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Rapid, Simple, and Cost-Effective Treatments to Achieve Long-Term Hydrophilic PDMS Surfaces

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This paper describes rapid, simple, and cost-effective treatments for producing biocompatible and long-term hydrophilic polydimethylsiloxane (PDMS) surfaces identified in an experimental study investigating 39 treatments in all. The wetting of the surfaces was monitored during six months. Changes in surface morphology and chemical composition were also analyzed. Some of the treatments are presented here for the first time, while for earlier presented treatments the selection of investigated

parameters was wider and the observation period for the surface wetting longer. The PDMS surfaces were modified by surface activation, physisorption, and synthesis of both “grafting to” and “grafting from” polymer brushes. In surface activation, the PDMS sample was exposed to oxygen plasma, with several combinations of exposure time and RF power. In the physisorption and synthesis of polymer brushes, three commercially available and biocompatible chemicals were used: 2-hydroxyethyl methacrylate (HEMA), polyethylene glycol (PEG), and polyvinylpyrrolidone (PVP). Thirty-three of the 39 treatments rendered the PDMS hydrophilic, and in 12 cases the hydrophilicity lasted at least six months. Seven of these long-term hydrophilic coatings supported a contact angle of 30° or less. Three of the long-lasting hydrophilic coatings required only minutes to prepare.

Keywords: PDMS; surface treatment; hydrophilization; contact angle; FTIR; SEM

1. Introduction

Not so long ago, all microfluidic structures were fabricated from glass and silicon. Owing to the relatively high cost and complex processing techniques, however, new materials have been eagerly sought. Among materials used to fashion microfluidic devices during the last decade are polymers such as polydimethylsiloxane (PDMS) [1-3], polymethyl methacrylate (PMMA) [4,5], polycarbonate (PC) [6,7], and polyethylene terephthalate (PET) [8,9].

PDMS is attractive for the prototyping of microfluidic and other microscaled structures because of its low cost and the fast and easy fabrication techniques [10-12] that it supports. PDMS also offers biocompatibility [13], mechanical properties similar to human soft tissue (elastic modulus ~2 MPa) [14], optical transparency down to 280 nm [15], and good thermal and chemical stability. These properties are particularly favorable in cell applications [16-18], enabling the fabrication of integrated systems with microactuators (pumps, valves, and mixers [1,19-21]) and allowing the use of detection methods such as ultraviolet absorbance [22] and fluorescence. PDMS products have commercial

potential, as demonstrated by BioNavis Ltd (Finland), Celectricon Ab (Sweden), Fluidigm Ltd (USA), Fulence Co. Ltd (Japan), GE Healthcare Ltd (UK), and Vitae LLC Ltd (USA).

The large-scale commercial breakthrough of PDMS is still awaited owing to certain shortcomings of the material. The main disadvantages, especially from a biomedical perspective, are the poor wetting and heterogeneous surface charge, properties that may lead to surface fouling through the adsorption of small molecules [23], such as fluorescent dyes [24,25], organic solvents [25,26], and proteins [27,28]. The interaction is especially strong with polar samples, where hydrogen bonding can occur between the siloxane group of PDMS and alcohol/acidic hydrogens in the analyte or through polar-polar interactions [29]. Part of a sample flowing in a PDMS microchannel may in this way attach to the channel surface [30]. In addition to the uncontrollable filtering effect, adsorption of the sample may lead to clogging and thereby to changes in the flow properties of the microchannel [27]. Other disadvantages of hydrophobic PDMS are the rather extensive bubble trapping [31] and poor cell adhesion [14,31]. Overall, these factors reduce device performance and cause sample loss, which in turn will skew experimental outcomes.

Given these drawbacks, much effort has been devoted to the development of surface treatments to improve the wetting properties of PDMS [28,32,33-38]. Despite the many published studies, present PDMS surface modification techniques are not without their shortcomings. Simple and popular surface activation, such as use of radiofrequency (RF) oxygen plasma, renders PDMS only temporarily hydrophilic. In addition, it is still unclear how RF power and duration of the activation influence the wetting properties of PDMS [35,39-44]. Physisorption treatments, involving the adsorption of molecules via hydrophobic or electrostatic interaction, suffer from weak interactions between the formed surface and the bulk of the material, which lead to thermal, mechanical, and solvolytic instabilities in the material [28]. Although polymer brushes [45] offer superior properties to the other modifications, the techniques for synthesizing long-term stable hydrophilic polymer brushes tend to be complex and time-consuming. Other shortcomings of PDMS surface modification studies have been

ignoring of the long-term durability of the coatings and poor justification of the parameters selected for treatments.

In this experimental study, the disadvantageous properties of PDMS were tackled by studying the long-term (six months) effects of four simple surface modification techniques. Activation and physisorption treatments were investigated, and both “grafting to” and “grafting from” approaches for the synthesis of polymer brushes. Three commercially available and biocompatible chemicals were employed in the adsorption and grafting experiments: 2-hydroxyethyl methacrylate (HEMA), polyethylene glycol (PEG), and polyvinylpyrrolidone (PVP). Altogether, 39 different PDMS surface modifications were studied. To our knowledge, this is the widest selection of PDMS surface treatments and the longest observation period included in a single study.

2. Materials and Methods

2.1 Materials

PDMS (Sylgard 184, Dow Corning, USA) was acquired from Ellsworth Adhesives AB (Sweden). 2-Hydroxyethyl methacrylate (HEMA) (stabilized with hydroquinone monomethyl ether) for synthesis and polyvidone 25 (PVP) powder (Merck MGaA, Germany) and polyethylene glycol (PEG) (Acros Organics BVBA, Belgium), average Mw 200, were obtained from VWR International Oy (Finland). For PVP coatings, a 22.2% (w/v) solution of polyvidone 25 powder was prepared in deionized (DI) water. The water was purified using a Direct-Q 3 system (Millipore Corp, USA). Vision 320 Mk II reaction ion etching (RIE) (Advanced Vacuum AB, Sweden) was used for surface activation.

2.2 Fabrication of PDMS Samples

Sylgard 184 base polymer and curing agent (10:1 w/w) were thoroughly mixed in a plastic cup, and 10 g of the liquid PDMS was measured into a Petri dish and degassed in vacuum. The degassed mixture was cured at 60 °C for at least 10 h and cut into rectangular pieces (approximately 11 mm × 11 mm × 1.6 mm).

2.3 Surface Activation

PDMS samples were activated with oxygen plasma to study how the RF power and the duration of the activation influence the hydrophobic recovery. Three RF powers (30, 60, and 90 W) and three exposure times (15, 90, and 180 s) were tested. The maximum power was kept below 100 W to produce smooth surfaces suitable for microfluidic use [39]. Chamber pressure (30 mtor) and oxygen flow rate (30 sccm) were kept constant.

2.4 Physisorption

Coating via physisorption was studied by pouring HEMA, PEG, or PVP onto PDMS samples in a Petri dish. The samples were left in the hydrophilic monomer or polymer for 1 min or 10 h to determine the rate of the adsorption. Samples were then rinsed liberally with DI water to remove unattached chemical residues, and wiped gently with absorbent paper to remove superficial water.

2.5 “Grafting to”

“Grafting to” is the more straightforward method for formation of polymer brushes. In this method, typically end-functionalized polymers are attached to reactive groups (anchors) on a material surface via chemical bonding or by physisorption [45]. Here, PDMS samples in a Petri dish were treated with oxygen plasma to generate anchors on their surfaces. Two exposure times (15 s and 180 s) were used to study the formation rate and the influence of the number of surface anchors. After the plasma exposure, “grafting to” process was initiated by covering the sample surface with HEMA, PEG, or PVP. The chemicals were left on the surfaces for 1 min or 10 h to clarify the rate of molecular attachment. After the grafting, samples were rinsed liberally with DI water and gently wiped dry. Constant chamber pressure (30 mtor), oxygen flow rate (30 sccm), and RF power (30 W) were used for plasma oxidation.

2.6 “Grafting from”

“Grafting from” polymerization, also called surface-initiated polymerization (SIP), is the more robust technique for forming polymer brushes. Since the formation of brush polymers commences with the anchoring of an initiation species on a material surface, monomers added to the polymer chains growing

from the surface will not endure much molecular hindrance, and this facilitates the production of thicker and denser coatings [28]. The versatile and effective free radical polymerization (FRP) method continues to be the most popular approach in PDMS surface modification [28,34]. A still more robust technique [45] for the synthesis of “grafting from” polymer brushes has also been reported.

In this study, PDMS samples were prepared for FRP by treating them with oxygen plasma. They were then covered with HEMA, PEG, or PVP. Two plasma (15 s and 180 s) and two chemical (1 min and 10 h) treatment times were studied to determine their effect on the adsorption rate. The prepared samples were then thoroughly rinsed with DI water, gently wiped dry, and again exposed to oxygen plasma to initiate FPR from the surface bound molecules. The influence of two initiation times (90 s and 180 s) was studied. Chamber pressure (30 mtor), oxygen flow rate (30 sccm), and RF power (30 W) were kept constant.

2.7 Wetting Analysis

Wetting of the modified samples was monitored by the sessile drop method, using a Attension Theta Lite optical goniometer (Biolin Scientific AB, Sweden) with attached GASTIGHT® precision syringe (Hamilton Inc, USA). The sample was placed under the syringe, and a drop (approximately 5 μ l) of DI water was injected onto its center. A side profile photograph of the formed droplet was captured with the goniometer and analyzed to determine static and dynamic contact angles. The values were obtained with two decimal places and rounded to the nearest whole digit for presentation. As the dynamic contact angle measurements suggest the static contact angle values to characterize the samples well (supporting information), only extensive static contact angle measurements were performed.

The long-term effects of the treatments were investigated by measuring the contact angles after aging of the samples for 10, 30, 60, 100, 150, 200, 300, 500, 1500, 2000, 5000, and 10000 min, and for 1, 2, 3, and 6 months at room temperature. Every measurement was replicated with three samples to guarantee the reliability of the test. Thus, a total of 1872 static contact angle measurements were performed during the experiment.

2.8 Surface Morphology Analysis

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to study morphology changes caused by the surface treatments. SEM micrographs taken with an XL-30 SEM (Philips Nv, the Netherlands) were used to illustrate the morphology changes caused by the seven most hydrophilic coatings. For comparison, four coatings that showed notable hydrophobicity recovery were also imaged. The surfaces were imaged at the center, with a perpendicular camera angle. Acceleration potential was 15 kV and the magnification 1000 times. Before the imaging, the samples were aged six months at room temperature and then made conductive by sputter-coating with gold.

Random mean squared (RMS) surface roughness values were obtained using a XE-100 atomic force microscope (Park Systems Corp, USA) in a tapping imaging mode, to complete the surface morphology analysis. NSC 11 cantilevers (MikroMasch Ltd, Estonia) with a tip radius of 24 nm and a resonance frequency of approximately 330 kHz were used to scan $5 \times 5 \mu\text{m}$ areas. Characterization included five long-lasting hydrophilic coatings, and one coating that showed notable hydrophobicity recovery. The samples were aged for six months at room temperature before the AFM analysis.

2.9 Surface Chemistry Analysis

Fourier transform infrared spectroscopy in attenuated total reflectance (FTIR-ATR) mode was used to analyze the effects of treatments on the surface chemistry of PDMS. Coatings providing long-term hydrophilicity and coatings suffering from hydrophobicity recovery were characterized, and a pristine PDMS sample was analyzed for comparison. The FTIR spectra of samples aged at room temperature for one week and two months were recorded with a Spectrum One infrared spectrometer (PerkinElmer Inc., USA). Spectra are the average of 16 scans at 4 cm^{-1} resolution accumulated in wavenumber range $4000 - 650 \text{ cm}^{-1}$ using an ATR diamond crystal.

3. Results and Discussion

3.1 Wetting Properties

Wetting properties of the four types of fabricated samples were studied from contact angle plots presenting average contact angle values and standard deviations of three parallel PDMS samples as a function of aging time.

3.1.1 Surface Activated Samples

Contact angle plots for PDMS samples activated with oxygen plasma are presented in Fig. 1. As the plots reveal, longer exposure to oxygen plasma increased the wetting of PDMS up to 5000 min of aging. An increase in RF power reduced the short-term differences due to the different exposure times. However, after 5000 min aging, all samples exhibited approximately the same contact angle, regardless of the treatment parameters. Thus, though a short-term increase in wetting was achieved with longer exposure to oxygen plasmas or higher RF power, neither factor influenced the long-term hydrophilicity of PDMS. None of the oxygen plasma activated samples ever recovered their full hydrophobicity ($113^\circ \pm 3^\circ$), as the contact angle values after six months varied from 95° to 102° .

These observations agree with previous findings in which elongated exposure [35,39,40] or higher RF power [39] enhanced the wetting of PDMS in the short term. Divergent results in regard to short term effect of exposure time and RF power have also been published [41,42]. In agreement with earlier work [43], the choice of parameters did not affect the rate of hydrophobic recovery of PDMS. One group [44] concluded that PDMS samples activated in oxygen plasma are likely never to recover their full hydrophobicity, although an elongated exposure to oxygen plasma was proposed to accelerate the hydrophobic recovery. In another study [43], oxygen plasma activated PDMS did recover its full hydrophobicity. Overall, however, our results and those in the literature are in agreement. The divergence in results could be due to differences in the equipment used for the plasma treatment. As well, surface roughness, which was not been reported in many studies, may be important for the wetting properties.

The fundamental reasons for the hydrophobic recovery of PDMS remain unclear. Usually migration of uncured low Mw species from the bulk polymer to the surface is considered to be the main cause

[44,46-49]. In addition, a loss of hydrophilic groups to the atmosphere under high-vacuum conditions [46] and reorientation of the oxidized side group [44,47] have been suggested. Although the rate of the hydrophobic recovery can be slowed by thermal aging [48], aqueous storage environment [35,43,50], and certain preprocessing techniques [31,51], ultimately alternative surface modifications of PDMS are required to avoid the recovery.

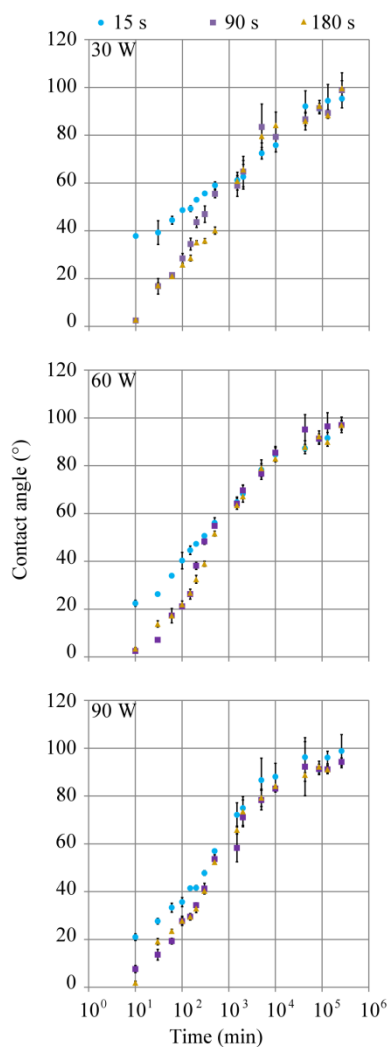


Fig. 1. Average contact angles with standard deviations for surface activated PDMS samples exposed to oxygen plasma at different RF powers and for different times as a function of aging time.

3.1.2 Samples Prepared by Physisorption

As shown in Fig. 2, the 1 min and 10 h physisorption treatments did not render the surface of PDMS hydrophilic with any of the chemicals. The extended adsorption (10 h) of PEG and HEMA nevertheless

reduced the contact angle of the samples to some extent, suggesting that the amount of compound adsorbed increases with adsorption time. The better results with PEG and HEMA than with PVP also indicate the relevance of low Mw (Mws for PVP, PEG, and HEMA are ~3500, 200, and 130, respectively.) After six months, the contact angle value was lowest ($107^\circ \pm 2^\circ$) for PDMS samples treated 10 h with PEG.

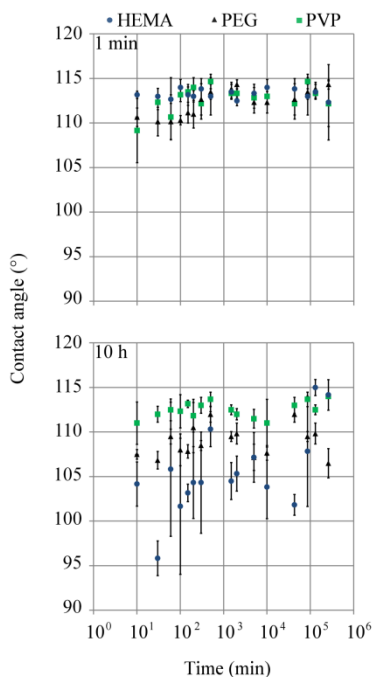


Fig. 2. Average contact angles with standard deviations for PDMS samples coated by physisorption method as a function of aging time.

3.1.3 “Grafted to” Samples

As Fig. 3a depicts, all 12 coatings prepared by “grafting to” technique rendered the PDMS hydrophilic. For the eight PVP and PEG “grafted to” samples, the effect lasted over six months. All HEMA “grafted to” samples, in contrast, recovered hydrophobicity before three months of aging. The most stable hydrophilic polymer brushes were synthesized with use of PVP: two coating modifications carried out with this polymer provided low and nearly constant contact angle values over a six month period.

The observations suggest that an increase in Mw increases the thickness of the formed coating, and thus the duration of the hydrophilicity. Similar conclusions have been drawn earlier [28,52]. Nevertheless, Mw of the coating material cannot be increased indefinitely because the viscosity of a solution increases with Mw, and rinsing of the unattached polymer residues from the surface would become difficult. Polymers with very high Mw are thus impractical for coating purposes.

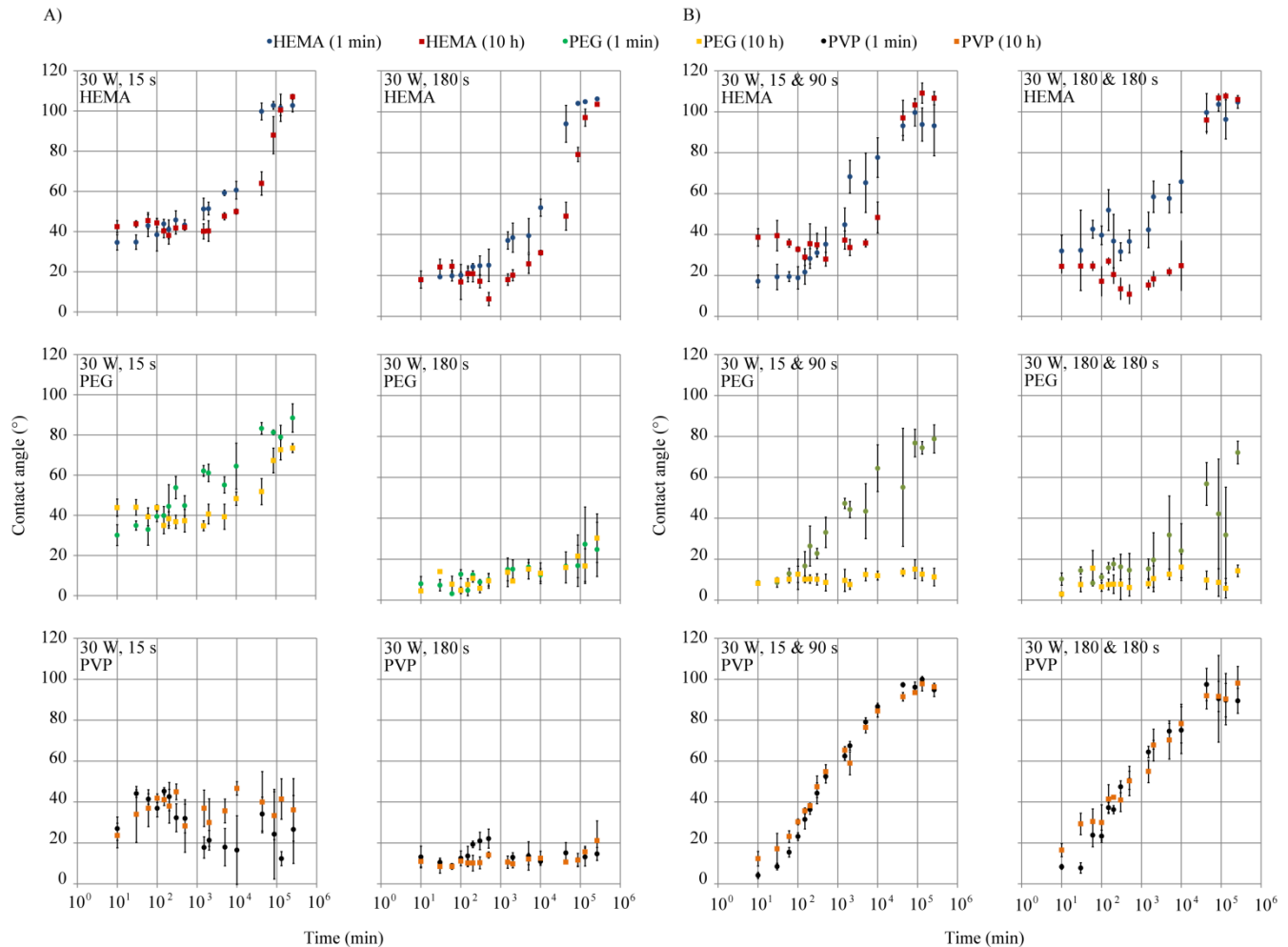


Fig. 3. Average contact angles with standard deviations for (a) “grafted to” and (b) “grafted from” PDMS samples as a function of aging time.

No clear difference in hydrophilicity was seen between chemical treatments of 1 min and 10 h, suggesting that the coating molecules attach only slowly after one minute. This could be due to increasing molecule concentration at the formed interface, which quickly becomes larger than the

concentration in solution. The coating molecules would then have to diffuse against the concentration gradient, and their rate of attachment would slow down. After this point, additional polymer molecules are linked to the surface on a logarithmic time scale [45].

Increase in the number of surface anchors on PDMS through use of a longer (180 s) surface activation period led to clear improvement in wetting properties (lower contact angle values) and coating homogeneity (lower standard deviations), indicating that an increased number of surface anchors allows the formation of thicker and denser coatings. However, since density of the coating is ultimately limited by the concentration gradient at the coating interface, surface activation longer than 180 s is unlikely to improve the coating further.

3.1.4 “Grafted from” Samples

As seen in Fig. 3b, all 12 coatings prepared by “grafting from” method rendered the PDMS samples hydrophilic, but only the PEG coatings remained hydrophilic for at least six months. Clearly lowest contact angle values (less than 20° after six months) and highly homogeneous coatings were achieved when the samples were exposed to PEG for 10 h before initiation of the FRP.

The findings suggest that the “grafted from” polymer brushes are synthesized only if the surface adsorbed compound is present in high concentration during the oxygen plasma initiation. This agrees with the physisorption results presented above (Section 3.1.2), which showed PDMS to adsorb HEMA and PEG but not PVP, and the amount of adsorbed molecules to increase with adsorption time. Thus, free radicals may be generated during the oxygen plasma initiation when longer treatment time (10 h) with PEG or HEMA is used to guarantee the presence of surface bound molecules. Possibly, the process could be accelerated by spin-coating a thin layer of PEG or HEMA on the surface of PDMS instead of adsorbing the chemicals. This would reduce the treatment time by almost ten hours. In the case of PVP, the attempted initiation of FRP only etched the surface anchored polymer molecules, and hydrophobicity was rapidly recovered. For successful grafting, free radical formation would be required on the surface of PDMS and in PVP.

The duration of the first plasma activation (15 or 180 s) seems to have had little effect on the amount of adsorbed molecules, and 90 s initiation with oxygen plasma appears to be long enough to guarantee possible FRP.

Table 1. Summary of the contact angle measurements.

Chemical	Preprocessing		Exposure time to chemical	Post processing		Short- term contact angle [°]	Coating homogeneity number [°]	Duration of hydrophilicity [months]	Long-term contact angle [°]	
	Treatment [s]	[W]		[s]	[W]					
-	Surface activation	15				39	2.5	< 1	95	
		90	30			10	3.2	< 2	99	
		180				10	2.1	< 2	100	
		15				24	2.0	< 2	97	
		90	60	-		5	2.2	< 1	97	
		180				9	1.4	< 2	97	
	PS ^a	15				24	2.9	< 1	102	
		90	90			11	2.9	< 1	100	
		180				11	1.8	< 2	96	
		-		1 min			113	1.3	-	112
		-		10 h			100	3.1	-	114
		-		1 min			35	4.1	< 1	103
HEMA	"Grafting to"	15				43	3.3	< 2	107	
		180	30			19	3.6	< 1	106	
		180				21	3.8	< 3	104	
		15		1 min	90		18	7.2	< 1	93
		15		10 h	90	30	39	4.7	< 1	107
		180		1 min	180		32	8.3	< 1	105
	PS ^a	180					25	4.1	< 1	106
		-		1 min			110	1.1	-	110
		-		10 h			107	1.1	-	107
		15					33	5.2	> 6	89
		15					44	4.2	> 6	74
		180	30	1 min			8	4.8	> 6	25
PEG	"Grafting to"	180				9	4.6	> 6	30	
		15		1 min	90		9	7.3	> 6	79
		15		10 h	90	30	9	2.8	> 6	11
		180		1 min	180		12	9.0	> 6	72
		180		10 h	180		5	4.4	> 6	14
		-		1 min			111	1.3	-	112
	PS ^a	10 h					112	1.1	-	114
		15					36	7.7	> 6	27
		15					29	8.7	> 6	36
		180					12	3.5	> 6	15
		180	30	1 min			10	2.8	> 6	21
		15		1 min	90		6	2.4	< 1	95
PVP	"Grafting from"	15				15	3.0	< 1	97	
		180				8	5.5	< 1	90	
		180				23	6.9	< 1	98	

^aPhysisorption (PS)

3.1.5 Summary of Wetting Properties

Table 1 summarizes the wetting properties of the formed coatings with four values calculated from the contact angle data. These are 1) the short-term contact angle, which is the average of the first and second contact angle measurements of three parallel samples (after 10 and 30 min aging); 2) coating homogeneity number, which is the average of the standard deviations of all contact angle measurements (at all aging times from 10 min to 6 months); 3) duration of hydrophilicity, which indicates how long the average contact angle of three parallel samples was 90° or below; 4) the long-term contact angle, which is the average contact angle value for three parallel samples after six months aging. The error marginal in the presented results is a few degrees, caused by the user controlled curve fitting needed for the determination of the contact angle values.

3.2 Surface Morphology

Fig. 4a-d presents SEM micrographs of four modified PDMS surfaces that showed considerable hydrophobic recovery. Fig. 4e-h, in turn, shows the surface morphologies of the four most hydrophilic PEG coated samples. Comparison of the images shows how longer exposure to oxygen plasma increases the surface roughness of PDMS through the formation of wavy patterns (observed also earlier [53,54]); no crack formation was detected. Thus, less than 180 s exposure time (Fig. 4a,b, and e) led to very smooth surfaces, whereas surfaces exposed 180 s or longer, (Fig. 4c,d,f-h) exhibited wavy structures. The observation was confirmed by the AFM analysis, as the RMS value for a sample with less than 180 s exposure time was 1.0 nm (Fig. 4e), while the RMS values for samples exposed 180 s or longer were 7.3 nm (Fig. 4d), 4.4 nm (Fig. 4f), and 3.0 nm (Fig. 4h). The wavy structures are assumed to be generated by buckling of the SiO_x layer that forms on top of the soft PDMS substrate during the oxygen plasma treatment [54,55]. Since smooth and rough surfaces appeared in both hydrophobic and hydrophilic PDMS samples, differences in the surface morphology cannot explain the improved wetting properties of the modified PDMS surfaces.

Comparison of published images of solely plasma exposed samples recorded right after exposure [54] (wavy structures are clearly visible) with our image of a similar sample imaged six months after the treatment (Fig. 4c, structures have smoothed) suggests that the wavy structures will smoothen in time. However, “grafted to” and “grafted from” samples treated with oxygen plasma for 180 s or longer (see Fig. 4d,f-h) still exhibit the wavy structure. Possibly the formation of polymer brushes prevents the smoothing of the wavy structures on PDMS.

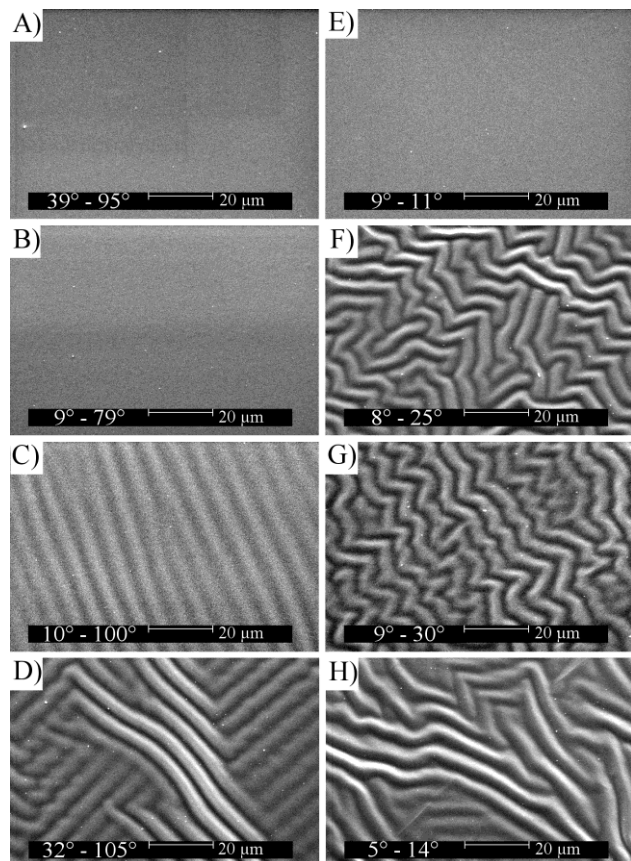


Fig. 4. SEM images of modified PDMS surfaces (a)-(d) recovering hydrophobicity and surfaces (e)-(h) retaining hydrophilicity during six months aging. Sample (a) is solely oxygen plasma exposed (30 W, 15 s), (b) is 1 min PEG “grafted from” (30 W, 15 & 90 s), (c) is solely oxygen plasma exposed (30 W, 180 s), (d) is 1 min HEMA “grafted from” (30 W, 180 & 180 s), (e) is 10 h PEG “grafted from” (30 W, 15 & 90 s), (f) is 1 min PEG “grafted to” (30 W, 180 s), (g) is 10 h PEG “grafted to” (30 W, 180 s), and (h) is 10 h PEG “grafted from” (30 W, 180 & 180 s). The short-term and long-term contact angle values of each sample are included in the figure.

RMS values measured using AFM showed increased surface roughness due to elongated oxygen plasma exposure also for PVP treated surfaces. The values measured for surfaces illustrated in Fig. 5b and c were 6.7 nm and 4.2 nm, respectively. However, SEM micrographs (Fig. 5) did not demonstrate as pronounced wave structures as the corresponding PEG and HEMA samples (Fig. 4).

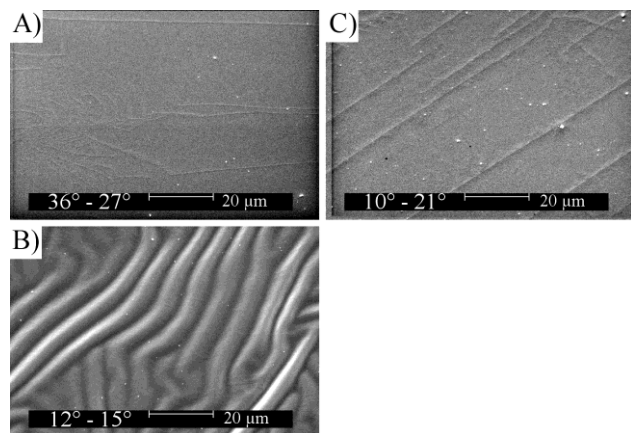


Fig. 5. SEM images of three highly hydrophilic PVP “grafted to” PDMS samples. The parameters for surface activation and chemical treatment were (a) 30 W, 15 s, and 1 min, (b) 30 W, 180 s, and 1 min, and (c) 30 W, 180 s, and 10 h. The short-term and long-term contact angle values of each sample are included in the figure.

3.3 Surface Chemistry

Fig. 6 presents the FTIR spectra of six differently treated samples: pristine PDMS (Fig. 6a), HEMA “grafted from” (Fig. 6b), PEG “grafted to” (Fig. 6c), and PVP “grafted to” (Fig. 6d-f). Wavenumbers for the adsorption bands, with assignments, are presented in Table 2. Peak values for pristine PDMS are included.

As compared with pristine PDMS, the surface of the HEMA “grafted from” sample (Fig. 6b and Table 2) showed additional infrared adsorption peaks at 3415 cm^{-1} (OH), 2881 cm^{-1} (CH_2), 1717 cm^{-1} (C=O), 1637 cm^{-1} (C=O), 1321 cm^{-1} (CH_2), 1298 cm^{-1} (C–O), and 1169 cm^{-1} (C–O). These adsorptions strongly indicate the presence of HEMA monomer after one week of aging. However, as the wetting

study suggested, the effect of HEMA FRP on PDMS is only temporary: no signs of the monomer were seen in the spectrum measured two months after the treatment.

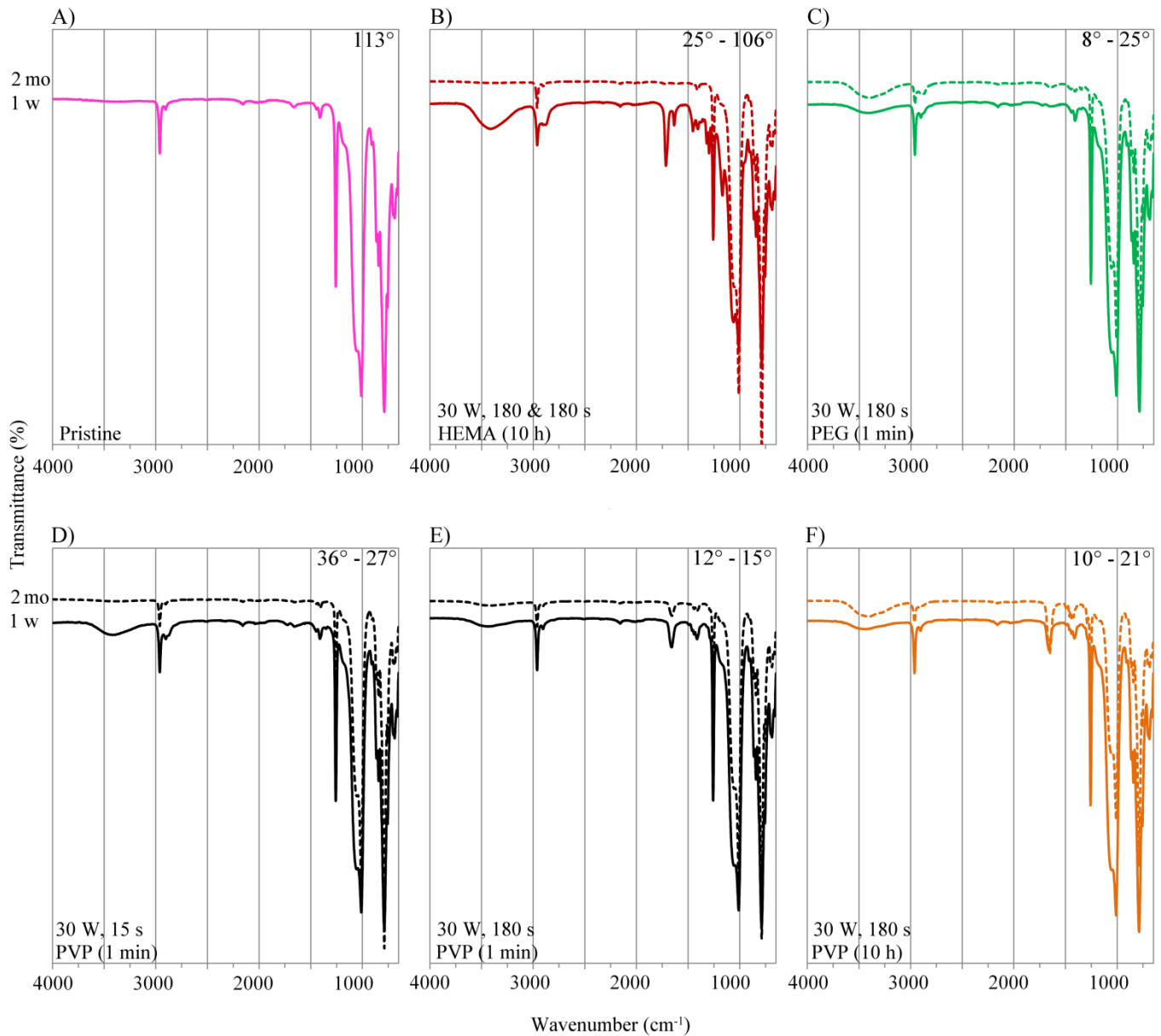


Fig. 6. FTIR spectra of differently modified samples one week (solid line) and two months (broken line) after the treatments. (a) pristine, (b) HEMA “grafted from”, (c) PEG “grafted to”, and (d)-(f) PVP “grafted to” PDMS samples. The short-term and long-term contact angle values of the samples are included in the figure.

Table 2. ATR-FTIR spectral values of selected surface treated and pristine PDMS samples after 1 week and 2 months aging. Infrared adsorptions are given in wavenumbers (cm^{-1}).

Assignments	Sample age	Pristine	O ₂ plasma (30 W, 180 s) + HEMA (10 h) + O ₂ plasma (30 W, 180 s)	O ₂ plasma (30 W, 180 s) + PEG (1 min)	O ₂ plasma (30 W, 15 s) + PVP (1 min)	O ₂ plasma (30 W, 180 s) + PVP (1 min)	O ₂ plasma (30 W, 180 s) + PVP (10 h)
OH stretch	1 w	-	3415	3405	3427	3440	3427
	2 mo	-	-	3401	-	3392	3411
CH ₃ symmetric stretch	1 w	2963	2962	2962	2962	2963	2963
	2 mo	-	2963	2963	2963	2963	2962
CH ₃ asymmetric stretch	1 w	2905	2905	2905	2905	2905	2905
	2 mo	-	2905	2905	2905	2905	2905
CH ₂ asymmetric stretch	1 w	-	2881	-	-	-	-
	2 mo	-	-	2887	-	-	-
C=O stretch	1 w	-	1717	-	-	-	-
	2 mo	-	-	-	-	-	-
C=O stretch	1 w	-	1637	-	-	1662	1660
	2 mo	-	-	-	-	1657	1657
CH ₃ asymmetric deform	1 w	1445	1455	1446	1446	1442	1442
	2 mo	-	1446	1452	1445	1443	1442
CH ₃ asymmetric deform	1 w	1412	1407	1412	1407	1414	1414
	2 mo	-	1412	1412	1412	1414	1424
CH ₂ in plane deform	1 w	-	1321	1353	-	-	-
	2 mo	-	-	1351	-	-	-
C-O stretch	1 w	-	1298	-	-	-	-
	2 mo	-	-	-	-	-	-
CH ₃ symmetric deform	1 w	1258	1258	1258	1258	1258	1258
	2 mo	-	1258	1258	1258	1258	1258
C-O stretch	1 w	-	1169	-	-	-	-
	2 mo	-	-	-	-	-	-
Si-O-Si asymmetric deform	1 w	1011	1011	1011	1011	1011	1011
	2 mo	-	1011	1011	1011	1009	1011
Si-C	1 w	843	843	843	843	843	864
	2 mo	-	843	843	843	843	864
Si-(CH ₃) ₂	1 w	788	785	788	789	788	788
	2 mo	-	788	788	788	787	788
Surface	1 w	688	688	688	688	688	688
	2 mo	-	688	688	688	689	688

In the case of PEG “grafting to” (Fig. 6c and Table 2), new adsorption peaks were observed after both one week and two months aging. These included a broad adsorption from 3200 to 3600 cm^{-1} and peaks at approximately 2890 cm^{-1} and 1350 cm^{-1} , indicating the presence of OH and CH_2O groups of PEG [56]. Thus, the improved wetting properties of PEG “grafted to” samples are suggested to be due to surface attached PEG molecules. Further analysis of the PEG “grafted from” samples (spectra not presented) is needed to determine the reason for their hydrophilicity.

All the PVP “grafted to” samples showed changes relative to pristine PDMS. When the preprocessing with oxygen plasma was short (15 s) (Fig. 6d and Table 2), the only change was the appearance of the broad adsorption, corresponding to OH, due to adsorbed water. This suggests that there was very little PVP on the surface. The samples exposed to longer (180 s) pretreatment (Fig. 6e,f, and Table 2) showed much clearer evidence of PVP on the surface: additional peaks appeared at approximately 1670 cm^{-1} , indicating the long-term presence of $\text{C}=\text{O}$. Thus, like the contact angle measurements, also the FTIR results indicate that long-term surface activation with oxygen plasma increases the amount of PVP on the PDMS surface. These findings suggest that the lower contact angle values of PVP “grafted to” samples are due to surface attached PVP molecules.

3.4 Proposed Reaction Schemes

3.4.1 Surface Activation of PDMS

Despite the common use of oxygen plasma in PDMS surface modifications, its effect on the surface chemistry of PDMS has not been fully clarified. The most common suggestion is that oxygen plasma treatment generates a thin and brittle SiO_x layer, also referred to as a “silica-like” layer, on the surface [12,42,44,46,57]. The elimination of methyl groups ($\text{Si}-\text{CH}_3$) with simultaneous formation of silanol functional groups ($\text{Si}-\text{OH}$) also has been reported [12,41,42].

Here, on the basis of the literature, we propose two alternative schemes for oxygen plasma activation of PDMS (Fig. 7). With CH_3 elimination hydroxyl (OH) groups form on the PDMS surface, and with no elimination methylol groups (CH_2OH). In the former case, also free radicals (O^\cdot) can be produced and

then converted to peroxides (ROOH). Further oxidation of the recently formed hydroxyl group can produce carboxylic moieties (COOH), peroxides (SiOOH or CH₂OOSi) or even peroxy radicals (COO[•]).

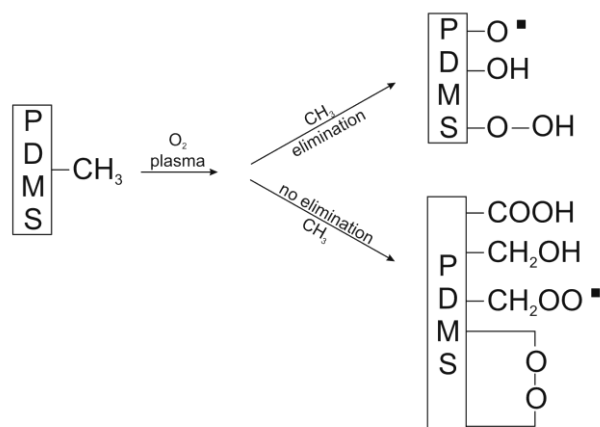


Fig 7. Two possible reactions for PDMS surface activation with oxygen plasma.

3.4.2 Formation of Polymer Brushes

The formation of long-term stable PEG and PVP “grafting to” polymer brushes is proposed to occur according to Fig. 8, where the coating polymers are covalently attached to oxygen radicals formed in the surface activation of PDMS. Another possibility is that PEG and PVP are hydrogen bonded to hydroxyl groups of surface activated PDMS, as presented in Fig. 9. As the schemes demonstrate, these coatings do not require usage of end-functionalized coating polymers, whose synthesis is both time-consuming and difficult [45].

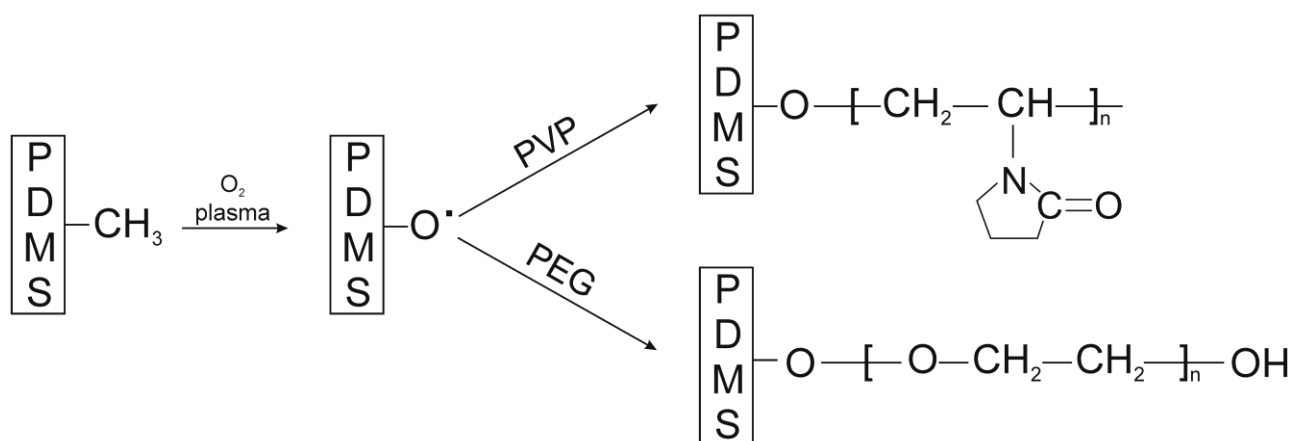


Fig 8. PVP and PEG “grafting to” PDMS surface via covalent bonding.

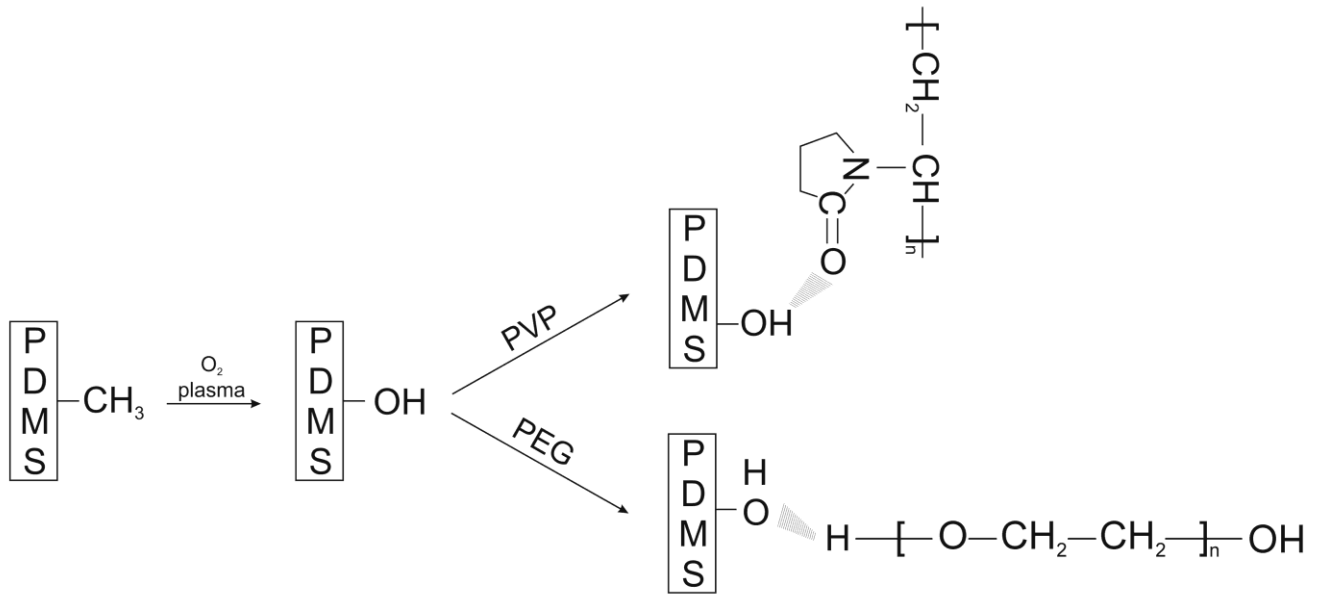


Fig. 9. PVP and PEG “grafting to” PDMS surface via hydrogen bonding.

“Grafting from” polymerization that rendered PDMS long-term hydrophilic was initiated from surface adsorbed PEG. The FRP reaction, we suggest, is initiated by the free radicals generated during the second oxygen plasma exposure, as depicted in Fig. 10. This results in increased coating thickness compared to PEG “grafting to” technique. Another possibility is that the second oxygen plasma exposure increases the coating density, as presented in Fig. 11. A combination of these two schemes is also possible.

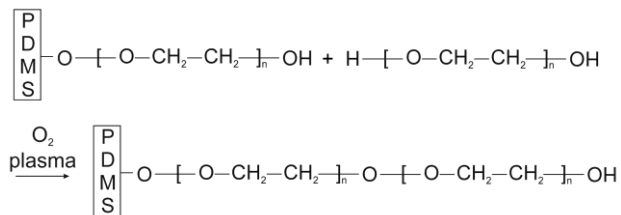


Fig. 10. PEG “grafting from” is initiated during the second oxygen plasma treatment: adsorbed PEG molecules attach to covalently tethered PEG on PDMS surface.

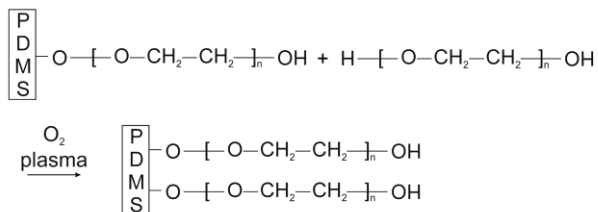


Fig. 11. PEG “grafting from” is initiated during the second oxygen plasma treatment: adsorbed PEG molecules attach to oxygen radicals forming on PDMS surface.

4. Conclusions

This study identified two simple and cost-effective techniques for producing PDMS surfaces exhibiting contact angle values of 30° or less that persist for at least six months. The more straightforward and quicker technique (requiring only a few minutes) is to tether PVP or PEG onto PDMS that has been activated with oxygen plasma. Free radicals (O·) or hydroxyl groups (OH) generated in the plasma treatment phase serve as surface anchors, enabling rapid attachment of PVP and PEG onto PDMS. For our knowledge, no simpler and more rapid methods to achieve constantly hydrophilic PDMS surfaces for at least six-months have been published.

Investigation of the grafting of the polymers by FTIR analysis confirmed that the attachment of PVP occurs very slowly after 1 min. This finding is in agreement with the contact angle measurements. The factors found to influence the “grafting to” coatings were the Mw of the grafted polymer and the number of anchors: larger Mw provides a thicker coating and, up to a certain point, increase in the number of surface anchors increases the density and thickness of the coating.

The second simple technique for producing long-term hydrophilic PDMS surfaces was FRP of adsorbed PEG molecules in a “grafting from” reaction. Compared with “grafting to”, this technique is more time-consuming, as adsorption of the coating material is a fairly slow process. Possibly the process could be accelerated by spin-coating rather than absorbing the polymer on the PDMS surface. The presence of PEG on the PDMS surface could not be confirmed by FTIR spectrometry (results not presented here). Moreover, surface morphology investigation failed to reveal the reason for the strong

and long-lasting hydrophilicity of the PEG “grafted from” samples. Further study is needed to clarify the reasons for the clearly improved wetting.

A sufficiently long observation period is required to demonstrate the long-term effects of a surface treatment. A good example of this is the HEMA “grafting from” samples, which showed clearly improved wetting properties and notable changes in surface chemistry during the first month after treatment but not thereafter.

Physisorption provided a rather slow coating process, and the amount of adsorbed molecules depended on the molecular weight of the absorbing monomer or polymer: the lower the molecular weight the more molecules were adsorbed. In the surface activation with oxygen plasma, RF power and duration of the exposure did not influence the long-term hydrophilicity of PDMS. However, short-term increase in wetting was achieved with elongated plasma exposure or increased RF power.

The described “grafting to” and grafting from” treatments offer an effective and versatile toolbox for easily and quickly modifying the PDMS surface and enhancing the applicability of PDMS. Uses for the coated PDMS include modification of PDMS microchannels for capillary based pumping, enhanced with reduced bubble trapping properties. In addition, since the wetting of a material is directly related to other important properties, such as cell adhesion and separation efficiency, the treatments should significantly improve the usability of PDMS in a wide range of common biomedical applications.

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