



## Nano-exploration of organic conditioning film formed on polymeric surfaces exposed to drinking water



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### ABSTRACT

Adsorption of organic macromolecules onto surfaces in contact with waters forms a so-called conditioning film and induces modifications of the surface properties. Here, we characterized conditioning films formed onto two hydrophobic materials (used as pipe liner) and immersed for 24 h in tap water. Using combination of atomic force microscopy (AFM), and chemical force microscopy (CFM), we detected some changes in roughness and hydrophilic/hydrophobic balance of the surface of the tested coupons, and also the deposition of numerous organic polymers (few millions/cm<sup>2</sup>) randomly distributed on the surface. The maximum molecular extension of these organic polymers was in the range of 250–1250 nm according to the tested materials. Systematic analysis of the force curves with the theoretical models (WLC and FJC) allowed determining the proportion of rupture events related to the unfolding of both polysaccharide and polypeptide segments, which represented 75–80% and 20–25% of the analyzed curves, respectively. The number of autochthonous drinking water bacteria, which attached to the material within the same period of time was 10000-folds lower than the detected number of polymers attached to the surface. Even in drinking water systems with relatively low organic matter (dissolved organic carbon < 1.1 mg/L), the potential of formation of a conditioning biofilm is important.

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### 1. Introduction

Adsorption of dissolved and colloidal organic matter onto surfaces in contact with natural waters has been reported since the 1970s and was called adsorbed layer or conditioning film (Baier, 1972; Loeb and Neihof, 1975; Taylor et al., 1997). Such deposits formed in a few hours (before any major bacterial adhesion) are very thin (a few nanometers). They seem intimately involved in pioneer microbial colonization and biofilm formation on biomaterials and industrial materials.

The deposition of any organic matter onto the surfaces in contact with water induces modifications of the surface properties. On the whole, the wettability of hydrophobic surfaces was found to increase and that of hydrophilic surfaces to decrease after

immersion in water for a few hours (Schneider and Marshall, 1994; Bakker et al., 2004; Abe et al., 2011; Hwang et al., 2013). Other authors observed that the chemical characteristics of the polymers forming this conditioning film strongly differed with the environment and the polymer source, e.g. seawater versus freshwater, season, water treatment (Beech et al., 2000; Compère et al., 2001; Garg et al., 2009). However, carbohydrates were systematically found to be the most abundant constituents of the conditioning film formed on coupons immersed in seawater, with carbohydrate concentrations ranging from 0.02 to 0.25 µg/cm<sup>2</sup> (D'Souza and Boshle, 2003; Bakker et al., 2004; Hwang et al., 2013). Additionally, occurrence of uronic acids, proteins, humic acids, and fulvic acids was frequently reported (Jain and Boshle, 2009; Landoulsi et al., 2008).

The effect of the conditioning film on bacterial adhesion is currently a source of debate, as it was shown to either increase or decrease initial bacterial adhesion (Schneider, 1997; Bakker et al., 2003; Long et al., 2009; Hwang et al., 2012; Bauer et al., 2013;

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Wang et al., 2014). Indeed, such contradictory results can be caused by the wide variety of variables: materials (hydrophobic/hydrophilic balance, roughness), conditioning film itself (environmental film or polymer models, density of polymers), microorganisms (gram-/gram+, exponential or stationary phase), and environmental conditions (ionic strength, temperature, hydraulic regime).

As far as we know, no studies on conditioning films have been reported on materials used in water industry under conditions relevant to drinking waters. Yet, there are significant concentrations of organic matter in tap waters (from 1 to 3 mg/L of organic carbon, in average) and some authors measured around 10–20 µg/L xanthan gum-equivalent of transparent exopolymer particles (TEP) (Van Nevel et al., 2012). This organic matter is able to stick to many surfaces, and preliminary assays with glass coupons immersed in drinking water gave rise to small hydrophobic adhesion forces with a tight distribution (Abe et al., 2011). The effects of such initial organic soiling on surface properties of materials used in drinking water pipes (from stainless steel to polymeric liners), and its contribution to bacterial deposition are unknown. Better mechanistic understanding of such initial fouling and its contribution to biofilm formation should help in designing new anti-adhesive materials to be used in water transport. Indeed, biofilm accumulation and growth in water distribution systems generate many negative effects (e.g., high bacterial counts in water), which may disqualify water characteristics and use.

As a result, this study represents a pioneer contribution to the characterization of the conditioning film formed in a short period of time (24 h) under conditions relevant to drinking water distribution systems. We aimed to characterize the drinking water organic polymers accumulated on relatively hydrophobic polymeric materials, named PO and PF used as pipe liners. As XPS, Raman, and FTIR technics were not sensitive enough in our conditions for detecting the low amount of organic matter adsorbed onto polymeric material, we used specifically atomic force microscopy (AFM) and chemical force microscopy (CFM). Thanks to these techniques, most of stretchable molecules should be detected. Then, we determined (i) the number of organic polymers attached to the surface, (ii) some of their conformational properties, and (iii) their distribution on the surface. Additionally, we checked the number of bacterial cells attached in 24 h in order to discuss the potential interference of the conditioning biofilm on bacterial cell adhesion.

## 2. Materials and methods

### 2.1. Tested materials and assays

Two materials produced by Arkema (France) to be used in drinking water distribution systems were tested in this study: a copolymer of polyolefin grafted with polyamide 6 (PO) and a homopolymer made of vinylidene fluoropolymer (PF). SEM micrographs of cross-sections of these materials are shown in Fig. S1 (Supplementary data). All coupons were cleaned before use by combining immersion in 0.1% SDS at 60 °C for 30 min, rinsing in milli-Q water (3 times), immersion in 0.1 M HCl at 60 °C for 30 min, rinsing in milli-Q water (3 times), and finally drying under nitrogen flow. The surfaces of two materials (PO and PF) were investigated before drinking water contact through quantification of their roughness and hydrophilic/hydrophobic balance. Then, the coupons made of PO and PF films (400 µm in thickness, 75 mm × 25 mm) were immersed in drinking water at 20 °C in a flow cell-like reactor (laminar flow, flow rate of  $2.2 \times 10^{-3}$  m/s) fed with tap water from the city of Nancy (France), with a water residence time of 12 h. The average characteristics of Nancy's tap water were: pH  $8.0 \pm 0.2$ ; conductivity  $379 \pm 35$  µS/cm; CAT (complete alkalimetric title)  $8.2 \pm 0.3$  °f; calcium  $47 \pm 2$  mg/L; magnesium  $6 \pm 0.8$  mg/L; DOC

(dissolved organic carbon)  $1.1 \pm 0.3$  mg/L; chlorine not detectable; autochthonous bacteria  $2.2 \times 10^4 \pm 0.75 \times 10^4$  cells/mL. After 24 h immersion, coupons were taken from the reactor and immediately placed in a sterile box containing milli-Q water for further analyses.

### 2.2. Atomic force microscopy (AFM): topographical images and force measurement

Roughness of the surfaces before and after immersion in tap water was assessed using AFM. Measurements were done in milli-Q water using an Asylum MFP-3D BIO atomic force microscope (Oxford Instrument, Mannheim, Germany) with IGOR Pro 6.04 (Wavemetrics, USA) as operating software. Roughness measurements were addressed via AFM imaging in contact mode with an applied force lower than 200 pN, using silicon nitride cantilevers (MLCT-AU, Bruker-nano AXS, Palaiseau, France) with a spring constant of approximately 0.010–0.012 N/m. Images were acquired at a scan rate of 1 Hz and scan size of  $80 \mu\text{m} \times 80 \mu\text{m}$ . The surface topography and the average root-mean square roughness (rms) of the surfaces before and after their immersion in drinking water were measured by imaging in milli-Q water three areas of  $80 \mu\text{m} \times 80 \mu\text{m}$  per coupon, randomly selected near the center of the coupons (3 coupons per materials).

### 2.3. Chemical force spectroscopy (CFM) and data processing

AFM was used in force volume mode in order to quantify the hydrophobic and hydrophilic interactions between the sample surfaces and either the bare AFM-tips or the chemically modified AFM-tips. These models could be used for investigating the physical properties of the polymers in the range of weak adhesion forces (<2 nN) (Camesano and Abu-Lail, 2002; Abu-Lail and Camesano, 2003). Briefly, adhesion forces were determined by recording force volume images consisting of a grid of  $32 \times 32$  force curves obtained upon approach and, subsequently, retraction of the tip onto a corresponding surface area of  $6400 \mu\text{m}^2$  (in such a situation one pixel was equal to  $2.5 \mu\text{m} \times 2.5 \mu\text{m}$ ). All force experiments were performed in milli-Q water.

- Hydrophobic forces were measured in Milli-Q water with gold-coated AFM tips (NPG-10, Bruker-Nano AXS, Palaiseau, France) functionalized with 1-dodecanethiol ( $\text{CH}_3\text{-C}_{11}\text{H}_{22}\text{-SH}$ ) as hydrophobic probes (Alsteens et al., 2007). Control of the contamination of the hydrophobic tip was done systematically before and after surface analysis by using a gold-coated glass substrate functionalized with 1-dodecanethiol.
- Hydrophilic interaction measurements were performed in Milli-Q water with bare silicon AFM-tips (MLCT, Bruker-Nano AXS, Palaiseau, France).

For each material, measurements were done on three to five areas of  $80 \mu\text{m} \times 80 \mu\text{m}$ /coupon (three coupons per material). The measures with the AFM probe have been done approximately every 2.5 µm (an *a priori* experimental choice done in order to avoid duplication in the detection of the same polymer because of the maximal polymer extension never exceeded 1.5 µm).

### 2.4. Force-curve analysis with WLC and FJC models

Force-displacement curves were analyzed on the formalism of the Freely Jointed Chain (FJC) and Worm Like Chain (WLC) models (Janshoff et al., 2000). These models could be used for investigating the physical properties of the polymers in the range of weak adhesion forces (<1 nN) (Camesano and Abu-Lail, 2002). Briefly, the FJC model describes macromolecules consisting of rigid segments

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