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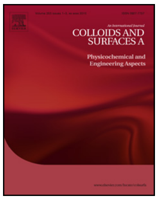

Chemical modification of PDMS surface without impacting the viscoelasticity: Model systems for a better understanding of elastomer/elastomer adhesion and friction

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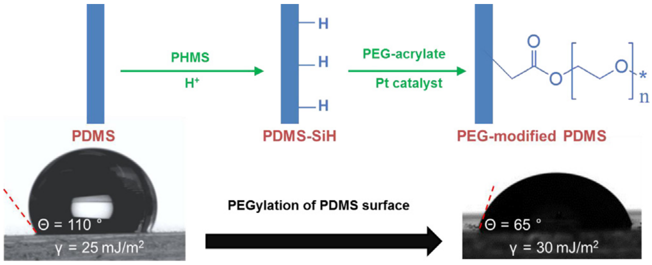
HIGHLIGHTS

- Poly(dimethylsiloxane) surfaces were modified with poly(ethylene glycol).
- Surface modification via hydrosilylation has no impact on viscoelastic properties.
- Modified surfaces exhibit lower contact angle and higher surface energy.

GRAPHICAL ABSTRACT



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ABSTRACT

The influence of both viscoelastic and interfacial parameters on the surface properties of elastomers is difficult to study. Here, we describe a simple route to achieve surface modification of PDMS without impacting the viscoelastic properties of the bulk. PEG modified PDMS surfaces were synthesized by two step surface modification based on hydrosilylation. The covalent grafting of PEG on the surface has been evidenced by AFM and ATR-FTIR, and its effect on the hydrophilicity characterized by static and dynamic contact angle. The static water contact angle of the PEG-modified PDMS decreases from 110° (for unmodified PDMS) to 65°. Dynamic contact angles also show a significant decrease in both advancing and receding contact angles, along with a significant increase in the contact angle hysteresis, which can be related to an increase in the surface energy as estimated by JKR measurements. The viscoelastic properties of modified PDMS are found to be quantitatively comparable to those of the unmodified PDMS. This simple method is an efficient way to prepare model materials which can be used to get a better understanding of the exact contribution of the surface chemistry on surface properties of elastomers.

1. Introduction

The frictional and adhesive behaviors of elastomers depend on the viscoelastic properties but also on interfacial parameters such as the surface chemistry and the surface topography of the two materials in contact [1–5]. The role of chemical interactions at the interface [6] and surface patterning [7–11] as well as viscoelasticity effects [12,13] on adhesion, friction, and also on other surface properties such as wetting, has thus started to be investigated extensively over the last years, but mostly independently from each other. However a real deep understanding of the coupling between these properties remains a challenge, and in consequence there is still a lack of prediction of the global effect of such properties.

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To identify the incidence of patterning on wetting, adhesion, and friction mechanisms, commercial polydimethylsiloxane (PDMS)-based elastomers have often been chosen as candidates as they have good mechanical properties, good thermal and chemical stability, transparency, and can be easily fabricated and patterned with good reproducibility. These features make these materials perfectly suited for applications in microfluidic or transfer printing. However, PDMS is rather chemically stable and has a low surface free energy (measured between 21 and 25 mJ/m^2) [14]. Moreover, these materials lack reactive surface groups, and may present low-molecular-weight mobile components having a high tendency to migrate to the PDMS surface from the bulk. This results in relatively poor intrinsic adhesive properties for these materials.

On the other hand, chemical modification of PDMS interface can drastically alter its frictional, adhesive and wetting properties but will also, in general, affect its mechanical properties. Indeed, developing a simple route to change the chemical properties of PDMS surfaces only, without impacting the bulk modulus (or creating, from a mechanical point of view, a bilayer system), is a challenging task which would prove useful to design model systems for a better understanding of the exact contribution of the surface chemistry on surface properties (adhesion, friction and wetting) of elastomers.

To modify the properties of PDMS surfaces and confer hydrophilicity to PDMS surfaces, various surface modification methods have been explored. One of the easiest means for generating the hydrophilic PDMS surface is its exposure to an air or oxygen plasma treatment [15,16]. However, this treatment leads to the formation of a stiff SiOH layer at the surface, which will then make the physical analysis of surface properties difficult and can lead to uncontrolled wrinkling and associated phenomena like surface cracks and grooves [17]. Furthermore, the result of this kind of treatment is temporary, and the surface will usually recover its hydrophobicity within a few hours due to low molecular weight chains diffusing to the surface and rearrangement of polymer chains near the interface [18,19]. Vickers et al. [20] used a two-step process involving solvent extraction of the oligomers followed by oxidation as one approach to solve this problem, making oxidized PDMS surfaces stable for at least 7 days in air but this kind of treatment still generates a stiff SiO_2 layer.

Several other PDMS hydrophilic surface modification strategies have been explored, such as UV treatment [21,22], chemical vapor deposition [23], layer-by-layer (LBL) deposition [24,25], sol–gel coatings [26], silanization [27], dynamic modification with surfactants [28], and protein adsorption [29], but all result in the formation of what can be seen as a bilayer system unstable over time.

Another approach for altering the properties of PDMS consists in predoping PDMS with chemicals (such as acrylic acid and undecylenic acid) [30] that will infuse in the matrix. However, by doing so, the chemical groups can perturb the crosslinking reaction and induce a significant change in the bulk mechanical properties of the elastomer. This approach depends also on the applicability of the chemical to be mixed with PDMS and the weight ratio of the added chemical. Seo and Lee [31] improved the wettability of PDMS by directly incorporating a nonionic surfactant into the PDMS. The concentration of the surfactant at the surface could then be changed by surface migration upon exposure to various solvents. Surface-initiated ATRP has been also used. Typically it involves creation of reactive sites on the PDMS surface followed by covalent linkage of a preformed polymer or more commonly a monomer that can then be used as the initiation site for a polymeric chain [32]. PEG was also tethered onto PDMS surface by using a swelling–deswelling method with block copolymers comprising PEG and PDMS segments [33]. All these treatments are long, complicated and dramatically alter the bulk and mechanical PDMS properties (often by a factor of 2 or more on the modulus when compared to unmodified PDMS).

An easier path consists in coating PDMS surface with hydrophilic polymers such as poly(ethylene glycol) (PEG) and its derivatives. Several techniques have been proposed to achieve this grafting. Star shaped PEG was grafted on PDMS functionalized using ammonia plasma treatment [34]. Simpler, Brook et al. developed a route using poly(ethylene glycol) monoallylether [35]. This method is a two-step surface modification process. Since PDMS does not have appropriate functional groups on the surface available to react with PEG, modification is necessary to introduce first active sites for subsequent functionalization. PDMS is initially functionalized with SiH groups under acid catalysis to give PDMS–SiH, followed by a platinum catalyzed hydrosilylation reaction with PEG. This is an addition reaction between SiH and allyl groups of PEG to create SiC bonds, and it is a method to replace the methyl groups on PDMS with PEG. A similar reaction was used by Iwasaki et al. [36] to graft triblock copolymers composed of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) and poly(vinylmethyl siloxane-co-dimethylsiloxane) onto the PDMS surface.

Inspired by this two-step strategy, we chose poly(ethylene glycol) methyl ether acrylate (PEG-acrylate) to modify PDMS surfaces through covalent bonding of PEG-acrylate chains on PDMS surfaces. We chose poly(ethylene glycol) acrylate (PEG-acrylate) because of three reasons: (1) this molecule has a terminating acrylic group (2) it is inexpensive and commercially available from common chemical companies with various molar masses and (3) the lower molar masses are liquid at room temperature, making it easy to react with PDMS disks of relatively large proportions. Moreover, the layer formed, being only a few monomers long, could be added on flat or patterned surfaces, and has the potential to be “invisible” in terms of mechanical properties.

The changes of PDMS surface properties during and after PEGylation are analyzed at different reaction times using contact angle measurements, AFM and ATR-FTIR study. The effects of this surface modification in terms of hydrophobicity were studied using both static and dynamic contact angles measurements. JKR technique was also used to determine the surface free energy and was coupled with rheological experiments to determine and compare Young’s modulus and loss modulus of modified and unmodified PDMS.

2. Materials and methods

2.1. Materials

Sylgard 184, a PDMS kit containing two parts, a liquid silicon rubber base and a curing agent, was purchased from Dow-Corning. Polyhydromethylsiloxane (PHMS), trifluoromethanesulfonic acid (CF_3SO_3H) were purchased from Merck. Karstedt’s platinum catalyst (platinum(0)–1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, soln. in vinyl terminated polydimethylsiloxane), diethylene glycol dimethyl ether (99%), anhydrous methanol, hexane and toluene were purchased from Alfa Aesar and used as received. Poly(ethylene glycol) methyl ether acrylate (PEG-acrylate, M_n = 480 g/mol given by the supplier), a viscous liquid, was obtained from Sigma Aldrich.

2.2. Methods

2.2.1. Preparation and surface modification of PDMS films

2.2.1.1. PDMS substrates. PDMS samples used in the present study for the surface modifications experiments were prepared using the Sylgard 184 silicone elastomer kit by the classical procedure,