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A simple method for fabrication of filler-free stretchable polydimethylsiloxane surfaces

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ABSTRACT

We propose a simple method to elaborate a filler-free stretchable PDMS surface strong enough to resist to successive elongation/retraction cycles even at high degree of stretching. It consists in creating free radicals on a filler-containing PDMS surface by argon plasma exposure and reacting them with a filler-free PDMS resin during the crosslinking step. Changes of physical and chemical properties upon plasma modification are monitored by FTIR and XPS spectroscopies, contact angle measurements and atomic force microscopy. Electron spin resonance (ESR) is used to identify the nature of radicals involved in interfacial bonding. Although a brittle silica-like layer is created on the filler-containing PDMS surface after plasma treatment, an increase in the PDMS/PDMS interfacial strength is observed and a high interfacial resistance has been found under elongation/retraction (stretching/relaxation) cycles.

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1. Introduction

Due to an attractive combination of (i) hydrophobic surface, (ii) high electrical resistance, (iii) low toxicity and (iv) flexibility, polydimethylsiloxane (PDMS) is an excellent material for biomedical uses [1,2]. However, when specific interactions with the surface are required, these advantages become problematic [3–6]. This is particularly true when the PDMS substrate is used for designing smart materials. For example, new types of *mechano-responsive materials* made of functionalized PDMS substrates are considered in our team [7,8]. These materials can reversibly change their surface hydrophobicity [7] or their surface accessibility under mechanical stimulation (elongation/retraction cycles in our case) [8]. In each case, the inert character of the PDMS has been changed by incorporating reactive groups at the near surface region using maleic anhydride plasma polymerization [9–11]. The versatile chemistry of the anhydride groups allowed to graft a great range of functional molecules for specific uses [12–15]. It has been shown, in particular, that these stretchable surfaces can be rendered antifouling by tailoring them with poly(ethylene glycol) (PEG) and, because of dilution of PEG chains during stretching, it has been also shown that the antifouling strength depends upon the elongation of the substrate [8]. In other words, we have demonstrated that the surface concentration of PEG chains can be regulated by simply stretching the substrate. However, these surfaces suffered from limitations due to the presence of silica fillers which are necessary today for achieving elastic property of the PDMS material [8]:

- Because the kinetic of growth of plasma polymer depends on the chemical and mechanical properties of the surface [16], the surface concentration of maleic anhydride groups (and then the concentration of PEG molecules grafted onto the anhydride groups) differed between silica-rich and silica-poor areas.
- During stretching, the dilution of the poly(ethylene glycol) molecules was not homogenous and varied according to their location (i.e. “between” or “on” the fillers particles) [17,18]. The aggregates moved away from each other while the separation of poly(ethylene glycol) molecules which were grafted on these aggregates was less important. Then, we suppose that the macroscopic stimuli (here stretching) did not lead to uniform dilution at the molecular scale.

In order to avoid the negative effects caused by the presence of fillers and to be able to uniformly control the concentration of functional groups by playing with elongation one solution could be the use of filler-free PDMS networks. But their tear strength is very poor and the degree of stretching available is very low.

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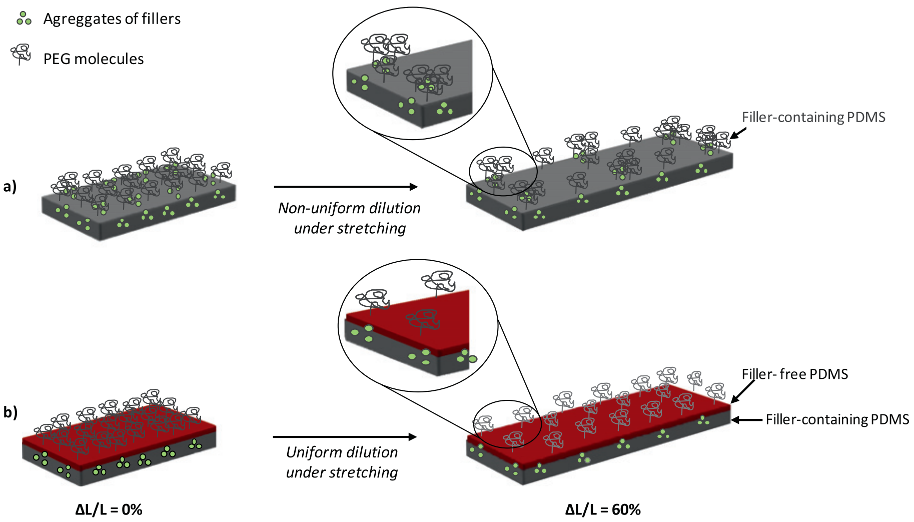

Fig. 1. Schematic representation of the surface dilution of PEG molecules induced by stretching (a) a filler-containing PDMS surface and (b) a filler-free PDMS surface anchored on the filler-containing PDMS substrate. $\Delta L/L$ corresponds to the stretching ratio where L is the initial length of the substrate and ΔL the difference in length before and after stretching.

To overcome all these problems we proposed here to elaborate a filler-free but always stretchable PDMS surface. It consisted in pouring a filler-free PDMS thin film on the top of a filler-containing PDMS substrate. Fig. 1 shows the advantages of using such filler-free PDMS substrate by illustrating PEG molecules dilution according to the presence or not of fillers at the interface. The PEG molecules should be more uniformly diluted under stretching when grafted onto filler-free PDMS surface.

The key point in elaborating such system was to strengthen the PDMS/PDMS interface in order to withstand the elongation step. Oxidation was the main surface modification process reported in the literature [19–26]. To do that and among several techniques involving physical or chemical treatments, plasma treatment (using air, oxygen or other oxygen-containing gas mixtures) is a simple and the most widespread technique applied [27–31]. However, the modifications are reported to be unstable. For example, the surface quickly recovers its native hydrophobic state [32]. More dramatic, a brittle silica-like layer can be formed at the PDMS surface leading to undesirable cracks under deformation and leading to deterioration of the PDMS/PDMS interfacial properties [10].

Besides, it is well known that exposure of polymers to inert gas plasma is sufficient to abstract atoms or chemical groups and to form free and highly reactive radicals. This result has been largely employed to convert the functional groups formed by plasma treatment at the PDMS surface with reactive molecules or polymers, or by plasma immobilization (crosslinking) of pre-deposited polymer nanofilms on top of the PDMS [33]. Here again, depending on the plasma conditions used, brittle silica-like layers or/and hydrophobic recovery have been observed. But surprisingly the presence of highly reactive free radicals has never been considered as a new opportunity to improve adhesion via interfacial bonding between two PDMS layers even if undesirable cracks were formed.

In this study, the modification of the filler-containing PDMS surfaces was performed by argon plasma treatment. The new idea here was to take advantage of the presence of free reactive radicals after plasma treatment and react them with the antagonist PDMS resin (here the filler-free PDMS) during the crosslinking step. After understanding the plasma effect and aging phenomena on PDMS surface modifications, we have highlighted the nature of free radicals in the plasma modified PDMS layer and we have shown the role of these radicals in improving adhesion between two PDMS components. Interestingly, the interfacial properties were maintained even if a brittle silica-like layer was formed and fragmented under elongation.

2. Experimental

2.1. Substrate preparation

The procedure for elaborating the filler-free stretchable PDMS surface is illustrated in Fig. 2.

Substrates of silicone containing silica fillers ($\text{PDMS}_{\text{fillers}}$) were molded by Statice Santé SAS (France) using MED-4750 from NuSil Silicone Technology LCC (Carpinteria, CA 93013, USA).

Plasma surface modifications were conducted using a radiofrequency (r.f.) inductive coupling plasma reactor (Plassys MDS 130) consisting in a cylindrical glass chamber (14.5 cm diameter and 5.5 L volume) enclosed in a Faraday cage. In the Ar plasma reactions the $\text{PDMS}_{\text{fillers}}$ substrate (with approximate dimensions of 15 mm × 45 mm × 0.3 mm) was placed into the plasma chamber at 27 cm from the gas inlet. The reactor was evacuated to 0.1 Pa, following by purging with Ar gas to the desired experimental pressure, typically 100 Pa. At this point, r.f. radiations were turned on (60 W) to induce plasma reactions. Upon completion (i.e. 30 s, 60 s or 120 s of exposure time), the r.f. generator was switched off. Then, the system was vented up to atmospheric pressure and the sample was immediately removed from the reactor and stored under nitrogen in order to minimize exposure with air (less than 10 s).

Besides, fillers-free PDMS resin ($\text{PDMS}_{\text{free}}$) were prepared from a linear polydimethylsiloxane, vinyldimethylsiloxy terminated (Mn = 28,000 g/mol, ABCR, AB109358, Germany) under nitrogen. The reaction between vinyl groups forming a crosslinked PDMS network was initiated by addition of (i) 0.9% (w/w) tetrakis(dimethylsiloxy)silane (97%, ABCR, AB11396, Germany) to the linear PDMS and (ii) 2 drops of 0.2% in volume of solution of 3 platinum divinyltetramethyldisiloxane (ABCR, AB 108773, Germany) diluted in heptane. Then the $\text{PDMS}_{\text{free}}$ resin was poured over against the $\text{PDMS}_{\text{fillers}}$ surface using a homemade PTFE mold (always under nitrogen) as illustrated in Fig. 1 in Supporting information. Finally, the $\text{PDMS}_{\text{free}}/\text{PDMS}_{\text{fillers}}$ bi-layer film was removed from the PTFE mold after 6 h at room temperature. The assemblies could not be removed before a minimum degree of crosslinking was reached and the crosslinking reactions were fully accomplished by

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