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ASSESSEMENT OF THE SURFACE ROUGHNESS OF CELLULOSE IONOGEL MEMBRANES USING ATOMIC FORCE MICROSCOPY

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Nowadays, ionogels are widely researched materials as they can be easily designed and varied as well as have a wide range of applications. Being composed of an ionic liquid and cellulose, they are biodegradable with properties dictated by the ionic liquid such as high conductivity and ion transport capabilities. Sometimes they are used in the aqueous phase, making their analysis very difficult due to the conditions surrounding them. The porosity and surface roughness of membranes are important properties. Atomic force microscopy is capable of avoiding the aforementioned difficulties and providing such essential data while providing images of the examined surface as well. The purpose of this work is to examine this novel material and how specific data can be recorded by atomic force microscopy.

Keywords: cellulose, ionic liquid, ionogel, AFM, surface roughness

1. Introduction

Ionic liquids are organic solvents which are non-flammable, thermally stable and good conductors at extremely low vapour pressures capable of carrying out ion exchange. Being environmentally-friendly solvents composed of an organic cation and an organic or inorganic anion, they are designable and offer a versatile range of applications. The majority of them are liquid below 100 °C and are referred to as room-temperature ionic liquids (RTILs) [1]. One of the most commonly used groups of RTILs are based on an imidazolium cation (*Figure 1*) usually with a halide anion, the most commonly used and researched being 1-Butyl-3-methyl-imidazolium chloride ([BMIM][Cl]).

In order to utilize the ionic liquid [BMIM][Cl] as a membrane, it must be immobilized since it cannot maintain the typical conformation of a cylindrical membrane. One method is to make an ionogel from a mixture of an ionic liquid and microcrystalline cellulose [2]. In doing so, the ionic liquid will become part of the grid structure of cellulose which acts as a matrix for the ionic liquid. This novel gel-like material, that is, ionogel, is biodegradable and cheap as cellulose is the most abundant organic material on Earth. Once spread, the fabricated ionogel can be used as a membrane, for example, in a microbial fuel cell (MFC) that may be subjected to microbial fouling due to certain strains attaching to its surface. A MFC is a galvanic cell in which the anode chamber is filled with electrochemically active anaerobic microorganisms that catalyse the oxidation of organic matter, leading to the conversion of hydrogen ions and electrons [3]. The protons migrate to the aerobic cathode chamber, where the oxygen on the cathode is reduced by the electrons released thus closing the circuit. During this process, these electrons can be harnessed and utilized. Since the anode chamber of the fuel cells is filled with a mixed culture, the membrane suffers from the formation of an inevitable layer of organic mass called biofouling which is affected by the composition of the microbial culture of the seeds and the properties of membranes such as surface roughness [4]. As a result of the aforementioned property, it is crucial to study the surface of the membrane. In the MFC, the membrane is in its wetted state, so in order to gain representative data it is necessary to also carry out an analysis of the membrane in its wetted form, which is impossible using certain analytical techniques such as scanning electron microscopy, the most common surface-imaging method for membranes. Other techniques, such as stylus instruments or optical methods like diffuse reflection or

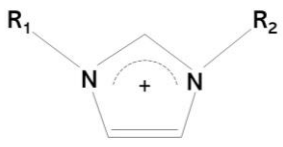

Figure 1: Imidazolium cation

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taper sectioning [5], are also unsuitable, because the surface of the samples is not conductive, cannot tolerate vacuums and is relatively easily damaged. On the other hand, atomic force microscopy (AFM) is a technique that is capable of providing information about the surface of the examined material, even in its wetted state since a vacuum is not required for the analysis unlike for scanning electron microscopy.

2. Experimental

2.1. Fabrication of the ionogel

5 grams of ionogel was fabricated by stirring 13 m/m % of microcrystalline cellulose (Molar Chemicals Kft., Hungary) and 87 m/m % of [BMIM][Cl] (IoLiTec-Ionic Liquids Technologies GmbH, Germany) together in a porcelain mortar until the product became a liquid of low viscosity. Next, it was poured onto a glass plate and spread to achieve the necessary thickness of 750 µm before being cured at 100 °C for an hour. During the heat treatment, the ionic liquid breaks the H-bonds between two glucose units before it is presumably wedged between them, forming a colloidal solution with the cellulose [6]. This process is not yet fully understood and remains a subject of research. The suspected mechanism whereby the H-bonds are broken can be seen in *Figure 2*.

After curing, the glass plate the mixture was submerged in distilled water for an hour. During that time, gelation took place resulting in the formation of an ionogel. Subsequently, the necessary shape needs to be cut out and can be used as can be seen on *Figure 3*.

2.2. AFM imaging

AFM is an imaging technique in where the surface topography of a solid sample is investigated by a probe consisting of a sharp tip attached to an elastic cantilever which moves over the surface of the sample. The interaction between the probe and this surface creates a morphological and topographic image by monitoring the changes in the vertical position of the probe as the sample is moved. Other than the surface morphology, AFM is able to investigate other aspects of the sample based on the tip-surface interactions such as adhesive forces, Young's modulus, electrical conduction, charge distribution and inhomogeneity [7]. The change in the position of the AFM probe vertically during imaging is shown in *Figure 4*.

In general, the surface of the sample must be flat with inclines that the cantilever can handle, that is, usually less than 10 µm, to prevent it from getting damaged. The surface of the sample must also be clean so a suitable degree of chemical purging is preferable [8]. In this study, the AFM imaging of ionogel membrane samples was carried out with the support of Dr. Zbynek Pientka from the Institute of Macromolecular Chemistry at the Czech Academy of Sciences.

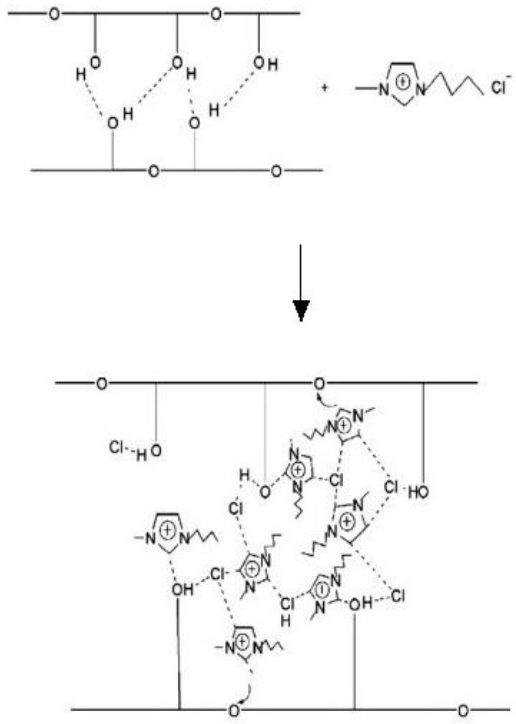

Figure 2: Mechanism of cellulose dissolution [6]

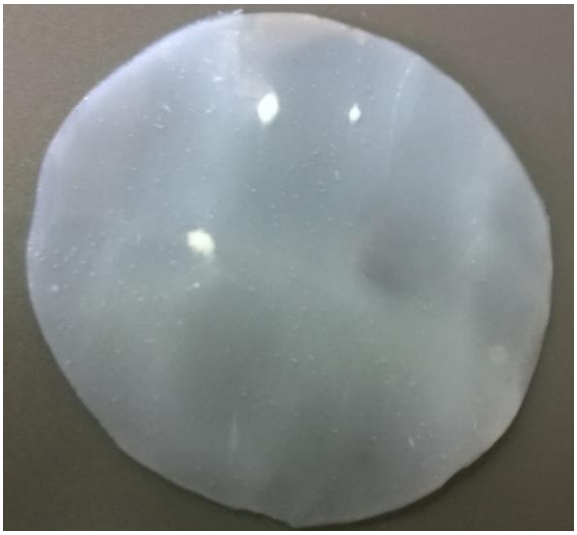

Figure 3: Ionogel membrane

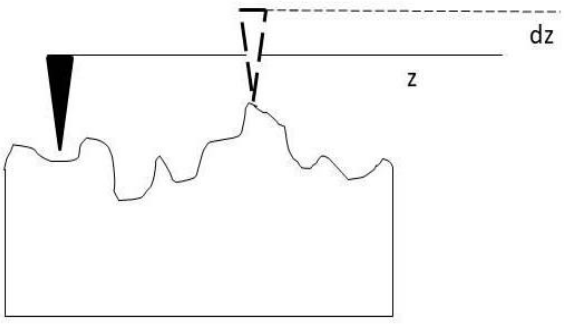

Figure 4: Interaction between the sample surface and the AFM probe

3. Results and analysis

The samples were examined in their wetted state. A scanning probe microscope Bruker Dimension Icon PT was used to observe the samples in PeakForce QNM tapping mode in water providing both i) the topography of the surface depicted and ii) local elastic/adhesive properties of the sample. Silicon nitride AFM cantilevers and a ScanAsyst-Fluid+ probe (Bruker) with a typical tip-apex distance of 2 nm (max 10 nm) were used. No damage to the samples caused by the scanning probe was observed. The resulting images were not processed further, except to compensate for tilt. An examined spot on the surface of the membrane is shown in *Figure 5* (Side A).

A 3x3 μm wide area was observed at a magnification suitable for observing distances 350 nm across. Darker spots indicate pores on average 200 nm in diameter on the surface of the membrane. The porosity could not be calculated precisely from these images. The average surface roughness R_A was 428 nm. In *Figure 6*, Side B of the membrane was observed using the same method and parameters as for Side A, revealing the same features except that the average surface roughness was no more than 222 nm due to the glass plate being in contact with the membrane during curing.

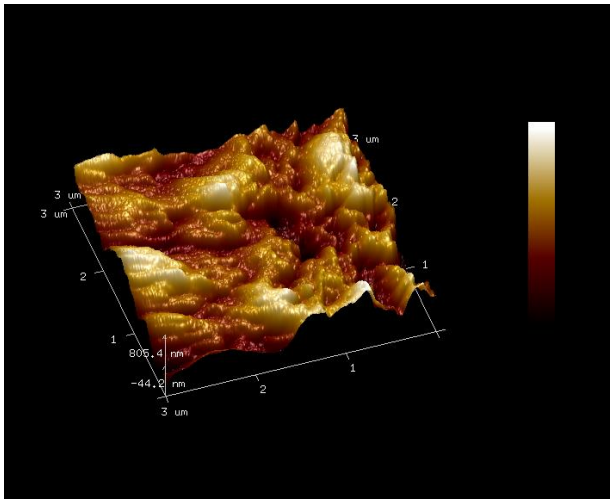

Figure 5: Ionogel membrane surface - Side A (AFM)

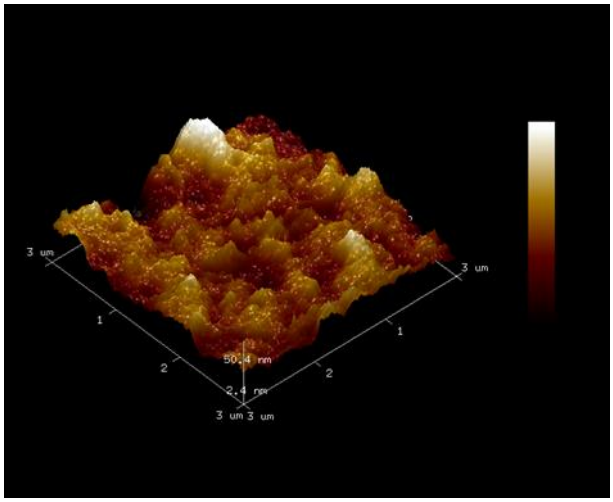

Figure 6: Ionogel membrane surface - Side B (AFM)

4. Conclusions

Wetted ionogel membranes were observed using AFM. The surface of one of the membranes was very corrugated, while the other was smooth. Local mechanic properties (adhesivity) did not reveal any material heterogeneity. The difference in surface roughness (428 vs. 222 nm) originates from the fact that one side was in contact with a glass plate which held the material during heat treatment, thereby making it smoother. Although the images revealed signs of pores, this method was not able to determine if they penetrate through the main bulk of the membrane nor provide information about their porosity. Nevertheless, it was able to determine their size which varied between 200 nm and 1-2 μm, sometimes even forming valleys. Knowing how difficult it is to analyse such materials, AFM has proven to be a useful method for gaining information directly about a gel-like material which usually requires pretreatment that alters the material, thereby altering the results.

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