# Polymer Surface Modification Using Microwave-Oven-Generated Plasma

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## Introduction

The treatment of polymeric materials with plasma is a frequently used technique to accomplish surface modifications that affect chemical composition as well as surface topography. Examples include the oxidation of polyolefins to enhance paint adhesion,[1] the synthesis of composite materials consisting of hydrophilic and hydrophobic components,[2] and the functionalization of polymers such as polystyrene.[3] Moreover, microwave discharges are routinely employed in the processing of materials to deposit films as well as coatings.[4−8]

In recent years, the modification of elastomer surfaces with oxygen plasma has also become an important tool in microfluidics where elastomers such as poly(dimethylsiloxane) (PDMS) are used as substrates for microreactors.[9] PDMS is a hydrophobic polymer for which exposure to oxygen plasma leads to oxidation and chain scission as well as cross-linking and the formation of a silica-like surface.[10] Additionally, oxygen plasma is utilized to adhere the polymer permanently to other silicon-based materials. The latter method is commonly employed to create sealed channels from open, microstructured surfaces obtained by soft photolithography.[11] Recent studies have also proposed reaction mechanisms for the functionalization of PDMS surfaces using a variety of plasmas created from gases such as Ar, $O_2$, and $CO_2$.[12]

Despite the advantages of this technique, the plasma treatment of surfaces requires the use of specialized equipment such as plasma strippers that are not available in many laboratories. We, therefore, devised and tested an inexpensive alternative to the use of these commercial products. Our approach relies on an unmodified "kitchen microwave oven" and standard laboratory glassware. The usefulness of our procedure is demonstrated for the surface modification of PDMS and the plasma-induced adhesion of PDMS to glass substrates.

## Experimental Section

**Materials and Equipment.** The silicon elastomer kit (Sylgard 184) and vacuum desiccator (Pyrex, diameter 160 mm) are from Fisher Scientific. Compressed oxygen and ethanol (100%) are from Air Products and Chemicals, Inc., and Florida Distillers Co., respectively. Nanopure water (18 MΩ cm) is prepared using a Barnstead EASYpure UV unit. Plasma is generated with a 1100-W countertop microwave oven (Amana, ACM2160AB), which emits radiation at a frequency of 2.45 GHz, and a Harrick PDC-32G plasma cleaner. In addition, a KLA-Tencor P-15 profilometer is used to measure the surface roughness of the PDMS samples obtained.

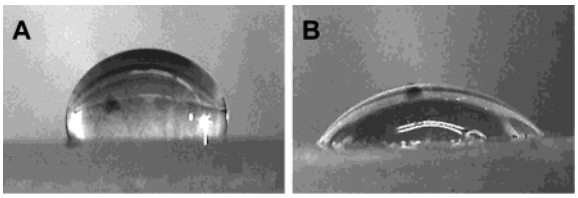


**Figure 1.** Water drops on the surface of two different PDMS samples. (A) 20-$\mu$L water drop on an unexposed PDMS surface. (B) 20-$\mu$L water drop on the surface of a sample exposed to oxygen plasma for 25 s.

**Sample Preparation.** Samples of PDMS are polymerized in accordance with the supplied instructions. A weight ratio of 10:1 is maintained by mixing 20.0 g of the polymer base with 2.0 g of the curing agent. The liquid mixture is placed in a vacuum desiccator for degassing. The unpolymerized mixture is then poured into a plastic Petri dish and degassed once more. To ensure thorough polymerization, the Petri dish is placed on a hot plate at 55 °C for 24 h. The resulting PDMS elastomer is removed from the Petri dish and cut with a straight razor into 1.0-cm$^2$ samples.

**Plasma Exposure.** To prevent any accumulation of surface residues, the PDMS samples are rinsed with ethanol and handled with tweezers prior to plasma exposure. After rinsing, the samples are dried with compressed air and placed on a glass microscope slide. The slide is then positioned on a sample stage in the center of the desiccator with a small piece of steel wire placed at the bottom to generate a spark and initiate $O_2$ dissociation. The system is purged with oxygen for 2 min before the desiccator is evacuated to a pressure of about $10^{-3}$ Torr. Last, the desiccator is placed into the microwave oven (turntable removed). In all the experiments shown here, the oven is operated at maximum power.

**Safety Precautions.** Because of the setup of these experiments, several safety precautions should be taken when using these methodologies. Long exposure times may cause the desiccator to become very warm. For this reason, a Pyrex desiccator should be used and oven mitts should be worn when removing the vessel from the microwave after lengthy exposures. Additionally, the desiccator should not be used if cracked or chipped to prevent implosion. A final precaution that should be taken is to avoid looking at the small steel piece at the bottom of the desiccator during exposure. The arc generated from the steel emits intense light.

## Results and Discussion

The radiation in the microwave oven sustains an oxygen plasma generated from the residual gas. The plasma is easily observed as a result of its emission of bright, colorful light. To analyze the effects of plasma exposure, we carry out systematic measurements of the contact angles between PDMS and 20-$\mu$L drops of water. These measurements are based on digital images that are recorded by a charge-coupled-device camera mounted in plane with the sample surface. Figure 1A,B shows the shapes of water drops placed on an unexposed and a plasma-treated PDMS sample, respectively. The result illustrates a profound increase in the hydrophilicity of the PDMS surface. This effect is due to the gain of $SiO_x$ groups during the plasma-mediated oxidation that renders a more hydrophilic surface.[10]

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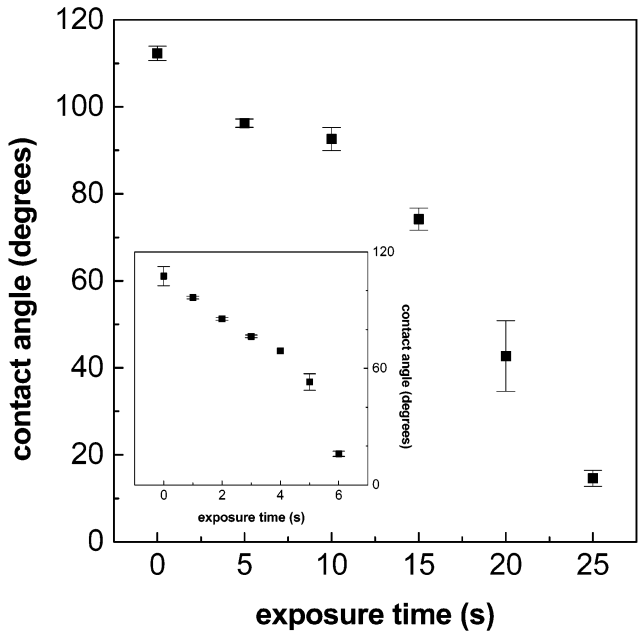


**Figure 2.** Contact angles between water and PDMS as a function of the plasma exposure time. The plot and its inset present data obtained using a microwave oven and a conventional plasma cleaner, respectively.

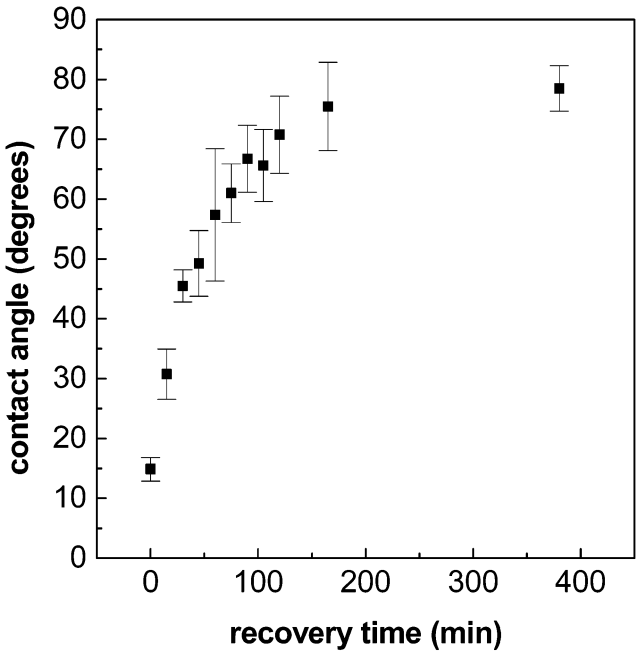


**Figure 3.** Contact angle as a function of time elapsed after a 25-s plasma exposure.

From images similar to those in Figure 1, we measure the contact angle as the angle between the polymer surface and the initial tangent of the curved water drop. The average contact angle for an unexposed sample is 112 ± 2°. Figure 2 shows the dependence of this angle on the duration of plasma exposure. It reveals that the contact angle decreases dramatically with increasing exposure time to values of less than 15°, which indicates the presence of a profoundly hydrophilic surface. The latter value is comparable to the contact angle of water on a clean microscope slide, which is a strongly wetting surface. Notice that a similar effect can be seen using conventional plasma-generating equipment and is shown as an inset in Figure 2. Additionally, control experiments without steel wire in the desiccator show no change in the contact angle with increasing time. These control experiments show that there are no apparent surface changes resulting from the microwave radiation. The corresponding values for the interfacial energy of the elastomer decrease from 28 to −70 mJ/m$^2$. This systematic change in the interfacial energy is accompanied by a mild decrease in the surface roughness of the PDMS samples. Profilometric measurements show a change in the root-mean-squared surface roughness from 3.7 ± 0.2 to 2.8 ± 0.1 $\mu$m with increasing exposure time (0−25 s).

We observe that the plasma-treated surfaces recover their hydrophobic character if allowed to react with ambient air. A typical example for this slow process is shown in Figure 3. In this experiment, a PDMS sample is exposed to the oxygen plasma for 25 s, yielding a contact angle of 15 ± 2°. Within a period of 2−3 h, this value increases to saturate at approximately 79°. Recent studies suggest that this phenomenon is due to passive transport of low-molar-mass PDMS species from the bulk to the surface and possibly a reorientation of the polar species.[10] Notice, however, that the polymer never fully regains its initial hydrophobicity. The saturation limit is about 34° lower than the contact angle measured for untreated PDMS, which is most likely caused by the formation of a silica-like surface.[10] These results agree with the recovery-time measurements in the literature that employed conventional plasma sources.[13]

In addition to the surface modification of polymer samples, our economic experimental procedure also allows for the sealing of PDMS to flat glass plates. To achieve strong adhesion between these two materials, we expose PDMS to the oxygen plasma for 25 s. The freshly prepared PDMS surface is then placed on a clean microscope slide, and the two components are pressed against each other to ensure full contact. While the adhesion is initially weak, the bonding reaches remarkable strength after several hours, and subsequent peeling tests reveal that the composite samples are more likely to rupture within the PDMS bulk than at the PDMS/glass interface.

In conclusion, our results provide a reliable and inexpensive alternative to the oxidation of polymer surfaces with commercial plasma devices. Our measurements of contact angles between water and PDMS reveal a profound increase in the hydrophilic surface properties of PDMS after plasma exposure. Moreover, the observed partial recovery of the initially hydrophobic surface is in good agreement with the reported performance of conventional techniques.[13] In conjunction with the importance of plasma treatment as an adhesion-promoting procedure, our experimental technique should aid and benefit future studies in the emerging field of microfluidics and related disciplines.

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