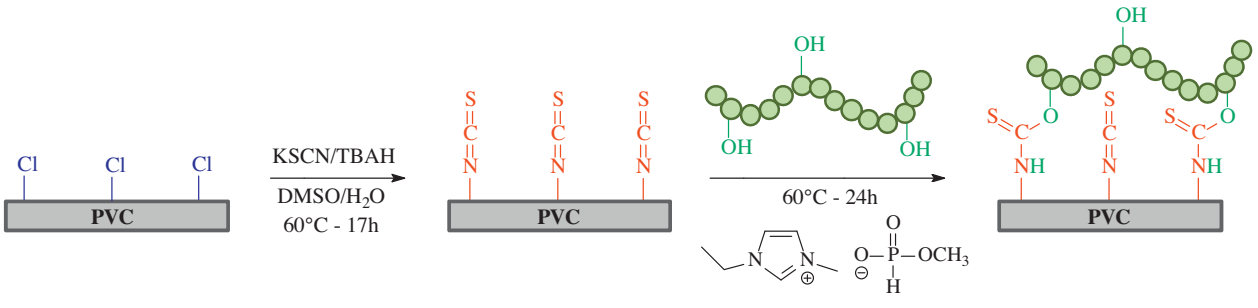
### 3.1. Preparation and characterizations of PVC–NCS surfaces

The reaction of thiocyanate ions with an alkyl halide is a nucleophilic substitution ($SN_2$) 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 be shown (James & Jayakrishnan, 2003) 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 confine 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.

Reaction was followed by ATR-FTIR. The appearance of a new band at ~2050 cm$^{-1}$ attributed to isothiocyanate groups, according to literature (Kameda, Ono, Grause, Mizoguchi, & Yoshioka, 2010), indicated that the reaction was successful.

The elemental compositions of PVC and PVC–NCS surfaces were determined by XPS analysis. Results are shown in Table 2. 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. PVC–NCS surface revealed the presence of N (1.5%) and S (1.3%) suggesting that the thiocyanation reaction




**Scheme 1.** The chemical process developed for grafting polysaccharides onto PVC surfaces.

**Table 2**
XPS elemental analysis of the prepared surfaces.

| Surface | %Cl | %C | %O | %N | %S |
|---|---|---|---|---|---|
| PVC | 33.4 | 66.6 | 0 | 0 | 0 |
| PVC–NCS | 15.5 | 81.7 | <1.0[a] | 1.5 | 1.3 |
| PVC–MeCell-1 | 14.6 | 70.0 | 11.8 | 2.1 | 1.0 |
| PVC–Lam822 | 6.7 | 67.2 | 17.6 | 2.4 | 2.3 |
| PVC–Ulv901 | 8.4 | 65.9 | 16.8 | 4.8 | 1.4 |
| PVC–Ulv815 | 6.9 | 65.0 | 20.5 | 2.8 | 2.2 |
| PVC–Ulv816 | 25.8 | 65.7 | 5.3 | 2.4 | 0.4 |
| PVC–Fuc812 | 10.0 | 68.4 | 16.1 | 2.5 | 1.5 |
| PVC–Zost900 | 14.9 | 69.3 | 11.7 | 2.1 | 1.2 |

[a] Not detected from the XPS survey spectra.

was successful. However, the percentage of Cl decreased indicating a PVC dechlorination (elimination of HCl), which was not observed by FTIR. Kameda et al. (2010) also observed this side reaction and have shown that the presence of phase transfer agents, such as TBAH, largely favored the substitution reaction over the elimination one.

The XPS survey scans for the main components were analyzed to assign the peaks C 1s, N 1s and S 2p to chemical functions. Typical examples are presented in Fig. 1.

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, O, S or Cl. The contribution of this peak is too weak (6.2%) 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 and thiocyanate groups. The peak at 401.5 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. As usual, 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.

Static and dynamic contact angle measurements performed on modified and unmodified PVC surfaces are reported in Table 3. In comparison with PVC, PVC–NCS surface showed a significant decrease of static and dynamic contact angles with water. 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. The balance between the two parts was reduced as suggested by the decrease of hysteresis value (from 48 to 33°). This indicated that thiocyanation increased considerably the hydrophilicity of the PVC surface. In addition, the surface polarity increased from 2.3 to 32.7%.

AFM data of the PVC and PVC–NCS surfaces are depicted in Fig. 2 and Table 3. One can observe that the surface treatment with NCS led to changes in surface morphology without significant variation in the surface roughness.

### 3.2. *Preparation and characterizations of PVC–NCS surfaces grafted with polysaccharides*

In a second step, the selected polysaccharides were reacted with PVC–NCS surfaces (Scheme 1).

[C2mim][(MeO)(H)$PO_2$] was chosen since it solubilized polysaccharides and not PVC. Further, ammonium salts have catalytic activities in nucleophilic addition reactions, such as the reaction between hydroxyl and isocyanate groups (Kébir et al., 2007; Mallakpour & Rafiee, 2007). Thus, it was assumed that [C2mim][(MeO)(H)$PO_2$] could have a catalytic effect in our reaction conditions. This hypothesis was checked in a preliminary study by reacting methylcellulose with PVC–NCS surfaces in different conditions. Water contact angle measurements were used to point out if the grafting reaction succeeded (Table 4).

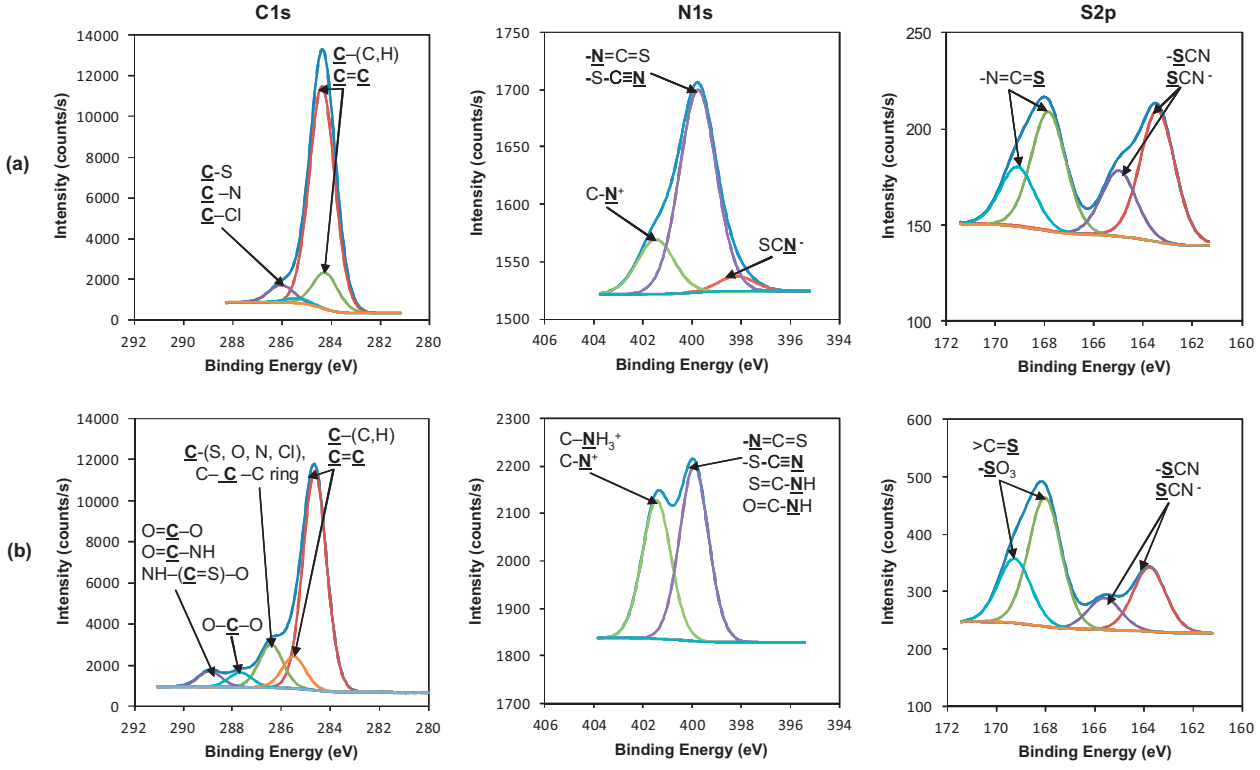



**Fig. 1.** C 1s, N 1s and S 2p high resolution spectra of (a) PVC–NCS and (b) PVC-Lam822.

**Table 3**
Contact angle data and roughness of the prepared surfaces.

| Surface | Static $\theta_{water}$ (°)[a] | Dynamic $\theta_{water}$ (°)[a] | | | $\gamma^d$ (mN/m)[a] | $\gamma^p$ (mN/m)[a] | Polarity (%)[a] | Roughness by AFM[b] (nm) | |
|---|---|---|---|---|---|---|---|---|---|
| | | AA | RA | Hyst | | | | Ra | RMS |
| PVC (control 1) | 89 ± 5 | 90 ± 3 | 43 ± 5 | 48 ± 2 | 42.2 ± 0.2 | 1.0 ± 0.8 | 2.3 ± 1.8 | 3.0 | 4.5 |
| PVC–NCS (control 2) | 44 ± 1 | 46 ± 2 | 13 ± 2 | 33 ± 3 | 38.9 ± 1.3 | 18.9 ± 0.1 | 32.7 ± 0.7 | 3.4 | 5.1 |
| PVC–MeCell | 63 ± 4 | 62 ± 1 | 15 ± 2 | 47 ± 2 | 42.3 ± 0.1 | 7.9 ± 1.6 | 15.7 ± 2.6 | 4.2 | 6.6 |
| PVC–Lam822 | 56 ± 3 | 55 ± 1 | 20 ± 1 | 35 ± 1 | 41.1 ± 0.9 | 12.1 ± 1.1 | 22.7 ± 1.1 | 5.2 | 8.7 |
| PVC–Ulv901 | 61 ± 2 | 61 ± 1 | 17 ± 1 | 44 ± 1 | 37.5 ± 1.8 | 10.7 ± 0.6 | 22.1 ± 0.4 | 3.7 | 5.2 |
| PVC–Ulv815 | 56 ± 1 | 55 ± 1 | 16 ± 1 | 39 ± 1 | 38.9 ± 0.8 | 13.9 ± 0.6 | 26.3 ± 0.3 | 4.4 | 6.7 |
| PVC–Ulv816 | 59 ± 3 | 59 ± 1 | 17 ± 2 | 42 ± 2 | 39.0 ± 0.6 | 10.5 ± 1.0 | 21.2 ± 1.2 | 5.6 | 9.2 |
| PVC–Fuc812 | 59 ± 5 | 59 ± 1 | 16 ± 1 | 43 ± 1 | 39.4 ± 0.9 | 10.5 ± 2.2 | 21.0 ± 3.1 | 7.8 | 11.2 |
| PVC–Zost900 | 60 ± 2 | 59 ± 1 | 15 ± 1 | 43 ± 2 | 40.5 ± 0.5 | 9.8 ± 0.7 | 19.5 ± 1.0 | 6.5 | 10.3 |

[a] $\theta_{water}$: contact angle with water; AA: advancing angle; RA: receding angle; Hyst: hysteresis; $\gamma^d$: dispersive component of the surface energy; $\gamma^p$: polar component of the surface energy; polarity = $100 \times \gamma^p/(\gamma^p + \gamma^d)$.
[b] Ra: arithmetic roughness, RMS: mean square roughness.

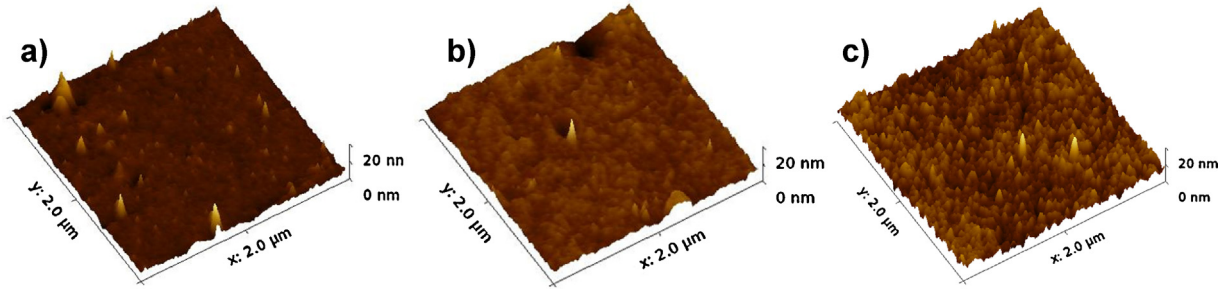



**Fig. 2.** IC-AFM height images (2 µm × 2 µm) of (a) PVC, (b) PVC–NCS and (c) PVC-Lam822, acquired in intermittent contact mode. The height scale was 20 nm.

When the reaction was conducted in a mixture of classical organic solvents such as DMSO/acetonitrile (1/6) without catalyst, no changes in the surface properties were observed indicating that grafting did not occur (Table 4, entry 2). On the other hand, adding dibutyltin dilaurate (DBTL) to the mixture led to modified surfaces (Table 4, entry 3).

In contrast, when using [C2mim][(MeO)(H)$PO_2$] the reaction was successful in the absence of catalyst (Table 4, entry 5). The addition of DBTL to the reaction medium did not change the final surface properties (Table 4, entry 6). Further, [C2mim][(MeO)(H)$PO_2$] alone did not react on PVC–NCS surfaces (Table 4, entry 4). All these convergent results suggested a catalytic effect of the IL on the reaction between hydroxyl and isothiocyanate groups.

Methylcellulose and sulfonated (Ulvans, Fucans) or non sulfonated (Laminarin, Zosterin) seaweed polysaccharides were used. Their dissolution conditions in [C2mim][(MeO)(H)$PO_2$] were optimized and reported in Table 1. Chemical grafting was then operated by immersion of the PVC–NCS samples in the polysaccharide solution (1 mg/mL) during 24 h at 60 °C. The obtained PVC-polysaccharide surfaces were thoroughly cleaned before characterizations.

In comparison with the PVC–NCS surfaces, the elemental analysis by XPS of the grafted surfaces showed the presence of oxygen and the increase of nitrogen percentage, attesting the presence of polysaccharides and their residual proteins onto the surface (Table 2). However, the grafting of the Ulvan 816 seemed to be less efficient since it exhibited the lowest percentages of O and S (Table 2). This result could be linked to the high molecular weight of this polymer limiting its mobility and reactivity onto the surface.

As a typical example, Fig. 1 shows the high resolution XPS spectra of the C 1s, N 1s and S 2p regions for the PVC–NCS surface grafted with Lam812.

Additional peaks belonging to the polysaccharide moieties were observed in the XPS C 1S region at 286.4 eV (C—O, C—N, C—S bonds as well as C—C—C bond from polysaccharide rings), at 287.7 eV (C in acetal or hemiacetal functions) and at 288.9 eV (C in the thiocarbamate links (NH—(C=S)—O)).

In the N 1s XPS region, the intensity of the peak at 401.5 eV increased because of the presence of residual proteins (C—$NH_3^-$). The main peak at 399.9 eV was assigned to the thiocarbamate link and to the thiocyanate and isothiocyanate groups.

The S 2p high resolution XPS spectra of the grafted surfaces exhibited the same peaks than PVC–NCS surface but with different

**Table 4**
Effect of DBTL on the contact angle data relative to PVC–NCS surfaces grafted with methylcellulose in acetonitrile/DMSO mixture or in [C2mim][(MeO)(H)$PO_2$] as ionic liquid.

| Entry | Medium | Surface | DBTL (eq/OH) | Static $\theta_{water}$ (°)[a] | $\gamma^d$ (mN/m)[a] | $\gamma^p$ (mN/m)[a] | Polarity (%)[a] |
|---|---|---|---|---|---|---|---|
| 1 | Acetontrile/DMSO (6/1)[b] | PVC–NCS (control) | 0 | 44 ± 1 | 38.9 ± 1.3 | 18.9 ± 0.1 | 32.7 ± 0.7 |
| 2 | | PVC–MeCell | 0 | 47 ± 2 | 36.9 ± 0.7 | 18.1 ± 0.1 | 32.9 ± 0.3 |
| 3 | | PVC–MeCell | 0.05 | 59 ± 2 | 39.0 ± 1.6 | 11.9 ± 0.2 | 23.3 ± 0.9 |
| 4 | Ionic liquid (IL) | PVC–NCS in IL | 0 | 46 ± 3 | 39.1 ± 2.0 | 17.0 ± 1.2 | 30.2 ± 1.1 |
| 5 | | PVC–MeCell | 0 | 63 ± 4 | 42.3 ± 0.1 | 7.9 ± 1.6 | 15.7 ± 2.6 |
| 6 | | PVC–MeCell | 0.05 | 65 ± 2 | 39.7 ± 1.0 | 7.9 ± 0.8 | 16.6 ± 1.1 |

[a] $\theta_{water}$: contact angle with water; $\gamma^d$: dispersive component of the surface energy; $\gamma^p$: polar component of the surface energy; polarity = $100 \times \gamma^p/(\gamma^p + \gamma^d)$.
[b] Experimental conditions are reported in the supplementary data.

contributions. The peak at 163.8 eV arose from thiocyanate groups and ions. In the case of surfaces grafted with the seaweed polysaccharides, the peak at 168.1 eV was more intense than the peak at 163.8 eV. This was ascribed to the presence of thiocarbamate functions, to sulfonate groups present in some polysaccharides and to unreacted isothiocyanate groups.

PVC–NCS surface grafted with polysaccharides exhibited increased contact angles with water and decreased polarities, in comparison with the ungrafted surfaces (Table 3). The static contact angles varied in the range of 56–61°, suggesting that these surfaces kept their hydrophilic character. AA with water was very close to static angle, whereas RA was in the range of 15–20°. Thus, polysaccharide surfaces exhibited hysteresis in the range of 35–47° which was higher than the PVC–NCS hysteresis. This behavior is likely to be associated with the hydrophobic backbone of the polymer chains that increase the hydrophilic–hydrophobic balance of the surface. Besides, hysteresis can also be explained by surface heterogeneity, texture and roughness.

AFM data of the PVC–NCS surface grafted with polysaccharides are also depicted in Table 3. A typical example of 3D AFM height images is given in Fig. 2 (PVC-Lam822). These images revealed a modification of surface morphology after polymer grafting. The PVC surfaces grafted with polysaccharide exhibited roughness values slightly higher than those of the PVC–NCS surface. While there are obvious variations in grafted surface roughness, AFM images at nanoscale resolution suggest that the surfaces are fully populated with polymer chains.

## 4. Conclusions

This work showed the possibility of grafting a range of bioactive polysaccharides onto PVC surfaces using a green and straightforward process. This process involved a reaction between alcohol groups of polysaccharides and isothiocyanate groups covalently bounded to PVC surfaces. [C2mim][(MeO)(H)$PO_2$] was used as solvent for polysaccharides and as catalyst for the grafting reaction. This process is expected to be used to graft any polysaccharide or polymer bearing alcohol, amine or thiol groups onto a surface bearing isothiocyanate groups.

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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.carbpol.2013.07.079.

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