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Characterization of natural rubber membranes using scaling laws analysis

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ABSTRACT

Natural rubber extracted from the *Hevea brasiliensis* tree is an exclusive natural polymer with many applications of strategic importance. Membranes of the In-Nature latex were prepared by the casting method in petri dishes and also dissolved in different solvents (water, chloroform and toluene) after centrifugation. The centrifugation process enhances the transparency of the membranes, which is required for optical applications. Analysis based on atomic force microscopy coupled with the scaling laws was used to characterize the morphological properties of the membranes, where the interfaces formed in contact with air and with the glass substrate were investigated. The scaling laws parameters obtained demonstrated that the dynamics of the membrane formation are directly dependent on the solvent and influence the final surface morphology. This report offers new insights regarding appropriate procedures for membrane production depending on the desired application.

1. Introduction

Natural rubber (NR) is a unique renewable biopolymer mainly obtained from natural latex of the *Hevea brasiliensis* tree, which allows the sustainable use of a natural resource. NR consists of isoprene units $(C_5H_8)_n$ linked in a 1,4 cis-configuration, *i.e.*, poly-1,4-cis-isoprene with a high molecular weight of 1300 kDa and its *n* value is approximately 18,000 [1]. In addition, NR is a colloidal system containing rubber particles suspended in an aqueous medium (around 50–60% water) composed of approximately 96% hydrocarbons, 1–2% proteins, 0.4–1% neutral lipids, 0.5–0.6% polar lipids and 0.4–0.6% inorganic components (including trace metals such as magnesium, potassium and copper) [2,3]. NR can be separated into three characteristic phases according to the centrifugation: rubber cream, serum (also known as C-serum) and bottom fraction. The rubber cream is mainly composed of the poly-1,4-cis-isoprene corresponding to approximately 40% of the total dried volume. In addition, it contains a small portion of hevein proteins (Hev b1 and Hev b3) with low allergenicity [4]. The serum is comprised of different compounds including carbohydrates, proteins, amino acids, enzymes and nitrogen [3,5]. Finally, the bottom fraction contains a high portion of lutoids. When the latex is stabilized with more than 0.7% of ammonium, it releases these lutoids to the serum phase producing the so-called B-serum [4,6].

NR has been applied for a long time in several industrial and medicinal segments. More recently, NR compounds and membranes have attracted attention due to their great potential for biological and technological applications. Modified NR has been investigated as a source of gel polymer electrolytes for lithium polymer batteries and revealed excellent suitability, with 4.2 V of maximum charge [7]. An NR/C_{60} blend has been shown to offer good properties in transistors able to perform write-erase and read functions [8]. Also, NR membranes have been

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successfully applied as catalysts in the synthesis of gold nanoparticles and showed notable potential to reduce the *Leishmania brasiliensis* promastigotes in a culture medium [9]. Moreover, NR membranes have been applied as a support matrix for nanometric TiO_2 (rutile phase) and demonstrated antibacterial action against *Escherichia coli* and *Staphylococcus aureus* [10]. NR can also be employed to produce transdermal drug delivery systems where it is the controlling layer membrane [11].

The chemical potential and physical interactions at different NR membrane interfaces, involving liquids, micro and nanoparticles, bacteria and/or microorganism, are strongly dependent on the morphology and surface roughness. A surface with greater roughness and/or porosity has a larger surface area and this can enhance the number of functionalized sites available for interaction with the medium. On the other hand, when we consider the application of the NR membranes to manufacture transparent and stretchable electrodes for optoelectronic devices, a low surface roughness is desirable because it is beneficial for charge injection or collection due to the reduced interface barrier [12]. Thus, understanding the relation between the morphology of the surface and the production method and/or the solvent used to obtain the NR membranes is essential for determining of the most adequate procedure for each specific application. Regarding this aspect, analysis based on scaling laws is a powerful tool for obtaining a quantitative description of the surface morphology.

Methods based on the scaling laws have attracted attention due to the possibility of describing the growth characteristics of thin films and other surface deposits [13,14]. Surfaces can be grown using distinct experimental techniques by adding or removing material from the surface (sputtering, casting, spin-coating, chemical vapor deposition, chemical etching, etc.). The morphology created is usually the result of competition between different growth dynamics, which can give rise to different forms depending on many factors known as the specific growth parameters. Thus, understanding the processes that control the growth of surfaces represents a considerable challenge. Statistical properties similar to those involved in scaling laws can be present, and the universality of these properties has been the target of many scientific studies [13–17]. The identification of this universality contributes to the description and understanding of the structure and the origin of a wide variety of rough surfaces.

In this study, NR membranes were produced using different solvents and methods. The optical and morphological properties were investigated by UV–Vis spectroscopy and atomic force microscopy (AFM). The AFM measurements were submitted to mathematical processing via computational software and analyzed using the formalism of scaling laws. It was observed that the preparation method and the solvent used for the membrane fabrication directly influence the optical and morphological properties. The analysis based on the scaling laws showed that the morphology characteristics of the interface formed by the evaporation of the solvent in contact with air can be explained by a model that considers the pushing force and the velocity of the fluid front during evaporation.

2. Experimental

The NR membranes were prepared using In-Nature latex from different rubber trees of the RRIM 600 clone, collected in the city of Indiana, São Paulo State – Brazil, and stabilized in ammonium hydroxide at a concentration of 2% (by volume). Four different NR membranes were produced with different solvents and methods, which were named as follows: the NR^{IN} membrane was produced using the stabilized In-Nature latex natural rubber while the NR^{C}_{Wat}, NR^{C}_{CLF} and NR^{C}_{TOL} membranes were prepared using a rubber cream phase of the centrifuged latex dissolved in Milli-Q water, chloroform and toluene, respectively. The rubber cream was obtained by submitting the In-Nature latex to centrifugation in a Cientec - CT 5000R centrifuge at 6000 rpm and at 4 °C for 90 min.

All NR membranes were produced by the casting method with 10 mL of the solutions on Petri dishes (90 mm in diameter) applying thermal annealing at 55 °C for 10 h in an oven. The concentrations of the solutions were 400 mg/mL for NR^{C}_{Wat} and 65 mg/mL for NR^{C}_{CLF} and NR^{C}_{TOL}. These concentrations provide viscosities similar to water for the NR^{IN} and NR^{C}_{Wat} solutions and of a gel for the NR^{C}_{TOL} and NR^{C}_{CLF} solutions. The NR^{IN} membrane was produced with 10 ml of the stabilized In-Nature latex solution. The final thicknesses of the NR membranes were measured with a digital micrometer.

Digital photographs were collected under ambient light conditions using a 16 mega-pixels digital camera. The morphology of both sides of the membranes was investigated: on the top (at the air interface) and on the bottom (at the glass interface). For this purpose, AFM measurements were performed using a Nanosurf FlexAFM microscope, operating in tapping mode under ambient conditions with a scanning rate of 1.0 Hz and 512 pixels × 512 pixels. The AFM data were analyzed with the WSxM 5.0 software and the mean surface roughness (RMS) was obtained.

The AFM images were mathematically processed in a computer program (C++) and analyzed according to the statistical methods of the scaling laws. In the most commonly applied approach the roughness exponent of the interface (α) is measured by plotting the interface width (W_L), which characterizes the roughness of the interface, as a function of the square matrix of size L, as defined by Eq. (1) [18]:

$$W_L = \left\{ \left[\frac{1}{L^2} \sum_{i,j} (h_{ij} - \overline{h_L})^2 \right] \right\}^{\frac{1}{2}}, \quad (1)$$

where h is the surface height at point (i, j) and the over bar denotes averages of h inside a given matrix of size L. The matrix of size L scans the whole image under analysis. This is also known as gliding matrix, where the scanning matrix moves one pixel each step and performs a new spatial average. If the surface presents a self-affine behavior, W_L scales with L according to the relation $W_L \sim L^{\alpha}$, where α characterizes the dynamic of the saturated interface roughness. The roughness exponent can be associated with the fractal dimension (D_f) following the expression $D_f = D_E - \alpha$, where D_E is the Euclidian dimension, which is equal