Applied Surface Science 268 (2013) 450–457

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Tuning the resistance of polycarbonate membranes by plasma-induced graft surface modification

Lukas Baumann[a,b], Dirk Hegemann[a], Damien de Courten[c,d], Martin Wolf[c], René M. Rossi[a], Wolfgang P. Meier[b], Lukas J. Scherer[a,*]

[a] Empa, Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, 9014 St.Gallen, Switzerland
[b] University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland
[c] Division of Neonatology, University Hospital Zurich, Frauenklinikstrasse 10, 8091 Zürich, Switzerland
[d] ETH Zurich, Rämistrasse 101, 8092 Zürich, Switzerland

ARTICLE INFO

Article history:
Received 11 September 2012
Received in revised form
17 December 2012
Accepted 20 December 2012
Available online 29 December 2012

Keywords:
Surface coating
Membrane permeability
Caffeine delivery
Controlled delivery
Surface hydrophilicity
Plasma induced surface modification

ABSTRACT

To tune the permeability resistance of porous polycarbonate (PC) membranes for caffeine, their surfaces were plasma modified with different monomers in a *grafting from* process. These coatings provided characteristic surface hydrophilicities. It was found that membranes with more hydrophilic surfaces have lower resistances to let caffeine pass through than membranes with hydrophobic surfaces. Additionally, it was possible to post-modify a poly(2-aminoethyl methacrylate) (AEMA) coated PC membrane with octanoic acid (Oct) under mild conditions. This post modification allowed transforming a slightly hydrophilic PC-AEMA membrane with a moderate permeability resistance into a hydrophobic PC-AEMA-Oct membrane with a high permeability resistance. Overall, it was possible to tune the PC membrane resistance for caffeine in a range from 5100 up to 15,100 s/cm.

1. Introduction

Neonatal caffeine therapy for new-borns suffering apnea is known to have a beneficial impact on the rate of survival without disability of preterm infants [1]. A membrane with a well-defined permeability resistance to let caffeine pass through could be a key unit of a transdermal caffeine delivery system [2,3].

Since polycarbonate (PC) membranes are known to be biocompatible and are widely commercially available, they are good candidates for drug delivery applications [4,5]. Being able to tune the resistance of PC membranes for caffeine to make them suitable for caffeine delivery systems or for more general drug delivery setups was the aim of this investigation.

The surface is the place where interactions of a material with its surrounding takes place. To tune the property of a polymeric material, it is essential to modify its surface in a predictable way [6–9].

Polymer surfaces can be modified by *grafting* of preformed polymers *to* a surface [10], by growing polymers from an activated surface (*grafting from*) [3,9,11–14] or by deposition of surface-active compounds [8,15]. The last modification often lacks long-term stability [11]. *Grafting to* approaches sometimes show limitations regarding coverage homogeneity of the surfaces due to steric repulsion of the preformed polymers [16]. Today, *grafting from* is one of the most promising approaches for surface modifications. There are several ways to achieve surface activation to induce polymerization, including plasma discharge methods [17–21], UV irradiation [11,22,23], ozone treatment [24] and γ-ray irradiation [13].

Plasma modification is a fast, dry and environment friendly technology which has become an important process step in many industrial fields. It enables the tailored surface functionalization of polymers, while maintaining their desirable bulk properties [25–27]. Besides the creation of active surface species, cleaning of the surface is an additional beneficial process which makes plasma a promising approach for creating homogenously coated polymer surfaces in a reproducible manner [25,28–30].

In order to optimize the plasma activation of polycarbonate membranes, the number of reactive species created in the plasma and their lifetime has to be regarded. Hence, the gas mixture and the pressure are important parameters beside power input and treatment time. Especially, argon/oxygen gaseous

* Corresponding author. Tel.: +41 58 7657469; fax: +41 58 7657762.
E-mail address: lukas.scherer@empa.ch (L.J. Scherer).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.12.125

mixtures were found to improve the adhesion on polycarbonate substrates [31,32].

In this work, the polycarbonate membranes were treated with an argon/oxygen ratio of 6:1 and moderate pressure. Similar plasma parameters have been previously reported for the treatment of different porous media such as textiles, non-wovens and membranes [33,34]. Polycarbonate is a polymer which typically shows linear etching rates with plasma exposure time [30].

The beneficial impact of chemical treatment of plasma coating concerning long term stability of polymeric surfaces is well known in literature and was also evident in this work [35–37]. In this study, we report on a novel plasma setup, which allows the modification of the activated membranes in solution under inert conditions. Thus nonvolatile monomers can be used in contrast to convenient gas deposition processes [18]. The herein reported surface-modification method allows the adjustment of the surface hydrophilicity, which leads to membranes with a range of permeabilities to the small molecule caffeine.

2. Experimental

2.1. Materials and methods

Polycarbonate (PC) Membranes Cyclopore Track Etched, 1.0 μm pore diameter, 47 mm membrane diameter, were purchased from Whatman. Methacrylic acid (MAA) and absolute ethanol, extra dry, was delivered by Acros Organics. Octanoic acid purris (Oct) was obtained from Riedel-de Haën. Anhydrous methanol, 2-Hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), 2-Aminoethyl methacrylate (AEMA), 2-Acrylamido-2-methyl-1-propane sulfonic acid sodium salt (AMPS-Na) and aluminum oxide, Type CG20, were obtained from Sigma Aldrich. All chemicals, unless stated otherwise, were used as delivered without further purification.

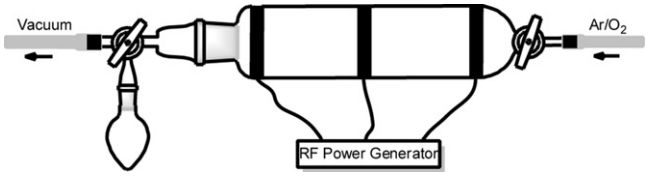
Argon (99.9995%) and Oxygen (99.9995%) were purchased from Alphagaz. A Dressler Cesar RF Power Generator, a MKS Multi Gas Controller 647C, two MKS Mass-Flo controllers and a Vacuubrand RE 2.5 rotary vane vacuum pump were used for the plasma set up.

The franz cell was purchased from SES Analyze Systeme with a receptor volume of 12 mL and an orifice area of 1.77 cm^2.

UV–vis measurements were performed on a Varian 50Bio/50MPR. Contact angle (CA) measurements were performed on a Krüss G10. For balancing, a Mettler Toledo AB204-S was used. IR measurements were performed on a BioRad FTS 6000 equipped with an ATR Golden Gate. NMR spectra were recorded on a Bruker 400 MHz. Scanning electron microscopy (SEM) pictures were recorded on a Hitachi S4800. X-ray photoelectron spectroscopy was performed on a PHI 5600 spectrometer. XPS data were analyzed using the program CasaXPS. Profilometric measurements were performed on a Dektak 150 from Veeco.

2.2. Plasma chamber

Scheme 1 shows the plasma chamber used to produce the surface modified membranes [18]. A glass tube (length: 16 cm, diameter: 4.5 cm) was equipped with three copper bands (length: 15 cm with: 2 cm). The first band was wrapped around the central part of the tube. The two others were fixed in a distance of 6.0 cm each on the left and right part of the tube to get a symmetrical setup. The central band (electrode) was connected to the RF power generator via a matching network, while the outer two bands (counter electrode) were connected to the grounded coaxial shield of the RF coupling. At one end, the glass tube was connected via a gas flow controller to argon and oxygen gas bottles. At the other end, a three-way valve connected the glass tube with the vacuum pump. There was a free connection, which allowed flooding the plasma chamber under defined conditions without opening the chamber. For these experiments, a round-bottom flask with a monomer solution was attached to this connection.



Scheme 1. Plasma set up for surface activation and modification in liquid phase.

To initiate the plasma, the vacuum pump was at full power and gas flow was set to 15.0 sccm argon and 2.5 sccm oxygen to reach a pressure of 52 Pa in the chamber. With 25 W and a radio frequency of 13.56 MHz the plasma could then be ignited. After initiating the plasma, it was possible to lower the power to a minimum of 10 W. The plasma expands symmetrically to both sides of the central electrode up to the outer electrodes.

2.3. Etching of PC-membranes

In order to examine the etching effect of the applied plasma conditions on the PC membranes, one membrane was positioned in the plasma chamber, with the shiny side pointing to the gas phase. While the vacuum pump was at full power, the gas flow was set to 15 sccm argon and 2.5 sccm oxygen. The chamber was rinsed under these conditions for two hours to remove other gases from the chamber and to stabilize the gas flow. Immediately after initiating the plasma (25 W, 13.56 MHz), the applied power was reduced to 12 W. The membrane was etched for a designated time span (between one and four minutes), removed from the chamber and then analyzed without further treatment.

2.4. Monomer solution

Inhibitors of stabilized liquid monomers were first removed by chromatography over aluminum oxide. 30 mL of a 3.17 M methanolic solution of the monomer was placed in the round-bottom flask and degased for 1 h by argon bubbling. Only AMPS-Na was used as delivered without further purification (50 wt.% in water).

2.5. Coating of PC-membranes

For the wet-chemical attachment of functional molecules on the plasma-activated membrane, two membranes were positioned in the plasma chamber next to each other, with the shiny side pointing to the gas phase. The chamber was evacuated and purged for two hours with 15 sccm argon and 2.5 sccm oxygen until a constant gas flow was obtained. After the plasma was initiated, the power was reduced to 12 W. After 4 min of plasma treatment, the power and the gas flow were switched off and the chamber was evacuated. Afterwards, the chamber was flooded with the prepared monomer solution via the foreseen connection of the three-necked valve and the reaction mixtures were stored under argon (100 kPa overpressure). The flooded chamber was then stored for 12 h at 20 °C in a conditioned room.

After removal of the left-over monomer solution, the membranes were washed with ethanol and water in an ultrasonic bath for 5 min each to remove residual monomers. Finally, the membranes were dried *in vacuo* over molecular sieves for at least 2 h before being analyzed.