Applied Surface Science 283 (2013) 411–416

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Facile grafting of bioactive cellulose derivatives onto PVC surfaces

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ARTICLE INFO

*Article history:*
Received 18 April 2013
Received in revised form 18 June 2013
Accepted 19 June 2013
Available online 29 June 2013

*Keywords:*
PVC
Methyl cellulose
Hydroxyethyl cellulose
Surface modification

ABSTRACT

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 (OBCS) onto PVC surface in order to improve blood compatibility. OBCS 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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http://dx.doi.org/10.1016/j.apsusc.2013.06.123

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.

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

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):

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

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 $\mu$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 × 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: $\nu_{max}$/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 gentile 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 be 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.