



The effect of direct fluorination of polydimethylsiloxane films on their surface properties

Sangyun A. Lee^a, Sang Hyup Oh^b, Woojin Lee^{a,*}

^a Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology, 335 Gwahak-ro, Yuseong-gu, Daejeon, Republic of Korea

^b Environmental Metrology Center, Korea Research Institute of Standard and Science, 1 Doryong-dong, Yuseong-gu, Daejeon, Republic of Korea

ARTICLE INFO

Article history:

Received 12 October 2008

Accepted 22 December 2008

Available online 25 December 2008

Keywords:

Polydimethylsiloxane

Surface modification

Direct fluorination

Surface energy

Contact angle

ABSTRACT

To investigate the effect of fluorination on the surface of polydimethylsiloxane (PDMS) film, direct fluorination was performed under a mild condition (approx. 2000 $\mu\text{mol/mol}$ F_2 in nitrogen) for 120 min. No structural damage of PDMS films was observed on the scanning electron microscopic images under the condition. Fourier-transform infrared/attenuated total reflectance (FTIR/ATR) and energy dispersive X-ray spectroscopy (EDS) results showed a successful fluorine introduction resulting in the structural change of PDMS. Surface property changes of PDMS films with respect to the extent of direct fluorination were also examined. Contact angles of water and alcohols on the PDMS surfaces decreased as fluorination time increased. Most alcohols showed greater decrease than water in the contact angle as a result of long-term fluorination, which sometimes results in zero contact angles of alcohols on the PDMS surfaces. Surface energy of PDMS films increased more than 200% after the direct fluorination for 120 min.

© 2008 Elsevier Inc. All rights reserved.

1. Introduction

Polydimethylsiloxane (PDMS) is one of the most widely used polymeric materials due to its low surface tension, hydrophobic property, stability against heat and oxidation, non-inflammability, and non-toxicity. In the field of environmental analysis, PDMS has been used as a GC column filler and solid phase micro-extraction (SPME) probe materials, etc. It has, however, disadvantages such as low mechanical strength, weak stability in acid, base, and organic solvents, and high gas permeability.

On the other hand, fluoropolymers have superior chemical and thermal stability, non-adhesive property, and barrier property [1]. It is also known that the synthesis and fabrication of fluoropolymers are difficult and they are generally expensive. Most benefit of fluoropolymers come from their surface properties, therefore surface fluorination methods for the enhancement of surface properties of non-fluoropolymers have been introduced to modify their thin top surfaces.

Direct fluorination is one of the most effective and promising method to fluorinate polymer surface using elemental fluorine [2, 3]. The method introduces fluorine gas or its mixture with inert gas (nitrogen or helium) onto the surface of polymeric materials and induces a spontaneous reaction. Fluorination is typically rapid

at room temperature without extra-heat or solvents. In addition, it is easy to control the initiation and termination of the reaction. Excessive direct fluorination, however, may damage polymer structure on the surface due to its high reactivity. To avoid the breakage of polymer backbone and irreversible deformation of polymer surface and to accomplish a maximum substitution of weakly bonded surface chemical species by fluorine, direct fluorination should be performed under a mild condition (low partial pressure of fluorine and room temperature) at an early stage and more forcing conditions at next stages [4].

The direct fluorination of polymer surfaces has been extensively studied and thoroughly reviewed by Kharitonov et al. [2,5–11].

It has been well known that fluorination gives better barrier property [12], chemical resistance, and gas selectivity of gas separation membranes [13–15]. Most studies on the direct fluorination have focused on the modification of the surfaces of glassy polymers such as polyethylene [16], polystyrene [11], polysulfone [17], and poly(phenylene oxide) [18] and their applications to date. However, relatively less attention has been paid to modify the surface of rubbery polymers [19] such as PDMS by the direct fluorination for the enhancement of its surface properties. We have identified the effect of direct fluorination of PDMS films on their surface properties under a mild condition in this research. The changes of PDMS surface structure as well as its surface properties due to the extent of direct fluorination have been observed and discussed.

* Corresponding author. Fax: +82 42 350 3610.

E-mail address: woojin_lee@kaist.ac.kr (W. Lee).

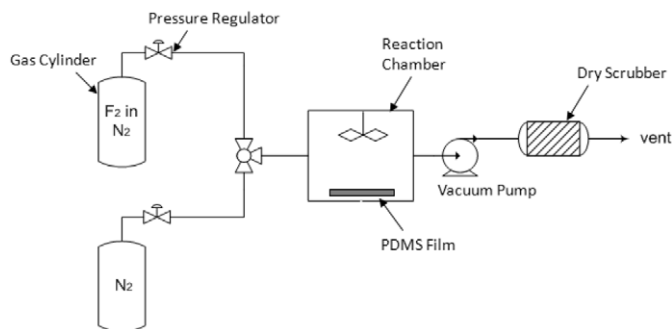


Fig. 1. Schematic diagram of experimental setup for direct fluorination.

2. Materials and methods

2.1. Film fabrication

PDMS (Dow Corning Sylgard 184® dual-component system) was purchased and used without further purification. *n*-Hexane (HPLC grade) was used as a solvent of PDMS polymer. PDMS base solution (18.1 g in 100 mL hexane) and curing agent solution (1.84 g in 100 mL hexane) were prepared and degassed using ultrasonication, separately. The two solutions were mixed at a volume ratio of 1:1 in short time before film casting. Approximately 1 mL of the mixture was introduced to the petri-dish and the solution was spin coated for 5 s at 2000 rpm. Coated films were stored in a forced convection oven at 80 °C for more than 24 h in a horizontal position to remove solvents and to finish cross-linking reaction.

2.2. Direct fluorination

Fig. 1 shows a schematic diagram of experimental setup for the direct fluorination of PDMS films. The direct fluorination was performed in a stainless steel chamber (27 L). The films were sparsely located in the chamber so that fluorine gas introduced to the chamber could fully and directly contact the films for an exact time period. Vacuum and nitrogen ([N₂] > 99.9999%) purging were performed more than three times to remove impurities such as dusts, water vapour, and oxygen in the chamber and on the polymer films. Diluted fluorine gas (2021 ppm in nitrogen balance) was introduced into the chamber and circulated by an internal fan to guarantee homogeneous environment. Different fluorination times (10, 30, 60, and 120 min) were applied to the PDMS films to investigate an effect of extent of fluorination on their surface properties, while temperature (25.0 °C) and fluorine concentration were kept constant for each experimental run. Vacuum was applied after the direct fluorination of PDMS films to terminate the reaction and nitrogen purging and vacuum were repeated three times to ensure complete removal of residual fluorine gas. Vent gas including fluorine was passed through a dry scrubber filled with activated alumina pellets before discard. Fluorinated PDMS films were stored in a desiccator at room temperature.

2.3. Surface analyses

The change of chemical species on the PDMS surface was observed by an energy dispersive X-ray spectroscopy (EDS, EDAX International Corp., Phoenix™). Chemical species on the polymer surfaces were qualitatively and quasi-quantitatively measured at the moments of fluorine introduction and elimination. Fourier-transform infrared spectroscopy (JASCO FTIR-4100)/attenuated total reflectance (ATR, PIKE MIRacle™) analysis was also performed to observe the modification of PDMS film surfaces before and after the fluorination. A silicone/ZnSe crystal plate was used as a reflecting element and an incident beam angle for ATR was set

to 45.0°. Surface morphology was observed by a scanning electron microscopy (SEM, Philips XL30S FEG). The surface of PDMS film was observed by SEM before and after the fluorination which can significantly affect physicochemical properties and morphology of PDMS surfaces. Contact angles of deionised water, methanol, ethanol, 1-propanol, 2-propanol, 2-butanol, 1-pentanol, 1-octanol, and diiodomethane were also measured before and after fluorination. Purity of alcohols used in this experiment was higher than 99.0%. The measurement of the contact angle was performed by a sessile drop method using the drop shape analyser (KRÜSS DSA100). Liquid droplets were deposited on the fresh surface of PDMS films and the angles of multiple droplets were measured and averaged. Contact angles of deionised water and diiodomethane were used to calculate the surface energy of PDMS film before and after the direct fluorination.

3. Results and discussion

3.1. Structural change after the direct fluorination of PDMS films

It is well known that the fluorination on the surface of polymer film induces the substitution of specific atoms and/or functional groups on the polymer by fluorine atoms [20]. Hydrogen in methyl group on the surface of PDMS film as well as methyl group itself is most likely to be substituted by fluorine (i.e., C–H to C–F (485 kJ/mol) and/or Si–CH₃ to Si–F (565 kJ/mol)) due to the weak bond energy between Si and C (306 kJ/mol) during the direct fluorination of PDMS [21].

The results of FTIR measurement of fluorinated PDMS films shown in Figs. 2(a) and 2(b) can verify the structural change of PDMS polymer. Variations of IR spectra in % reflectance were observed at 2960, 2906, 1258, and 800 cm^{−1} under the different extent of fluorination. Films with longer fluorination time showed higher % reflectance of IR spectra at the wavelengths (i.e., their band absorbance intensities decreased). It has been reported that IR spectrum at 2960 and 2906 cm^{−1} represents asymmetric and symmetric stretching of methyl groups, respectively [22] and that at 1258 cm^{−1} does a symmetric deformation vibration of methyl group [22,23]. The band absorbance intensities of IR spectra in this region decreased as the fluorination time increased, implying that C–H bonds were attacked by fluorine and transformed to C–F bonds on the PDMS film surface. It is known that IR bands around 800 cm^{−1} represent rocking of methyl group as well as stretching of Si–C bonds [24]. The change of band absorbance intensities in this area under the different fluorination time also indicates the removal of methyl groups. IR bands in the range of 1000–1060 cm^{−1} were merged as the fluorination time increased, which represents broad and strong asymmetric Si–O–Si stretching absorption [22]. This indicates that the introduction of fluorine atoms on the side chain of PDMS can affect the vibration of Si–O–Si backbone on the polymer surfaces.

In contrast, the decrease of % reflectance was observed at the following positions; 1725, 1626, 1180 shoulder, 940 shoulder, 899, 760 cm^{−1}. Weak absorption around 1725 cm^{−1} might due to the generation of carbonyl groups from unwanted oxyfluorination reaction. The change of % reflectance on the other wave numbers may suggest the formation of novel fluorinated chemical species bound on the PDMS film surface by the substitution by fluorine. IR bands observed in the range of 1000–800 cm^{−1} have been typically known as an existence of Si–F bonds [23,25]. However, no further efforts have been made for the identification of the novel fluorinated functional groups bound on the PDMS film surface in this research.

Fig. 3 shows EDS spectra of virgin and fluorinated PDMS films. No fluorine peak was observed on the surface of virgin PDMS film, while the intensity of fluorine peaks of fluorinated PDMS

Download English Version:

<https://daneshyari.com/en/article/610640>

Download Persian Version:

<https://daneshyari.com/article/610640>

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