



Enhancement of polycarbonate membrane permeability due to plasma polymerization precursors

Dilek Çökeliler*

Biomedical Engineering Department, Başkent University, Bağlıca Campus, 06530 Ankara, Turkey

ARTICLE INFO

Article history:

Received 12 August 2012

Received in revised form 10 October 2012

Accepted 24 November 2012

Available online 26 December 2012

Keywords:

Plasma polymerization
Polycarbonate membrane
Permeability
Allylamine

ABSTRACT

The diffusivity of different species through a membrane depends on several factors to illustrate the structure of the matrix, molecular size and concentration of the species and temperature. This study concerns the use of the low-pressure plasma process with different monomers to confer surface chemical character to polycarbonate membranes without altering their bulk properties for change membrane permeability. Track-etched polycarbonate membranes with 0.03 μm pore sizes were modified by plasma polymerization technique with two precursors; acrylic acid and allylamine in radio frequency discharge at certain plasma process conditions (discharge power: 20 W, exposure time: 10 min, frequency: 13.56 MHz). The transport properties of model organic acid (citric acid) was studied through unmodified and modified polycarbonate membranes by using diffusion cell system. Such plasma treated membranes were characterized by scanning electron microscopy, X-ray photoelectron spectroscopy and surface energy changes were studied by static contact angle measurements. These results showed that the change of surface properties could be used to improve the transport properties of the target substrates. The diffusion of citric acid through plasma treated polycarbonate membrane was increased about $54.1 \pm 3.5\%$ with precursor: allylamine while it was decreased $48.7 \pm 2.5\%$ with precursor acrylic acid. It was observed that the presences of proper functional group (like amino) in surfaces of pores can raise the affinity to citric acid and improve its transport rate.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Recently there is an increasing interest toward the integration of two or more varied processes into one process yielding new and better results. To give an example of such an integrated process is extractive fermentation, which combines fermentation products, e.g. organic acids, during the process favors the efficiency of the latter due to reduced inhibiting effect of the products. The aim of this study was to show how different chemical surface structure alters the citric acid permeability of track etched polycarbonate membranes. As a citric acid was chosen for reference organic acid since it is importance for the food industry. Moreover end-product of some process is almost accompanied by waste and/or recycling streams containing acid–water mixtures. Thus, the separation of aqueous acid mixtures is of interest to the chemical industry.

The facilitation of some ions and substrates in liquid membrane extraction instead of classical extraction allows the simultaneous recovery of the organic acid from the fermentation medium and its

pre-concentration in another solution appropriate for subsequent treatment [1]. The leaching of organic compounds is also inconvenient since the final product, present in the receiving aqueous. Bulk liquid membranes were often used to simulate membrane transport of organic acids of biological interest. These membranes displayed a high selectivity due to a specific complex (hydrogen bonding, electrostatic or hydrophobic interactions) of the solute by the selective carrier, but presented a low stability [2]. Usually, the carrier, the solvent or both suffer from continuous leaching out from the membrane support to the aqueous phases, therefore short lifetime of the liquid membrane reduces the industrial exploitation of these membranes [3]. The review of stability of supported liquid membranes clearly indicates that the stability is a major problem for its industrial application.

In this study the usage of hydroxyl group or amino containing chemicals as the vapor source at plasma polymerization was a new idea to improve basic transport characteristic of the polycarbonate membrane surface. Polycarbonate track-etched (PCTE) membranes were selected since novel applications have been proposed for these types with well-defined pore characteristics e.g. very sharp cut off allows their use in the filtration field, yet they were also useful as in vitro substrate in cell biology and also used to determine the reflection coefficients of rigid and partially flexible

* Corresponding author. Tel.: +90 312246666x1325; fax: +90 3122341051; mobile: +90 5334465576.

E-mail address: cokeliler@baskent.edu.tr

macromolecules [4]. PCTE membranes have been used in applications such as filtration, blood plasma separations, drug delivery, and flow control of reagents for assays. Several studies of these membranes have involved gas permeation/separation applications. PCTE membranes are unique in that they possess cylindrical pores in their fabrication process. Their pore morphology can be considered close to ideal with regard to the availability of uniform, straight cylindrical pores. Our objective was to examine the utility of employing these membranes as mechanically simple, yet precise, approach to control acid transport behavior for ultimate use [5].

In order to create membranes with controllable transport properties, one can use the ability of the macromolecules at the surface layer to make reversible conformational transitions. The research in this direction is related to a goal-directed formation of a membrane surface with tailored chemical structure. For this purpose, various methods are used: chemical methods [6] or radiation-induced graft polymerization [7], preliminary activation of the surface etc. [8]. With the same goal, membranes are successfully modified by deposition on the surface of thin polymeric layers obtained by plasma polymerization [9] that was the direct process from the monomer vapors fabricates plasma polymers for the practical use. Even though there are many ways to alter the surface chemistry, plasma treatment appears to be the most effective and convenient one. Plasma polymerization provides ultra-thin membranes composed of cross-linked structure, and the functions of membranes are due to the surface as well as the bulks. It is well known that plasma treatment can alter the physicochemical properties of the polymer surface. Such goals as improvements of wettability, permeability, conductivity, printability, adhesion or biocompatibility are easily achieved within very short time. Plasma polymerized layer has better thermal stability and adhesion properties than the layer formed by conventional methods and we previously reported a plasma treatment studies for sensor surfaces, biomaterials that achieves new permanent surface properties [10]. The usage of plasma provides a number of additional advantages such as: the control of the thickness of the polymeric layer deposited on the membrane surface, the high adhesion of the layer, the short treatment time and the opportunity of using of a wide list of organic and element-organic compounds for modification. Thus, the surface properties of the formed membranes appreciably depend on the type of discharge and nature of the chemical compound used for modification.

Focus of the presented work is on testing the differences from transport mechanism of citric acid from medium using thin film deposition on PCTE with monomers; acrylic acid and allyl amine as the precursors and understanding the mechanism. The modifications based on plasma polymerization of amino compounds are of particular interest for biomedical applications [11–19]. Membranes are rarely used as a substrate for such amino modifications yet in the literature, only membranes for gas separation [20–22] and filtration [15,23] are described, while not transporting properties of acids were tested previously. On the other hand, introduction of polar groups such as carboxylic acid has been interesting for the characteristic functions of adsorption, biomaterial and surfactants [24]. Fabrication of the acidic surfaces of substrates and the coating by plasma polymers containing the –COOH group was tested for the same motivations. PCTE membranes were modified in a glow discharge reactor by plasma polymerization technique at certain conditions with different monomers. Then, the effect of type of monomers on the membrane permeability was tested by a diffusion cell system. The chemical and physical structural characterization of the PCTE membranes before and after the surface modification is done by means of scanning electron microscopy and X-ray photoelectron spectroscopy. The surface wettability of the pure and plasma modified membranes were characterized using the surface contact angle of water.

2. Experimental

2.1. Plasma polymerization process

PCTE membranes with nominal pore size $0.03\ \mu\text{m}$ was obtained from Poretics (California, USA) and treated by plasma within a tubular type reactor containing a pair of plate copper electrodes separated by 5 cm (Fig. 1). A 13.6 MHz radio frequency generator was used to sustain glow discharge in the reactor and power losses were minimized by means of a matching network. PC membranes were located in the center of two electrodes. Monomer acrylic acid (AAc) of 99% purity was purchased from Merck Co. and allyl amine (AA) was obtained commercially (Sigma, Steinheim and Merck, Darmstadt, Germany). After the system was evacuated to a pressure of 10^{-3} Torr, first the AAc vapor was introduced to the system to a predetermined pressure of 5 Pa. Monomer vapors were allowed to flow at a rate of 25 ml/min. Then, RF power was adjusted to 20 W and the membrane was exposed to glow discharge for 10 min. At the end of the process the RF generator was turned off and the system was fed with Argon gas for 30 min to deactivate free radicals. After the one set of the plasma polymerization process, new polycarbonate membranes were inserted and monomer container was filled by new precursor; AA. The plasma was ignited at a frequency of 13.56 MHz with power 20 W for 10 min. All parallel modifications were repeated at the same plasma polymerization parameters (discharge power: 20 W, time: 10 min, flow rate: 25 ml/min). The monomers were chosen to provide surfaces differing greatly in their surface energies and stability. These factors were varied and their effects on acid permeability of PCTE membranes were studied using citric acid as permeate.

2.2. The characterization of PCTE membranes

The surface morphologies of PCTE membranes were investigated by using AFM (Burlleigh Metrisc 2001A-MS) and pore structures were characterized by SEM (JEOL, JSM 5600, USA). For the SEM analysis membranes were photographed in the electron microscope with $5000\times$ magnification. The polymeric surface usually has no electrical conductance; hence a 10–15 nm gold layer must be provided by sputter coating, to remove electrostatic charge from the surface due to electron beam radiation.

Analysis of polymer surface functional groups after plasma treatments was performed by X-ray photoelectron spectrometer in ADES-400 equipped by Al K α excitation sources and a hemispherical energy analyzer was used to obtain information about the composition and the chemical bonding of elements found in a surface region of untreated and plasma treated samples. The operating pressure was 1×10^{-7} Pa. Pass energies 50 and 15 eV were used for the survey and high resolution scans, respectively. The take-off angle was $\alpha = 45^\circ$. The HR envelopes were analyzed and peak-fitted after subtraction of a Shirley background using a Gaussian–Lorentzian peak shapes obtained from the Casa XPS software package. The signal of C 1s, 285 eV, was selected for energy calibration.

The water contact angles were measured using a NRL (Rame'–Hart) goniometry. The contact angle of a pure water (de-ionized with a resistivity of 18.2 MV cm) drop on the membrane surface was measured by sessile drop method. The membrane was placed over a micrometer bench and multiple droplets are formed on the surface using a syringe. The images of the water droplets on the membrane surface was captured by a high-resolution video camera and digitized. The contact angles were directly measured from the images using a software. For each specimen, the measurements were repeated in three different areas, 10 times each area. The measured values of the contact angles were averaged.

Download English Version:

<https://daneshyari.com/en/article/5360621>

Download Persian Version:

<https://daneshyari.com/article/5360621>

[Daneshyari.com](https://daneshyari.com)