

Creation of a Stable Hydrophilic Poly(dimethyl siloxane) Surface by the Plasma-Induced Crosslinking of Monomers

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ABSTRACT: A 3 : 1 composition of functional monomer (FM)–multifunctional acrylate was spin-coated and later crosslinked under the influence of oxygen plasma on the surface of poly(dimethyl siloxane) (PDMS) to generate a surface-anchored crosslinked network bearing functional moieties. Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and wetting angle measurements were used to analyze the crosslinked monomer surfaces. Scanning electron microscopy was used to visualize the

surface of the film after modification. The results of the surface reconstruction of the FM surfaces and plasma-treated PDMS reveal that long-term hydrophilic surfaces were achieved. Thus, the surface architecture could be favorably manipulated with this remarkable technique with a suitable combination of FMs and crosslinkers. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1426–1430, 2011

Key words: ESCA/XPS; FTIR; surfaces

INTRODUCTION

Polymers are of growing importance in microfabricated devices, especially those used in the fabrication of biosensors and labs-on-a-chip. Of the polymers used in fabrication, poly(dimethyl siloxane) (PDMS) is one that is widely used. The attractive properties of PDMS include transparency, low cost, ease of fabrication, capability of self-sealing, and compatibility with various biomaterials. However, despite its many advantages, the surface of PDMS is naturally hydrophobic and cannot be used as it is for a variety of applications.

Polymers with different surface properties are lately the most popular areas of research in polymer chemistry.^{1–3} Among all the techniques used for surface modification, functional group implantation with electron irradiation⁴ has emerged to be the most rational alternative because of its many obvious advantages, including uniform and controlled modification. However, it is often reported that the hydrophilic functionalities generated at the polymer interface as a result of electron implantation are temporary and are lost with storage time.^{5–7} This phenomenon, termed *surface reconstruction*, is the

major drawback associated with this technique. The surface dynamics that lead to hydrophobic recovery depend on many factors, including the polymer physiochemical properties, temperature, and storage time, and are, therefore, a feebly understood complex phenomenon, which differs from one substrate to another.^{8,9} The hydrophobic recovery is determined by an increase in the water contact angle, the rate of which varies with the nature of the polymer.

The loss of surface functionality with time is a major concern of researchers working in the area of surface modification. Although there are a large number of reports on the surface modification of polymers,¹⁰ there have only been a few studies on tailor-made permanently hydrophilic diene–elastomer surfaces.^{11,12} This article is a part of our study aimed at the fabrication of permanently hydrophilic surfaces via the controlled grafting of functional monomers (FMs). It is well known that the exposure of a polymer film to electron irradiation conditions leads to degradation and surface crosslinking.^{13,14} Taking advantage of the drawbacks of crosslinked surfaces, we accomplished the deliberate crosslinking of FMs and multifunctional acrylates (MFAs) onto the PDMS surface. In this study, functional vinylic monomers, along with functional crosslinkers, were spin-coated onto the surface of PDMS and exposed to oxygen plasma irradiation to obtain long-term hydrophilic surfaces with a crosslinked network of grafted monomers. Surface reconstruction was studied as a function of storage time under ambient conditions upon storage. All of the samples were analyzed with surface-sensitive techniques,

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TABLE I
Results of the Contact Angle (θ) Measurements

Sample	Gravimetric density (G_d) (mg/cm ²) ²¹	θ of the pristine film (°)	θ after treatment (°)
NVP + DAA	2.4	74	12
NVP + EGDMA	1.4	73	7
HEMA + DAA	0.3	70	7
HEMA + EGDMA	0.54	75	6

such as FTIR spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and contact angle measurements.

EXPERIMENTAL

A two-component PDMS from GE Silicones (Huntersville, NC) (RTV 615) with a 10 : 1 base-to-curing-agent mixing ratio was used. The two components were thoroughly mixed and degassed *in vacuo* to remove bubbles. The mixture was cured at a 100°C temperature for 1 h. All of the plasma treatments were conducted in a Plassys RIE system (Alcatel, Paris, France) with a radio-frequency (RF) power supply with a frequency of 13.56 MHz for the plasma excitation. Four different combinations of FM and crosslinker were used for the surface modification. They were 2-hydroxyethyl methacrylate (HEMA) plus diallyl amine (DAA), HEMA plus ethylene glycol dimethyl acrylate (EGDMA), *n*-vinyl pyrrolidone (NVP) plus DAA, and NVP plus EGDMA. All of the chemicals used to carry out the surface modifications were analytical-reagent grade purchased from Aldrich Chemicals, Ltd. (Lyon, France).

The surface modification was conducted in several steps. First, the surface modification of the PDMS surface was carried out with oxygen in a system with a pressure of 100 μ barr and a flow rate of 20 sccm. An RF power of 100 W was used for 30 s for the modification. A mixture of FM and MFA was then spin-coated onto the oxygen-modified PDMS surface at a spin speed of 1500 rpm for 15 s (thickness = 500–600 nm). The FM–MFA coated PDMS surfaces were finally treated with oxygen plasma at a constant pressure of 100 μ barr and with an oxygen flow rate of 20 sccm. The RF power was 100 W with a time of 3 min.

RESULTS AND DISCUSSION

The crosslinked FM–MFA network grafted onto the surface of PDMS was substantiated by contact angle measurements and surface-sensitive spectroscopic techniques. The results of the contact angle measurements are compiled in Table I. As shown by the results, EGDMA was a better crosslinker compared to DAA and led to better surface grafting and, therefore, hydrophilicity. Lens et al.,¹⁵ in a similar study carried out on polypropylene and polyethylene,

found that unsaturated surfactants, when coated along with crosslinkers, underwent efficient grafting; this resulted in a significant number of hydrophilic groups generating long-term wettable surfaces.

It was obvious from our contact angle measurements that the HEMA-grafted PDMS surfaces generated better hydrophilicity compared to those with NVP because of the greater number of freely available hydroxyl groups. The crosslinking of FM and MFAs onto the film surface facilitated the immobilization of functional groups at the interface, even after long-term storage, which was otherwise impossible. Oxygen, being easily converted into its biradical state in the plasma, expedited the crosslinking of the coated monomers and MFA with the film surface. Moreover, it also contributed to the hydrophilicity of the film surface via functional group implantation.

Attenuated total reflection–FTIR

The presence of surface-anchored FM and MFAs onto the PDMS substrate was evident from the FTIR spectra, shown in Figures 1(a,b) and 2(a,b). Figure 3

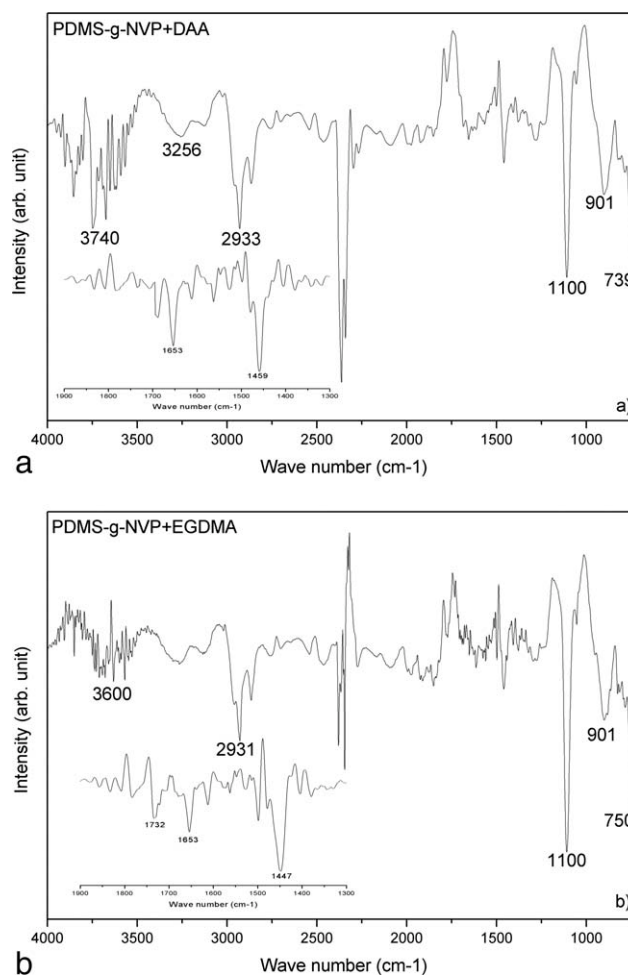


Figure 1 FTIR spectra for (a) PDMS-g-NVP + DAA and (b) PDMS-g-NVP + EGDMA.

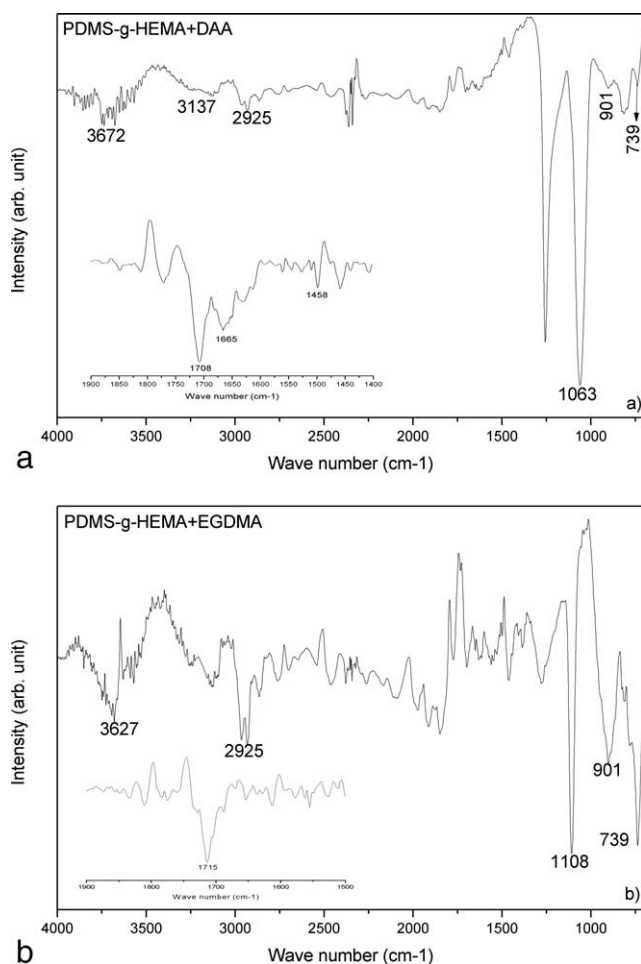


Figure 2 FTIR spectra for (a) PDMS-g-HEMA + DAA and (b) PDMS-g-HEMA + EGDMA.

shows the spectrum of the pristine PDMS. The peak assignments are given in Table II. As shown in Figure 1(a), the broad peak from 3400 to 3100 cm^{-1} corresponded to N–H stretching vibrations, and the peak at 1660 cm^{-1} implied N–C=O stretching vibrations for PDMS-g-NVP + DAA. The vibrational frequencies corresponding to 1732 cm^{-1} (O=C=O), 1653 cm^{-1} (N–C=O), and 1453 cm^{-1} (C–N) for PDMS-g-NVP + EGDMA are evident in Figure 1(b). The presence of humps from 3000 to 3250 and 3400

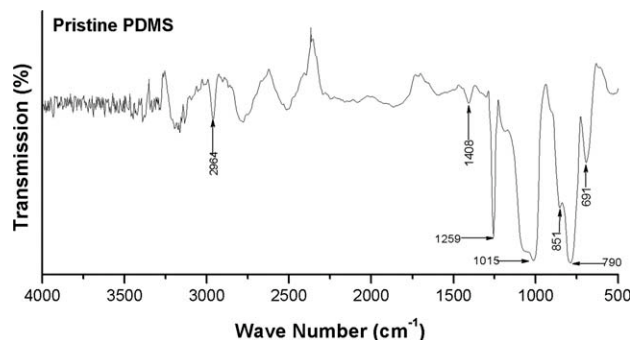


Figure 3 FTIR spectrum for the pure PDMS.

to 3800 cm^{-1} in Figure 2(a) indicate N–H stretching and the hydroxyl group of PDMS-g-HEMA + DAA anchored onto the surface of PDMS, respectively, whereas PDMS-g-HEMA + EGDMA [Fig. 2(b)] showed the presence of peaks at 3600–3800 and 1715 cm^{-1} for hydroxyl and ester groups, respectively. In all of the samples, a broad peak was observed around 3600–3750 cm^{-1} , which corresponded to the broad absorption band of O–H bond of water molecules and indicated a change in the surface characteristics of the plasma-treated PDMS. A peak shift in the FTIR spectra due to the presence of FM–MFAs on PDMS was observed. These H₂O molecules were adsorbed at the silanol interface of the surface of PDMS as a thin layer and as a consequence of plasma treatment. The broad peak corresponding to the –OH group of silanol moieties, expected around 3750 cm^{-1} ,¹⁶ was observed in this study.

XPS

The XPS analysis performed on the surface-modified PDMS showed the Si2p binding energies of the corresponding FM and crosslinker present at the film surface. The C1s peak at 285.0 eV in this spectrum referred to the carbon atoms of the repeat unit in the unmodified polymer. All of these spectra were corrected for charging effects that may have arisen by their reference to C1s (285.0 eV) as an internal standard, present in the sample. In Figure 4(a–c), peaks corresponding to C1s, O1s, and Si2p for PDMS-g-[HEMA + DAA] are evident. Figure 4(a–c) shows the spectra for the pure PDMS, HEMA + DAA coated PDMS films, and oxygen-plasma-modified PDMS-g-HEMA + DAA film. The spectra of pure PDMS showed C1s at 286.4 eV, which corresponded to C–O–Si; O1s at 533 eV, which corresponded to oxygen bonded with silicon; and Si2p at 102.1 and 103.2 eV, which corresponded to virgin PDMS.¹⁷ The spectra of PDMS-g-HEMA + DAA without oxygen plasma treatment showed C1s values of 286.2 (C–O), 286.8 (C=O), and 288 (N–C=O); O1s values of 532.2 (C–O) and 533.7 (O–C=O); and Si2p values of 102.2

TABLE II
Peak Assignments for the PDMS-Grafted FM–MFAs

Assignment	NVP + DAA	NVP + EGDMA	HEMA + DAA	HEMA + EGDMA
OH	3750	3600	3672	3627
N–H	3250	–	3137	–
Methyl CH	2933	2931	2925	2925
O=C=O	–	1732	1708	1715
N–C=O	1653	1653	1665	–
C–N	1459	1447	1458	–
Si–O–Si	1100	1100	1063	1108
Si–C	901	901	851	901
Si–(CH ₃) ₂	739	750	739	739

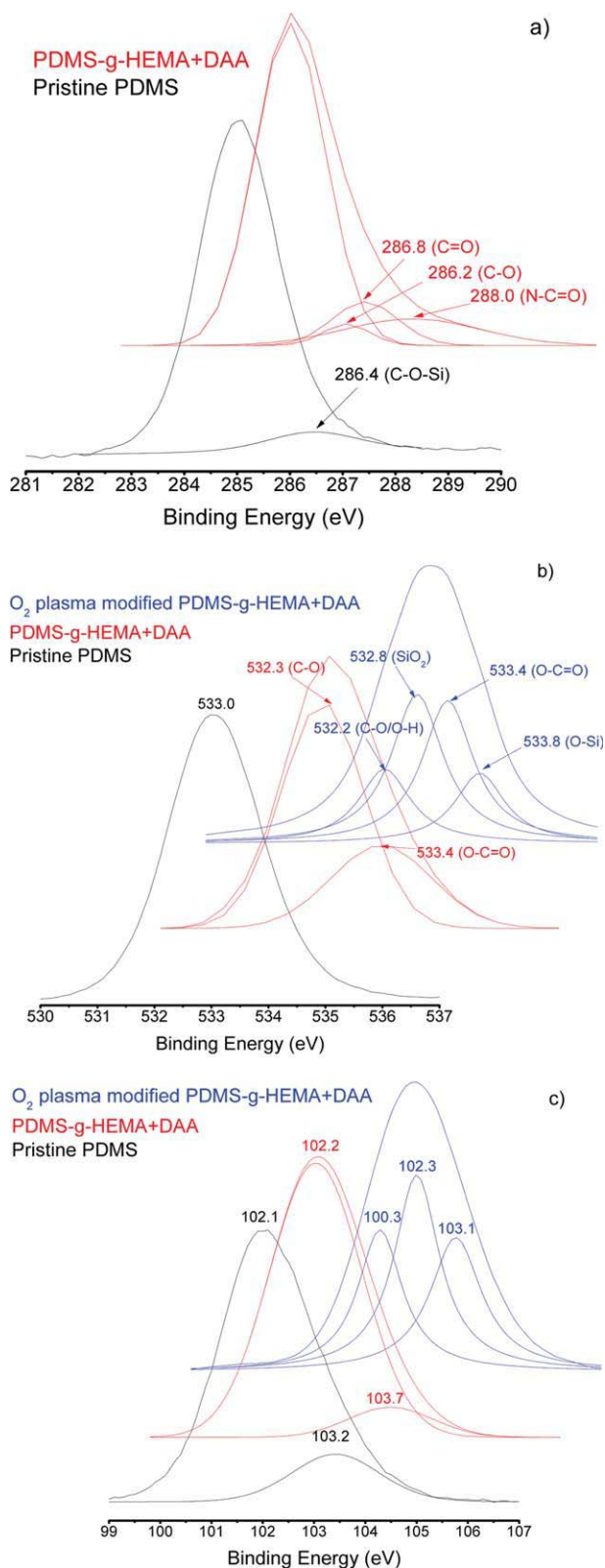


Figure 4 XPS spectra for PDMS-g-HEMA + DAA: (a) C1s, (b) O1s, and (c) Si2p. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and 103.7 eV. There was no change observed in the intensities of the Si2p spectra after spin coating on HEMA + DAA. After the oxygen plasma treatment,

there was no change observed in the C1s spectrum, but new moieties were observed in the oxygen spectrum. The oxygen spectrum showed peaks at 532.2, 532.8, 533.4, and 533.8 eV; these corresponded to OH overlap, SiO₂, O—C=O, and oxygen bound to silicon, respectively. Si2p binding energies of 100.3 eV (Si—O), 102.3 eV (O—Si—O), and 103.1 eV (silica structure) were observed for the oxygen-plasma-modified PDMS-g-HEMA + DAA. The results prove the formation of hydroxyl groups at the surface, which led to hydrophilicity. The Si2p spectra of the modified sample showed an increased peak intensity of oxygen-bound moieties; this indicated an increase in the oxygen content in the film. An OH peak was also observed in the spectra; this indicated the modification of the film. Similar peaks were observed for the remaining three compositions, and hence, indicative XPS for PDMS-g-HEMA + DAA is shown.

SEM

Figure 5(a,b) shows SEM of the pristine PDMS and PDMS-g-HEMA + DAA, respectively. The film

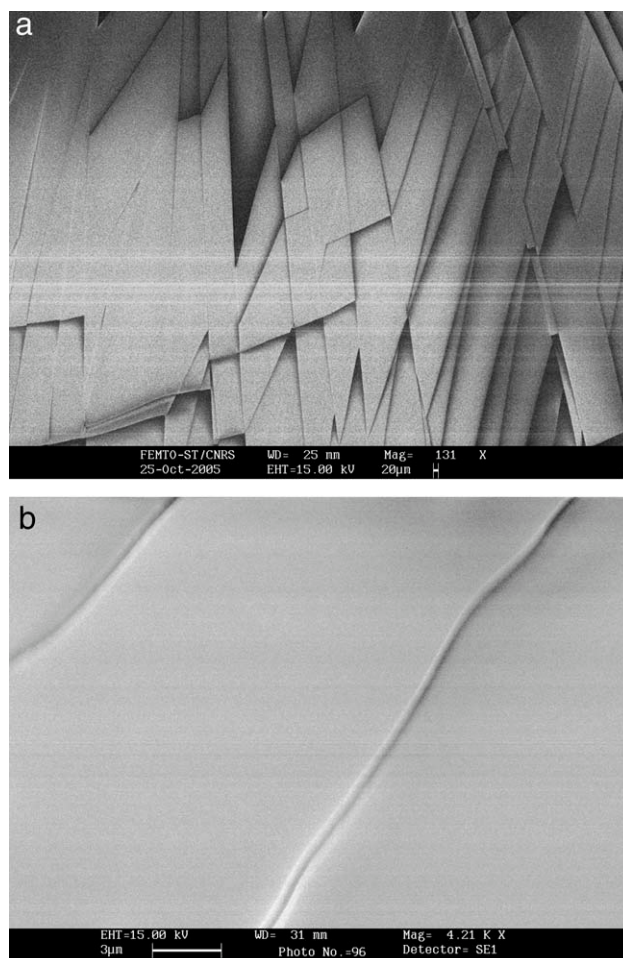


Figure 5 SEM of (a) the pristine PDMS and (b) PDMS-g-HEMA + DAA.

TABLE III
Effect of the Storage Time on the Hydrophilicity of the Surface of the PDMS-Grafted Films as a Function of the Water Contact Angle (°)

Sample	1 h	1 day	1 week	1 month
NVP + DAA	35	50	54	61
NVP + EGDMA	30	36	43	48
HEMA + DAA	32	46	48	50
HEMA + EGDMA	21	35	39	40

looked smooth compared to the PDMS pristine film.¹⁸ As reported in ref. 18, the hydrophobic recovery of PDMS is not only due to the reorientation of bulk molecules to the surface but also to physical destruction due to the bombardment of ions. The HEMA-coated film showed nanostructuring and, as reported, gave a stable contact angle, as there were stable silanol groups formed on the surface. A similar reason could be given for the films reported in this article. No nanostructuring was visible at higher magnification, unlike that reported in ref. 18.

Water contact angle

Attempts have been made in the past to fabricate permanently hydrophilic surfaces by the covalent grafting of FMs; however, uncertainty still prevails in the location of the functional groups. In this study, the hydrophilic stability upon storage was monitored by the changes in the water contact angle, the values of which are compiled in Table III. The water contact angle was measured with a contact-angle goniometer (Rame Hart, Netcong, NJ) with a measurement accuracy of $\pm 1^\circ$. A decrease in the surface hydrophilicity is a common symptom of surface instability encountered after electron bombardment. The functional groups generated initially due to bombardment are lost as volatile products or permanently buried below the crosslinked network.¹⁹

It was obvious from the contact angle measurements that the HEMA-grafted PDMS surfaces generated better hydrophilicity than those grafted by NVP because of the greater number of freely available hydroxyl groups. The behavior of FM-crosslinked surfaces was mainly due to the crosslinked network. A very small hydrophobic recovery may have been due to the free rotation of the functional groups generated on the grafted polymer chains due to bombardment. It was established that the surface state of the polymeric materials possessed far greater mobility than the bulk macromolecules. This enhanced mobility was achieved through the rotational motion of the functional groups about the polymer chain backbone rather than long-chain segmental motion of macromolecules. This mobility of the functional groups completely ceases in fully crosslinked surfa-

ces.²⁰ Therefore, when FM was crosslinked with MFA, hardly any room was left for the free rotation of the grafted monomer chains bearing the functional groups, unlike in grafting by other methods.

CONCLUSIONS

We have reported a very efficient technique for grafting a thin layer of FMs onto the surface of polymer films while retaining the monomer structure; this is often difficult in the case of simultaneous plasma grafting or any other plasma-based grafting technique. This technique also refrained from the use of solvent, initiators, or robust grafting conditions. Moreover, the use of MFAs facilitated the formation of a surface-crosslinked network, along with the generation of functional moieties on the film surface. These functional moieties in the crosslinked network, in turn, generated a long-term hydrophilic surface, which underwent hardly any surface reconstruction. Also, very stable hydrophilic films were obtained with this technique; this was a very crucial requirement.

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