European Polymer Journal 44 (2008) 2130–2139

Contents lists available at ScienceDirect

European Polymer Journal

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

Surface modification and aging studies of addition-curing silicone rubbers by oxygen plasma

Dhananjay Bodas, Jean-Yves Rauch, Chantal Khan-Malek *

FEMTO-ST/LPMO, CNRS UMR 6174, 32 Av. de l'Observatoire, 25044 Besançon Cedex, France

ARTICLE INFO

Article history:
Received 16 April 2007
Received in revised form 4 April 2008
Accepted 7 April 2008
Available online 14 April 2008

Keywords:
PDMS
Surface modification
Contact angle measurements
Hydrophilicity

ABSTRACT

Poly(dimethyl siloxane) (PDMS) has been focused on recently due to its variety of applications specifically in microsystems technology. Many companies market two-component PDMS, which is comprised of a base component and a curing agent. Widely known and used for microsystems applications is Sylgard 184 from Dow Corning. Present work deals with two-component Room Temperature Vulcanized (RTV) PDMS from three different companies. They are Sylgard 184 from Dow Corning, RTV 615 from GE Silicones and RTV 141 from Rhodia Chemicals. Temporary increase in wettability of these three different types of PDMS by oxygen plasma by varying the plasma power and exposure time has been studied and compared with results available in literature. The hydrophobic recovery of the modified surfaces was monitored as a function of time and quantified. The surfaces were characterized using contact angle measurements and ATR-FTIR and XPS spectroscopy, their behavior analyzed in term of free surface energy and work of adhesion.

1. Introduction

Poly(dimethyl siloxane) (PDMS), an elastomer, is most widely and one of the most versatile material used in the construction of microfluidic devices, in particular for rapid prototyping [1,2]. One of the reasons for the popularity of PDMS is the particularly straightforward manufacturing method where PDMS precursor and catalyst can be cast against a mold/master in liquid form followed by a polymerization step. Definite advantages of replica casting with PDMS are: (i) the possibility of a low temperature polycondensation; (ii) low-cost and versatility; (iii) an excellent fidelity of replication (sub-0.1 μm) and resolution compatible with applications in the nano-meter regime (soft lithography techniques of micro-contact printing and associated techniques); and (iv) masters can be produced by several techniques in a variety of materials such as SU8 resist patterned by photolithography, silicon master etched by anisotropic wet etching (e.g. KOH) or by deep reactive ion etching (DRIE) etc. Because of its elasticity and chemical inertness, PDMS replica can be pulled from micromoulds without damaging the master, which results in an increased longevity of the master. PDMS also seals reversibly to itself or irreversibly to other materials, making it suitable for constructing hybrid hetero-material chips.

Other well known beneficial properties of PDMS are (i) it may be transparent down to 280 nm, in which case it is suitable for detection at a wide range of optical wavelengths; (ii) it is biologically inert and non toxic, which makes it compatible with cell patterning on various substrates; (iii) it is permeable to gases, a property which is useful when supplying oxygen to cell cultures in closed systems.

However, in spite of the many advantages of PDMS, the surface of PDMS cannot be used as is for a variety of applications and requires functionalization. In particular, PDMS surface is naturally hydrophobic and a number of efforts

* Corresponding author. Tel.: +33 381 853 999; fax: +33 381 853 998.
E-mail addresses: dhananjay.bodas@gmail.com (D. Bodas), chantal.khan-malek@lpmo.edu (C. Khan-Malek).

0014-3057/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2008.04.012

are being made to modify the surface of PDMS micro channels, in order to enhance hydrophilicity and electro osmotic flow (EOF) which limit its applicability for devices in microfluidics technology.

It has long been recognized that in order to modify the surface properties of PDMS, various techniques can be utilized that involve, physical or chemical treatments [3–7] or a combination of both [7–9]. Particularly oxygen plasma has been widely used to modify the surfaces of PDMS [10,11]. These studies report that oxygen plasma treatment propagate deep under the polymer surface (about several hundred nanometers) [12,13] and cause chemical changes in the near surface region of PDMS: polar functional groups containing hydroxyl groups (Si–OH groups) are introduced into its surface, leading to the hydrophilic surface. However, its surface characteristics gradually change during aging and the surface recovers its hydrophobicity after a short time as has been observed by various groups [6,14,15].

1.1. State of the art in oxygen plasma treatment of PDMS

Modification using oxygen plasma on cured and uncured PDMS surface was done by Hollahan and Carlson in 1970 [16]. Since then several methods using oxygen and UV/ozone plasma treatments were reported. Plasma treatment of PDMS as reported by Owen et al. [12] shows increase in wettability to improve adhesion with various organosilicon thin films. They studied the effect of RF plasma treatment on PDMS elastomer. They used various gases like argon, helium, oxygen or nitrogen and concluded that with the use of all gases a thin brittle, silica like layer is produced on the surface of PDMS. Also the hydrophobic recovery of the surface is due to migration of untreated polymer chains from bulk to the surface through cracks in the silica like layer as reported by Owen et al. [12].

Also several articles on hydrophobic recovery of PDMS while using oxygen plasma treatment was reported by Fritz et al. [17], Murakami et al. [6], Efimenko et al. [4], Hillborg et al. [13] and many more. Fritz et al. [17] has studied hydrophobic recovery of PDMS surface using cold plasma with variation in plasma parameters with various gases like oxygen, argon, nitrogen and helium. According to Fritz et al. [17] PDMS surface can be treated to zero contact angle without cracking by adjusting appropriate plasma parameters with change in gases. They reported hydrophobic recovery of both the cracked and uncracked surface, but different gases used only changed the recovery rate.

Murakami et al. [6] has characterized the oxygen plasma treated and untreated PDMS by contact angle. According to them after oxygen plasma treatment the water contact angles decreased on the PDMS surface. As stated by the authors results suggested the introduction of hydrophilic functional groups into the polymer chains and/or formation of oxidation products of low molecular weight on the polymer surfaces. The polymer films seem to recover back to their original hydrophobicity with time due to the migration of oxygen containing functional groups from the sample surface to the bulk as reported by the authors.

Hillborg et al. [13] has reported hydrophobicity changes in silicone rubbers (PDMS). They have used FTIR, Contact angle measurements and XPS for recording changes in hydrophobicity. They reported several possible mechanisms of hydrophobic recovery of silicone rubber films after exposure to corona discharge or plasma. According to the authors recovery can occur due to (i) migration of low molar mass species from the bulk to the surface, (ii) reorientation of polar groups at the surface into the bulk, (iii) condensation of silanol groups at the surface, (iv) external contamination of the surface, (v) changes in surface roughness and (vi) loss of volatile oxygen-rich species to the atmosphere.

Efimenko et al. [4] have reported the surface modification of Sylgard 184 PDMS by UV and UV/ozone treatment. According to the authors PDMS when exposed to UV, underwent chain scission, involving both main backbone and the side groups. The radicals formed during this process recombined, forming a network whose wetting properties were close to those of untreated PDMS. In contrast the UV/ozone treatment caused very significant changes in the surface and subsurface structure of the PDMS which contained a large number of hydrophilic groups (OH).

The hydrophobic recovery of PDMS is an inherent disadvantage of using PDMS in microfluidics as reported. Work on hydrophilic stability of PDMS was reported by Whitesides group [10,18] which used plasma oxidation to modify PDMS stamps surface. Recently Bhattacharya et al. [19] have studied surface wettability of PDMS under oxygen plasma treatment by varying various parameters, such as plasma system, system pressure, power and time of exposure to optimize the hydrophobic recovery. According to them, PDMS recovers back to its original hydrophobicity under oxygen plasma under certain process conditions. According to authors oxygen plasma exposure at lower RF power with shorter duration makes a thin layer or undamaged oxide on the PDMS surface with active silanol groups. With prolonged exposure the treated PDMS forms excessive surface silanol concentration causing a reorientation of surface chemical bonds. As the bond density increases a chemical transformation on the surface known as chain scission results. In such a situation a marked reduction in the number of surface silanol bonds occur by back biting scission reactions, a physical surface cracking and a gradual migration of the mobile, low molar mass PDMS to the surface. To achieve greater hydrophilic stability variation of plasma parameters was focused on in many of the research articles.

Delamarche group has varied the base to curing agent mixing ratio in order to achieve greater stability. Donzel et al. [20] have reported use of PEG derivatized PDMS to achieve stable hydrophilicity of PDMS surface for its use in stamps for microcontact printing. Recently thermal aging effect to increase hydrophilic stability was reported by Eddington et al. [14] the authors have reported stable hydrophilicity of PDMS over a couple of weeks. According to the authors hydrophobic recovery is due to migration of lower molecular weight species to the surface from bulk. There are several recent publications which use chemical grafting on to PDMS surface in order to increase hydrophilic stability.