Polymer Testing 68 (2018) 350–358

Contents lists available at ScienceDirect

Polymer Testing

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

# The contributions of supramolecular organization to mechanical properties of chitosan and chitosan copolymers with synthetic polymers according to atomic force microscopy

Tatyana S. Sazanova, Ksenia V. Otvagina, Ilya V. Vorotyntsev*

*Laboratory of Membrane and Catalytic Processes, Nanotechnology and Biotechnology Department, Nizhny Novgorod State Technical University n.a. R.E. Alekseev, 24 Minin St., 603950, Nizhny Novgorod, Russia*

ARTICLE INFO

*Keywords:*
Atomic force microscopy
Material characterization
Mechanical properties
Mathematical statistics methods
Chitosan
Polymeric membrane

ABSTRACT

Biodegradable polymers represent a basic component of a large range of various application including membrane technologies for gas separation. Since one of the first stages in gas separation is a contact of gas mixture with a membrane surface, there is an important task to evaluate the relationship between physicomechanical properties of membranes and their surface structure. In this context, microscopy techniques such as atomic force microscopy (AFM) are emerging as fundamental tools to study deeply morphology and structural properties at micro- and nanoscale. In the present work, AFM was used for study of surface structuring features of chitosan (CS) graft and block copolymers with polyacrylonitrile (PAN) and polystyrene (PSt) modified with ionic liquids (ILs) based on a cation of 1-butyl-3-methylimidazolium ([bmim]) with various anions ($[BF_4]$, $[PF_6]$ and $[Tf_2N]$) at each stage of modification. Mathematical statistics methods were used for stability study of surface structure of the CS copolymers. There was shown that the block copolymers were better in comparison with the graft ones. Special impact of the original and modified copolymers surface structure on their mechanical properties were studied. It was shown that ILs immobilization caused the decrease of the surface packing density of the copolymers, and by this resulted in the overall deterioration of their mechanical properties. At that, the block copolymers were more resistant to this effect than the graft ones. However, the strength and elastic properties of the CS copolymers with PAN showed better than of ones with PSt.

## 1. Introduction

Nowadays, there is the trend to increase demand for biodegradable polymers, as a result of more severe legislation concerning petroleum-based polymers with high « carbon footprint». Lately, the development and application of biodegradable polymers in membrane gas separation field is receiving particular attention [1,2]. Cellulose and its derivatives have been extensively studied for gas separation tasks [3]. Another class of natural polymers – amino-polysaccharides, such as chitosan (CS), is now of interest for membrane development due to biodegradability and the presence of free amino group responsible for binding polar penetrants and ability to form films with impressive thermal properties [4–10]. CS is traditionally obtained by deacetylation of chitin, a natural mucopolysaccharide of major importance, which is produced by a high number of living organisms [5] and belongs to the most abundant natural polymers together with cellulose.

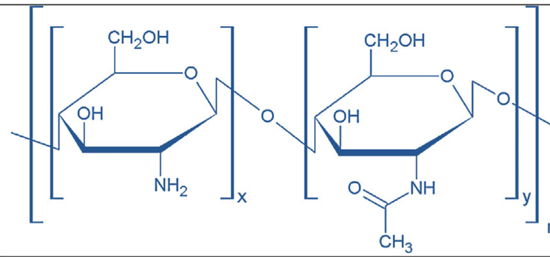
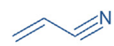
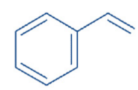
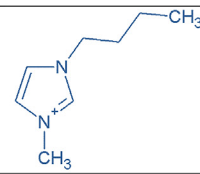
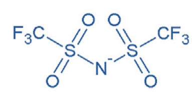
Still, the use of CS for applications in membrane gas separation has some limitations related to the low mechanical strength [11,12], comparatively low permeability [10] and hydrophilic surface character of CS films [5,12], which effect on membrane operational properties, performance and lifetime.

Recent development of synthetic approaches combined with physical modifications has led to a number of techniques to increase CS performance. For example, A. Ghosh, M.A. Ali and R. Walls [13] have shown that the CS film treated with ethylene glycol diglycidyl ether (EGDE) has an improved resistance to swelling in water at pH range from 5.2 to 9.1, and the treatment with a mixture of 0.25 EGDE in methanol increased the tensile modulus and decreased the ultimate elongation without affecting the maximum stress. N.S. Sambudi, S.B. Park and K.J. Cho [14] carried out mineralization of electrospun CS/poly(vinyl alcohol) (PVA) with $CaCO_3$ to obtain desired mechanical properties. As a result, the highest ultimate stress value was found to be 44 ± 3.2 MPa for the composite with 17 $_{wt.}$% of $CaCO_3$. Therefore, the maximum value of Young's modulus was 2328.35 ± 204.9 MPa for the composite with 34 $_{wt.}$% of $CaCO_3$. Other studies reported a notable change in CS mechanical properties was achieved by block and graft

* Corresponding author.
*E-mail address:* ilyavorotyntsev@gmail.com (I.V. Vorotyntsev).

https://doi.org/10.1016/j.polymertesting.2018.04.031
Received 7 February 2018; Received in revised form 26 March 2018; Accepted 20 April 2018
Available online 23 April 2018
0142-9418/ 

**Table 1**
Chemical structure of the primary materials.

| Name | Chemical structure |
|---|---|
| CS |  |
| AN |  |
| St |  |
| bmim |  |
| $Tf_2N$ |  |

copolymerization with vinyl monomers [15–17]. Moreover, CS gas separation properties can be improved by immobilization of ionic liquids (ILs) into polymeric matrix [10,16,18].

However, mechanical and physical properties of materials based on modified CS don't only depend on the chemical nature of polymer matrix but also strongly depend on their microphase-separated structure and supramolecular organization. The surface structure of CS-based films is widely studied to predict operational properties of a polymeric product. For example, C.C. Ryan, M. Bardosova and M.E. Pemble [19] have studied mechanical and structural properties of a range of CS-based interpenetrating network before and after modification with a tetraethylorthosilicate (TEOS) cross-linker and various-sized silica and polystyrene particles. M. Matet, M.C. Heuzey and A. Ajji [20] have studied morphology and antibacterial properties of materials based on blends of plasticized CS with metallocene polyethylene and have shown that mechanical properties of these blends were improved by compatibilization with ethylene vinyl acetate, while antibacterial properties were not affected. S.M. Luna and co-workers [21] have studied the cell behavior on CS membranes modified by argon and nitrogen-plasma treatments. There have shown the effect of their surface structure on the functioning of obtained biomaterials. In another study, A.E. Mochalova and co-workers [15] reported the effect of CS copolymers structure on the physical-mechanical properties of these films and biodegradability by micromycetes. O.B.G. Assis and co-workers [22] have studied the surface structure of self-assembled films obtained from water-soluble CS rich solution precursor at sputtering metallic deposition. However, the relationship between a surface structure and mechanical properties of modified CS still requires considerable efforts for better understanding.

A polymer surface structure can be efficiently studied by atomic force microscopy (AFM) [16,23–28].

This method is suitable for a research of polymers not only because of high lateral and vertical resolutions but also because of its ability to gain quantitative three-dimensional information about surface topography, roughness, height and tilt angle of topographic structures. Moreover, unlike such methods as scanning electron microscopy and tunneling probe microscopy, AFM doesn't require special sample preparation, doesn't impose conditions on sample conductivity and allows to study polymers without destruction of their soft surface. Also, the results of AFM scanning are presented in digital format, which allows them to be processed using mathematical statistics methods [23,29]. It is a critical point, because AFM results combined with ones of mathematical-statistical processing allows to assess a surface structure not only qualitatively but also quantitatively.

This novel study for the first time in the world represents the relation between particular surface structure of CS copolymers and their mechanical properties. In order to control the surface morphology, ILs based on the cation of 1-butyl-3-methylimidazolium (bmim) with various anions ($[BF_4]$, $[PF_6]$ and $[Tf_2N]$) were used. The resulted were obtained with use of advanced research technique – AFM supported by wettability measurements and mechanical testing.

## 2. Experimental section

### 2.1. Materials

Chitosan (CS) with a molecular weight of $1.05 \cdot 10^5$ and a deacetylation degree of 80% was supplied by Bioprogress CJSC (Russia). Acrylonitrile (AN) with purity of 99% was from Lukoil PJSC Subsidiary (Russia). Styrene (St) with purity of 99%, and also 1-butyl-3-methylimidazolium (bmim) with various anions – $[BF_4]$, $[PF_6]$ and $[Tf_2N]$, solvents of acetone, tetrahydrofuran, dimethylformamide were supplied by Sigma-Aldrich (USA). L-Ascorbic acid (pharmaceutical secondary standard) and hydrogen peroxide solution 30 $_{wt.}$% in $H_2O$ were obtained from Himreactive (Russia). Azobisisobutyronitrile (AIBN) 99% pure was supplied from Chemical Line (Russia) and was used after