Simultaneous Graft Copolymerization of 2-Hydroxyethyl Methacrylate and Acrylic Acid onto Polydimethylsiloxane Surfaces Using a Two-Step Plasma Treatment

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ABSTRACT: Acrylic acid (AAc) and 2-hydroxyethyl methacrylate (HEMA) mixtures were simultaneously grafted onto the surfaces of polydimethylsiloxane (PDMS) films using a two-step oxygen plasma treatment (TSPT). The first step of this method includes: oxygen plasma pretreatment of the PDMS films, immersion in HEMA/AAc mixtures, removal from the mixtures, and drying. The second step was carried out by plasma copolymerization of preadsorbed reactive monomers on the surfaces of dried pretreated films. The effects of pretreatment and polymerization time length, monomer concentration, and ratio on peroxide formation and graft amount were studied. The films were characterized by attenuated total reflection Furrier transformer infrared (ATR-FTIR) spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), zeta potential, surface tension, and water contact angle measurements. The ATR-FTIR spectrum of the modified film after alkaline treatment showed the two new characteristic bands of PHEMA and PAAc. Both increase the polar part of surface tension (γ_p) after grafting and the evaluation of surface charge at pH 1.8, 7, and 12 confirmed the presence of polar groups on the surface of grafted films with a mixture of HEMA/AAc. Morphological studies using both AFM and SEM evaluation illustrated various amounts of grafted copolymer on the surface of PDMS films. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2208–2217, 2007

Key words: two-step plasma treatment; surface modification; polydimetylsiloxane; hydroxyethyl methacrylate; acrylic acid; graft copolymerization

INTRODUCTION

The nature of surfaces plays a vitally important role in some specific applications. Many polymers do not have the surface characteristics required for biomedical applications. Therefore, to use these polymers, the surfaces must be modified while maintaining the key bulk properties. For example, surface modification of polymers to improve biocompatibility is becoming an increasingly popular method.[1,2]

Polydimethylsiloxane (PDMS)-based elastomers have been used in a wide range of biomedical applications in the past three decades, as a result of their physiological inertness, good blood compatibility, low toxicity, good thermal and oxidative stability, low modulus, and nonadhesive properties.[3,4] Surface modification of PDMS using hydrophilic monomers such as 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AAc), acrylamide (AAm), and many biological derivations as biomaterials have attracted great interest for many years.[4–16]

There are many techniques that can be used to alter surface properties using laser,[5,7,17–21] plasma,[6,8–15,22–29] and corona discharge.[30,31] Among the various surface modification methods, surface grafting has been widely used to modify the surface properties of the PDMS films. However, there has been growing interest in utilizing plasma in surface modification of polymeric biomaterials. This is because plasma-based techniques are usually reliable, reproducible, relatively inexpensive, and applicable to different sample geometries and location of modification is limited at the surface region of the polymeric material without altering the bulk properties. Also, plasma treatment not only may result in changes of a variety of surface characteristics (chemical, tribological, optical, and biological) but can provide sterile surfaces.[1,9,12]

According to the previous studies,[28,32,33] plasma graft copolymerization techniques include plasma-induced graft copolymerization and simultaneous plasma-treated graft copolymerization. In the former, a polymeric substrate is treated by plasma before it undergoes subsequent graft copolymerization in monomer solution. A mechanism of peroxide induc-

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tion is proposed for this reaction.[28,32] Whereas in the latter; a polymeric substrate preadsorbed with a layer of reactive monomer is treated by plasma. Therefore, the monomer with required functional groups is specifically introduced onto the surface of polymers.[28,33]

The rationale behind this work by using the mixture of HEMA and AAc is attributed to the grafted polyHEMA, which significantly improves the biocompatibility of PDMS films, and also carboxylic groups of grafted polyAAc play a very important role in immobilization of some biological derivations such as collagen. In our study, mixtures of AAc and HEMA were simultaneously grafted onto surface of PDMS films using oxygen plasma via a new method named ''two-step plasma treatment (TSPT).'' To the best of our knowledge, no attempts have been made using the mixture of HEMA and AAc with TSPT method. Briefly, the plasma pretreated film was first immersed in an aqueous monomers solution with different monomer ratios of HEMA/AAc and the second step the plasma graft copolymerization was carried out onto treated PDMS films. Finally, the grafted PDMS films were characterized by ATR-FTIR, SEM, AFM, zeta potential, surface tension, and water contact angle measurements.

EXPERIMENTAL

Materials

The silicone rubber used in this study was Silastic® MDX4-4210 medical grade elastomer, made by Dow Corning Corp., Midland, MI. The silicone was thoroughly mixed with 10% (w/w) of curing agent. After thorough mechanical stirring the mixture was degassed. The silicone rubber films were prepared by hot compression molding (250 psi, 75°C, 30 min), followed by post curing process at 90°C for a period of 3 h to establish the required physical properties.

HEMA and AAc were from Fluka, Buchs, Switzerland. Both HEMA and AAc were redistilled under vacuum to make them free from the inhibitor. All other solutions used were prepared by analytical grade reagents.

Plasma pretreatment—Step I

Emiteck, K1050X apparatus was utilized for both plasma pretreatment and copolymerization of silicone films. The silicone films were placed on the bottom of reaction chamber, which was evacuated to 6×10^{-1} mbar, and pretreated with 60 W of oxygen plasma for up to 180 s. Then, the plasma pretreated films were immersed in aqueous monomer solutions with the given ratios of HEMA/AAc for up to 30 min at room temperature, and then finally removed from solution and dried at 40°C for 5 min.

Plasma graft copolymerization—Step II

The dried plasma pretreated films with a preadsorbed layer of reactive monomer on their surfaces were placed into the reaction chamber for plasma graft copolymerization for up to 5 min. The residual monomers and homopolymers were removed by Soxhlet extraction in distilled water for 72 h. The amounts of grafted polymer were calculated with the microbalance (Precisa) according to the following equation:

$$\text{Grafted amount } (\mu g/cm^2) = \frac{W_g - W_0}{A} \qquad (1)$$

where W_g is the dry weight of grafted film, W_0 is the dry weight of untreated film, and A is the surface area of the grafted film.[9]

Peroxide determination

The amount of peroxide formed on the surface of pretreated films was measured using 1,1-diphenyl-2-picrylhydrazyl (DPPH).[12] The pretreated films were placed into a degassed toluene solution of DPPH at 80°C for 24 h to decompose the peroxides on the surface of films. The DPPH molecules consumed were determined from the difference in transmittance at 520 nm between the control and oxygen plasma pretreated films. The absorption coefficient of DPPH at 520 nm was measured 1.18×10^4 L mol^{-1} cm^{-1}.[12,34]

Contact angle and surface tension measurements

The static contact angles of the control (untreated), plasma pretreated, and grafted films were measured with the sessile drop method using Krüss G10 contact-angle measurement equipment.[17] The films were stored in distilled water and air for up to 10 days. The wet samples were dried with filter paper before contact angle measurements. A 5-μL double distilled water droplet was used for each point and the contact angle was recorded after 1 min. The average values of five measurements on different points of each sample were recorded.[17,18] Furthermore double distilled water and diiodomethane were employed to calculate surface tensions of the samples using Owens-Wendt equation.[35] The polar and disperse parts of surface tension were also calculated.

ATR-FTIR spectroscopy

To confirm the formation of graft copolymerization on the surface of the modified film, a Brucker IFS-48 attenuated total reflection Furrier transformer infrared (ATR-FTIR) spectrophotometer with a KRS-5 prism was employed. The incident angle was 45°and

scanning was carried out from 4000 (2.5 μm) to 650 cm^{-1} (15.4 μm).

Scanning electron microscopy

The morphologies of the control, plasma pretreated, and grafted PDMS films (gold-coated with a Polaron sputter coater) were studied using a Cambridge *S*-360 scanning electron microscope (operating at 10 kV).

Atomic force microscopy

The surface topology, microstructure, and homogeneity of the grafted PDMS films were also analyzed using an Autoprobe CP Multiple AFM (Park Scientific) in noncontact (tapping) mode working with a SiC tip and a frequency of 113 kHz.

Zeta potential measurement

Using an Anton Paar electro kinetic analyzer, the zeta potential of the silicone films was measured. The control, plasma treated, and grafted films with the thickness of 0.3 mm were cut into 4 × 3-mm pieces to use for clamping cell.[36] One piece of films was used for each measurement. Before the start of each experiment, the cell and film were rinsed with the electrolyte solution in both directions for 2 min. The measurements were carried out at 25°C and pH 1.8, 7, 12. One millimolar KCl solution was used as a background electrolyte in all experiments. Potassium hydroxide and hydrochloric acid were used for pH adjustment to study the variation of zeta potential with pH of electrolyte. Three measurements were taken and averaged and the zeta potentials were calculated from streaming potential using the Helmholtz–Smoluchowski equation.[36,37]

Statistical analysis

The samples used in all experiments were in three replicates and the results were given as ''mean ± standard deviation.'' The unpaired Student's *t*-tests were employed for all statistical analyses using Microcal Origin 3.5.

RESULTS AND DISCUSSION

Peroxide group formation

Several investigations have revealed that the peroxide groups could be efficient initiators of graft copolymerization on the plasma-treated surfaces.[12,17,26,27] Also some other studies revealed that application of DPPH was highly effective for determining the concentration of the peroxide groups on the activated polymer surface.[12,26,27,34]

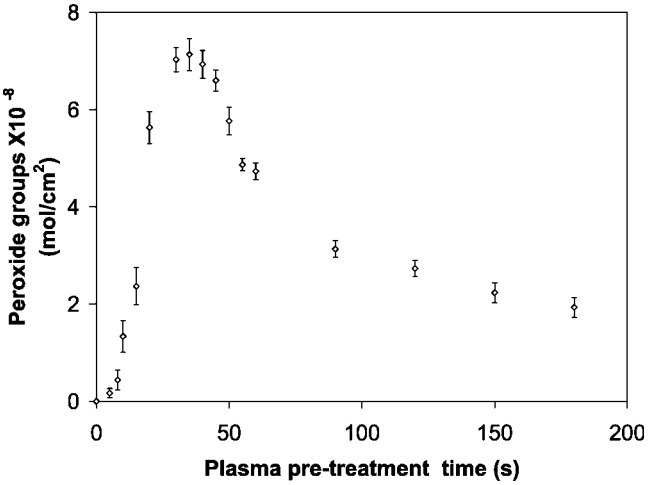

Figure 1 Formation of the peroxide groups on the surface of PDMS films pretreated by oxygen plasma; 60 W, 6 × 10^{-1} mbar, ($n = 3$, mean ± standard deviation).

According to our results, as shown in Figure 1, the concentration of peroxide groups increased with increasing pretreatment time, reached a maximum value after 35 s under 60 W, and then decreased with further increase in pretreatment time. As most peroxide groups must have been produced under oxygen plasma atmosphere during the pretreatment time, therefore, it should be expected that lower peroxide concentrations at longer plasma exposure time may be due to direct decomposition of the peroxide groups formed by plasma. In other words, this occurrence could be accounted by the produced peroxides that were partially converted into inactive species, and not as free radicals after prolonged plasma pretreatment times.[12,34]

Graft copolymerization

Poly(HEMA-*co*-AAc) with different monomer ratios were graft copolymerized onto silicone films using a two-step plasma treatment. This technique includes: oxygen plasma pretreatment of the PDMS films, immersing the films in the aqueous monomer solution (feeding solution) with different monomer ratios of HEMA/AAc, drying the film with a preadsorbed layer of reactive monomer on their surfaces, and plasma graft copolymerization (Fig. 2). The reasons for plasma pretreatment of the films before grafting are: (1) producing polar groups (hydroperoxide groups) on the surface of chemically inert PDMS so to physically react with hydrophilic monomers (HEMA and AAc) via hydrogen bonding, and (2) the production of peroxide groups which may act as initiators in polymerization step.

The amount of grafted copolymer was sensitively affected by pretreatment time length, monomers con-

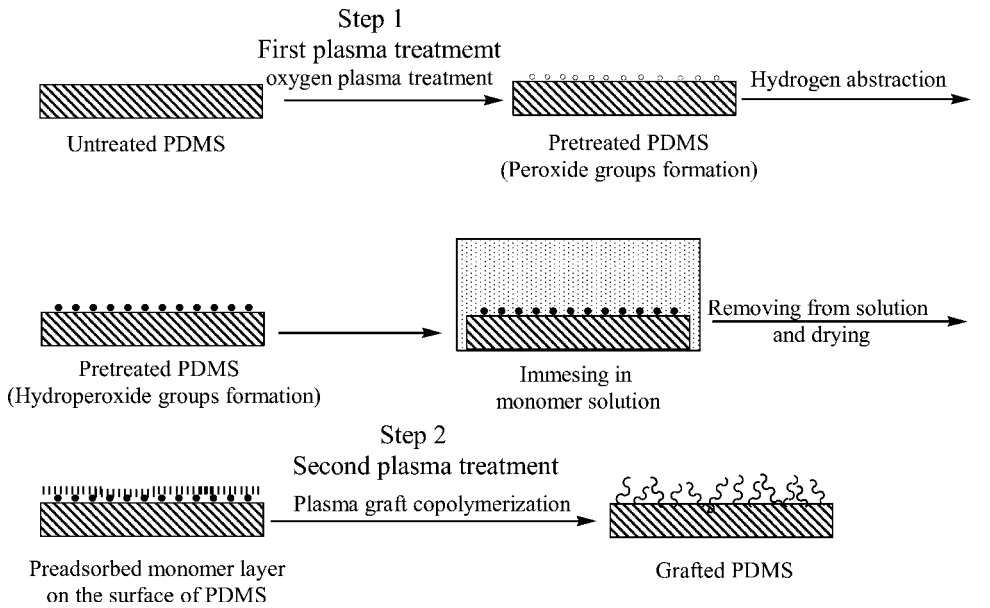

Figure 2 Schematic diagram of the graft copolymerization of HEMA and AAc mixture using a two-step plasma treatment (TSPT).

centration and their ratios, as well as polymerization time length. The relationship between the amount of grafted copolymer per square centimeter and plasma pretreatment duration is plotted in Figure 3. The analysis of experimental data indicates that the grafted amount has decreased after passing a maximum at 35 s (60 W). The previous studies have shown that the peroxide groups act as initiators in plasma-induced graft copolymerization.[12,17,28,34] According to our results, the changes of the grafted amount as a function of the pretreatment time directly depend on those of the peroxides concentration (Figs. 1 and 3).

The influence of the plasma graft copolymerization duration on the grafted amount was also studied. According to our results in Figure 4, when plasma graft copolymerization time is ''0,'' the grafting amount is ''0'' as well. In other words, the graft copolymerization was not carried out without second plasma exposure and it was a confirmation that during the drying stage (40°C for 5 min) graft copolymer was not created on the surface of films. Furthermore, the grafted amount increased with the increasing copolymerization time up to 3 min at 60 W of power and then it gradually decreased. This finding may be explained in terms of both polymerization process and etching rate of plasma, which can affect the amount of the grafted copolymer onto the PDMS films. During propagation step of the plasma copolymerization, the preadsorbed monomers react with radicals and graft onto the surface of silicone until the polymerization reaction terminates. In this step the etching rate of plasma is less than the increase of the grafting amount, which is a consequence of the polymerization process, the curve would go up to a maximum after 3 min. Then, the polymerization terminates, and the curve falls slowly because plasma etching is the predominant phenomenon.[38]

We believe that some advantages of a two-step plasma treatment (TSPT) over that of plasma-induced graft copolymerization are as follows

1. *Lower graft polymerization time length*: Plasma-induced graft copolymerization (one-step) takes about several hours while TSPT takes just 40 min.

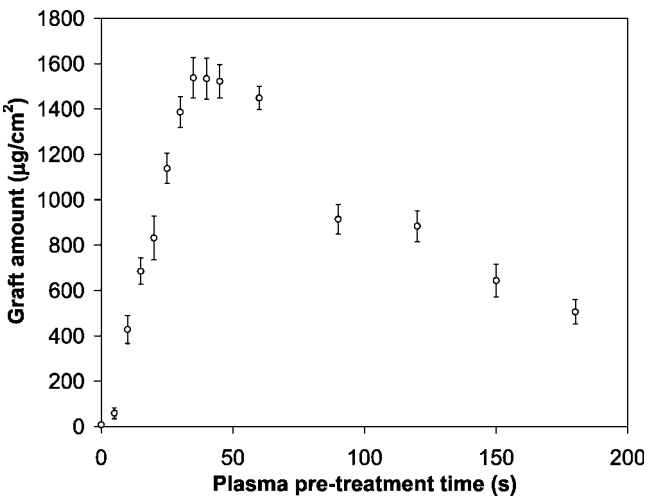

Figure 3 The Change of graft amount (μg/cm^2) during oxygen plasma pretreatment time (the first plasma treatment); 60 W, 6 × 10^{-1} mbar, (n = 3, mean ± standard deviation).

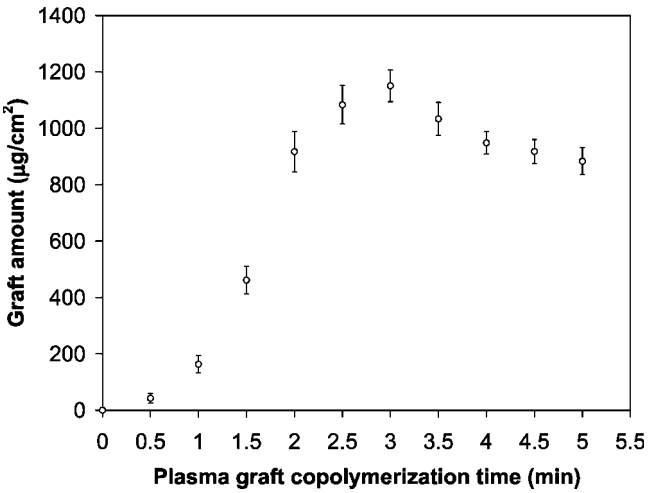

Figure 4 The change of graft amount (μg/cm^2) during plasma graft copolymerization time (the second plasma treatment); 60 W, 6×10^{-1} mbar, ($n = 3$, mean ± standard deviation).

2. *No controlling requirement on pH of monomer solution*: In plasma-induced graft copolymerization, a plasma treated substrate was immersed in a monomer solution at a temperature higher than 50°C for several hours. Because HEMA is an ester, in an acidic solution (aqueous monomer solution of HEMA and AAc) at these conditions, it can be hydrolyzed to acid and alcohol. Therefore, controlling pH value of the solution during the reaction plays a vitally important role in the ratios of HEMA/AAc in plasma-induced graft copolymerization.
3. *No need to remove oxygen from the monomer solution before polymerization*: In TSPT, graft copolymerization is carried out under oxygen plasma atmosphere and no vacuum is required to eliminate oxygen from the solution or PDMS before copolymerization process.

Moreover, some advantages of TSPT in comparison with simultaneous plasma-treated graft copolymerization are as following

1. *Higher grafting amount*: In simultaneous plasma-treated graft copolymerization, first a polymeric substrate is preadsorbed with a layer of reactive monomer and then it is treated by plasma. As PDMS is a hydrophobic polymer with high contact angle and low surface tension, the hydrophilic monomer solution (aqueous monomer solution of HEMA and AAc) cannot spread on the surface and the monomers are neither adsorbed nor the amount of the preadsorbed monomers on the surface is being high. However, in TSPT, plasma pretreated PDMS with low contact angle and high surface tension is used, therefore, the higher amount of preadsorbed monomers and consequently a higher graft amount is obtained.
2. *Producing more homogeneous morphology and topology of the grafted surface*: As aforementioned, in TPST a better and more homogeneous spreading of hydrophilic monomer solution on the surface of pretreated PDMS can lead to more homogeneous morphology and topology of the grafted surface.

It should be considered that the reaction of oxygen plasma with preadsorbed reactive monomers on the surface of PDMS during the plasma graft copolymerization process (the second step of TSPT) could lead to formation of two kinds of active site (radical), depending on dissociation of pi (π) or sigma (δ) bonds. As π bond of C=C in HEMA and AAc is weaker than δ bonds, then the reaction of the created radicals or plasma particles with these monomers can easily dissociate the former bond, which is covalently attached to two adjacent monomers. Now, it is expected that if other radicals or plasma particles react with these monomers, additional active site may be generated from dissociation of δ bonds and partial crosslinking may occur. Therefore, like simultaneous plasma-induced graft copolymerization, the possibility of crosslinking or creation of by-products can be considered as disadvantages of TSPT method.

Figure 5 shows the effect of the monomer concentration of the feeding solution on the amount of the grafted copolymer onto the PDMS films with two different peroxide concentrations of 6.4×10^{-8} mol cm^{-2} [Fig. 5(a)] and 4.1×10^{-8} mol cm^{-2} [Fig. 5(b)]. The grafting amount increases up to 70 wt % of the

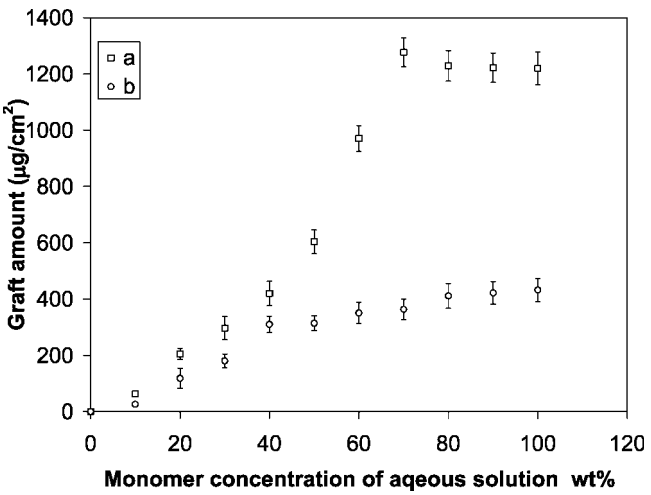

Figure 5 The effect of monomer concentration of the feeding solution on the graft amount with two different peroxide concentrations, (a) 6.4×10^{-8} mol/cm^2 and (b) 4.1×10^{-8} mol/cm^2. ($n = 3$, mean ± standard deviation).

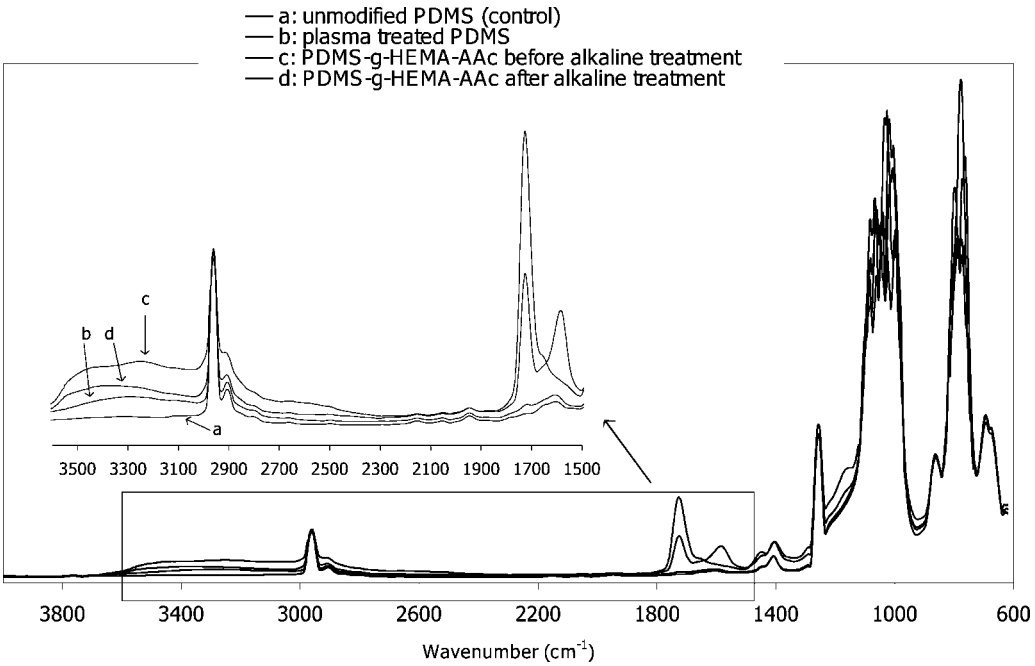

Figure 6 ATR-FTIR spectra of (a) unmodified PDMS (control), (b) oxygen plasma treated PDMS (3 min, 60 W, 6×10^{-1} mbar), (c) PDMS-*g*-HEMA-AAc before alkaline treatment, and (d) PDMS-*g*-HEMA-AAc after alkaline treatment.

mixture of HEMA and AAc concentration at 6.4×10^{-8} mol cm^{-2} peroxide groups, while it increases up to 40 wt % of the mixture of HEMA and AAc concentration at 4.1×10^{-8} mol cm^{-2} peroxide groups, and then it levels off. This is explained as a result of the consumption of the active sites on the polymer surface.[26] Because preadsorbed monomers on the pretreated film react with the peroxide groups by covalently grafting onto the surface, hence, the graft copolymerization of HEMA and AAc would no longer proceed when the surface peroxide groups are being consumed.[12,26]

ATR-FTIR spectra

The presence of the graft was confirmed by comparing the ATR-FTIR spectra of control, plasma pretreated, and modified samples (Fig. 6). A peak at about 3300 cm^{-1} due to peroxide groups was observed in the spectrum of plasma-treated PDMS in comparison with unmodified PDMS [Fig. 6(a,b)]. Probably because the absorbance of the carbonyl groups of AAc overlaps with that of HEMA, a single absorption peak at 1720 cm^{-1} was observed in the spectrum of PDMS-*g*-HEMA-AAc. Also, a broad adsorption peak at about 3100–3500 cm^{-1} due to —OH groups of HEMA and AAc appeared in this spectrum [Fig. 6(c)]. According to the previous investigations, alkaline treatment shifted the IR absorbance of the carboxyl groups of acrylic acids to 1576 cm^{-1}.[27,34] In our findings, after alkaline treatment the peak at 1720 cm^{-1} decreased and a new peak at 1576 cm^{-1} appeared because carboxyl groups of AAc reacted with NaOH and the peak shifted from 1720 to 1576 cm^{-1}, while HEMA remained intact. Furthermore, the peak at about 3100–3500 cm^{-1} decreased after this treatment, but it did not disappear completely because of the —OH groups of HEMA [Fig. 6(d)], which confirmed that both HEMA and AAC groups are successfully grafted onto the surface of PDMS.

Additionally using ATR peak areas, which were determined by integrating the areas under the peaks

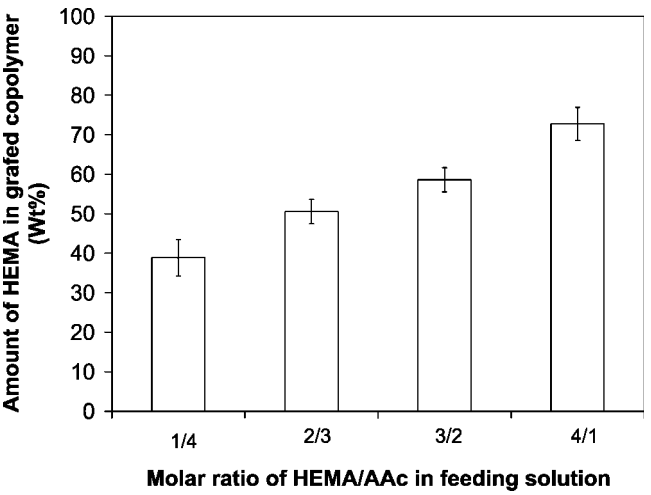

Figure 7 Amounts of HEMA in grafted copolymer of poly(HEMA-*co*-AAc) with different ratios of HEMA/AAc in the feeding solution, ($n = 3$, mean ± standard deviation).

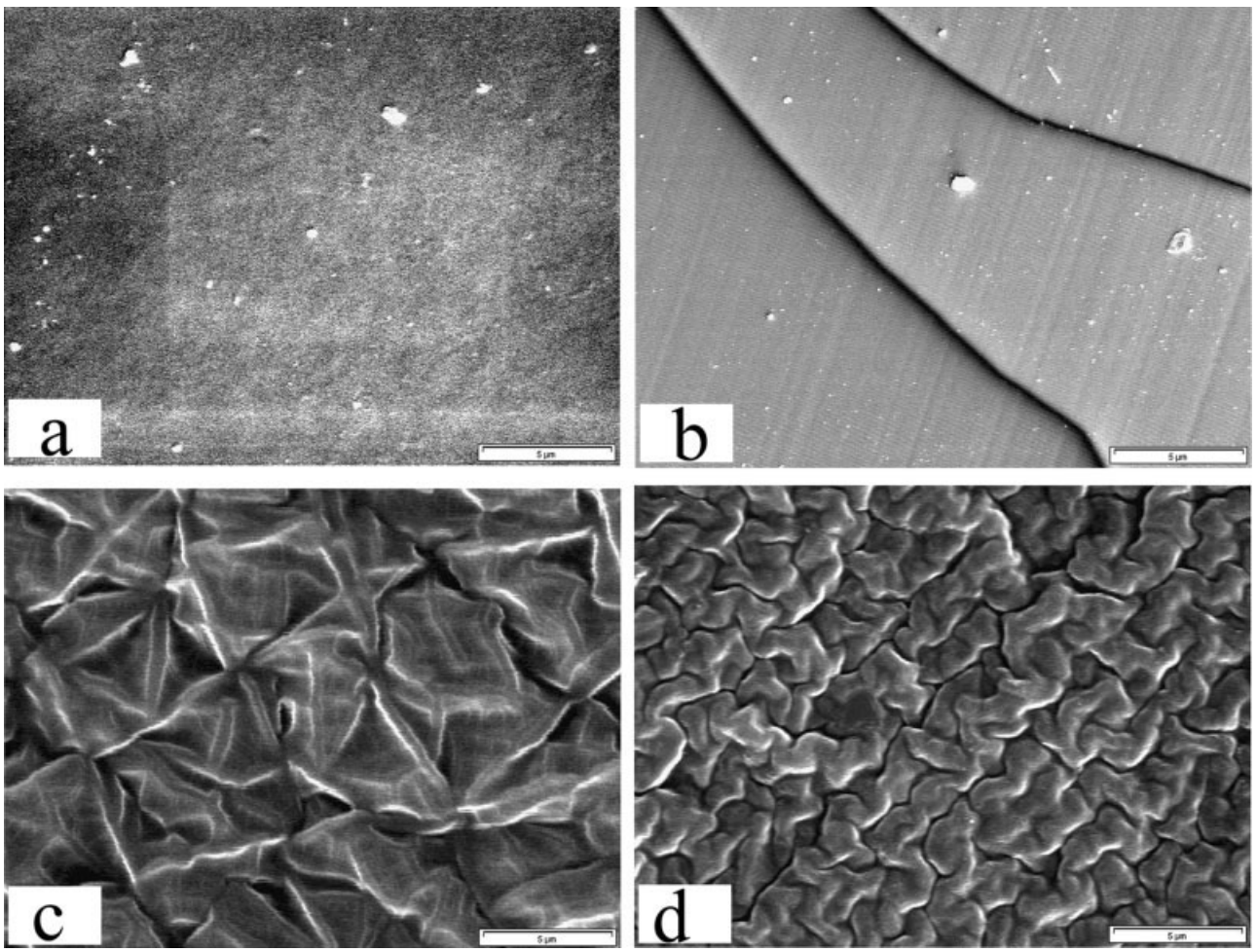

Figure 8 Scanning electron micrographs (magnification ×5000) of (a) unmodified PDMS, (b) oxygen plasma treated PDMS (3 min, 60 W, 6×10^{-1} mbar), (c) PDMS-*g*-HEMA1-AAc1 (modified PDMS with equal monomer ratio of HEMA/AAc), (d) PDMS-*g*-HEMA9-AAc1 (modified PDMS with the ratio of 9/1 for HEMA/AAc).

of 1720 and 1576 cm^{-1}, the monomer ratio (HEMA/AAc) of the grafted copolymer in different feeding ratios was calculated. As shown in Figure 7 the monomers ratio of the graft copolymer was obviously different from that of feeding solution, and thus an equal molar ratio in feeding solution did not produce an equal molar ratio in the graft copolymer.

SEM micrographs

The surface morphology can be seen through the SEM given in Figure 8. After oxygen plasma pretreatment the PDMS surface became cleaner and smoother. This was caused by the plasma etching effect, in which small molecules and occasional fragments attached onto the surface were removed. Furthermore, some cracks, which could correspond to the silica-like layer,[39] were observed on the plasma pretreated surface [Fig. 8(a,b)]. However, after graft-

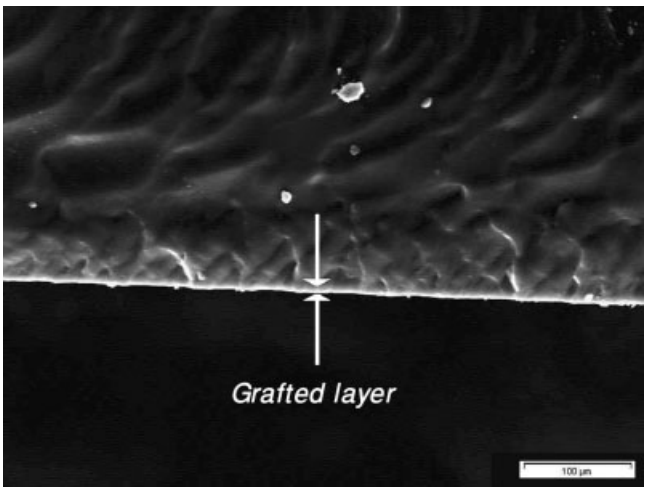

Figure 9 SEM cross-sectional micrograph of PDMS-*g*-HEMA1-AAc1 (grafted PDMS with equal monomer ratio of HEMA/AAc), magnification ×200.

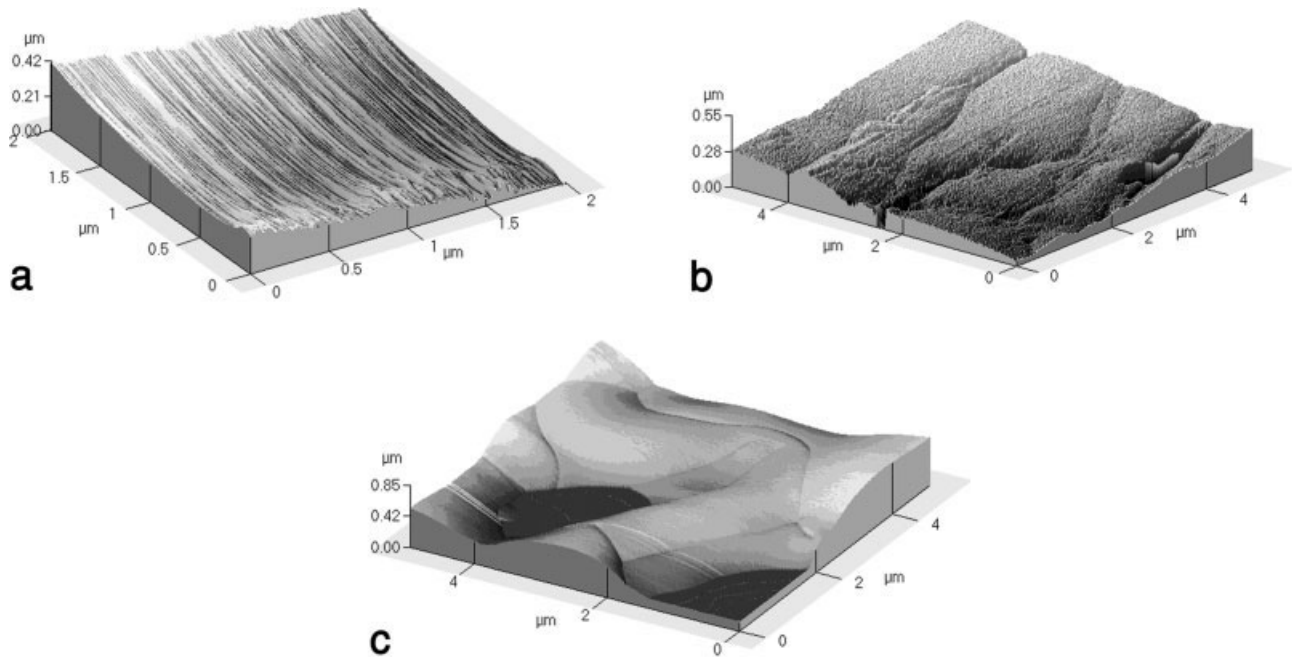

Figure 10 Surface topography of (a) unmodified PDMS, (b) oxygen plasma treated (3 min, 60 W, 6×10^{-1} mbar), and (c) PDMS-*g*-HEMA1-AAc1 (modified PDMS with equal monomer ratio of HEMA/AAc).

ing of poly(HEMA-*co*-AAc), the surface of PDMS films became rougher than that of control and plasma pretreated films [Fig. 8(c)]. The comparison of grafted surfaces with different monomers ratios revealed that their morphology were apparently affected by monomers ratios in the graft copolymer and consequently in feeding solution, respectively [Fig. 8(c,d)].

On the other hand, the thickness of the grafted layers was observed by cross-sectional SEM micrographs. These micrographs indicated that the thickness directly depends on the grafted amount. In other words, an increase in the grafted amount resulted in an increase in the thickness of the grafted layer. As shown in Figure 9(a) cross section of the grafted film is about 10-μm thickness, which is obviously an indication of being limited to the superficial region.

AFM study

Atomic force microscopy (AFM) images of the various films (unmodified, plasma treated, and modified) are shown in Figure 10. Like SEM micrographs, some cracks were observed on the AFM image of oxygen plasma treated PDMS film in comparison with unmodified film [Fig. 10(a,b)]. As it is explained earlier, it is believed that the creation of these cracks corresponds to the silica-like layer.[39] Other investigators reported that this layer was a thin, stiff surface-modified layer, which was formed when PDMS was exposed to oxygen plasma. The thickness of this layer reached a submicron depth. Because of a significant modulus mismatch between this layer and the compliant bulk of PDMS, the surface-modified layer developed cracks under tensile stress.[40] Moreover, a significant roughness and an altered morphology in comparison with the unmodified surface were created on the grafted surface with poly(HEMA-*co*-AAc) of

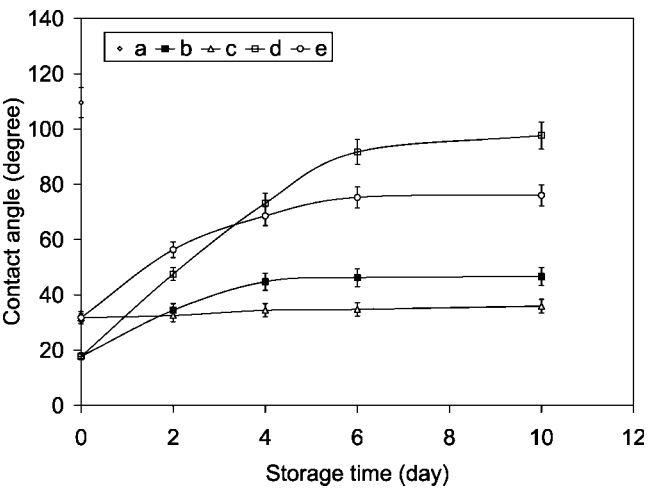

Figure 11 The effect of contact angle on the storage time ($n = 3$, mean ± standard deviation, P value < 0.0025 compared to untreated PDMS film): (a) control; (b) oxygen plasma treated PDMS (40 s, 60 W, 6×10^{-1} mbar), stored by wet method; (c) PDMS-*g*-HEMA1-AAc1 (modified PDMS with equal monomer ratio of HEMA/AAc), 1250 μg/cm^2), stored by wet method; (d) oxygen plasma treated PDMS (40 s, 60 W), stored by dry method; and (e) PDMS-*g*-HEMA1-AAc1 (modified PDMS with equal monomer ratio of HEMA/AAc), 1250 μg/cm^2), stored by dry method.

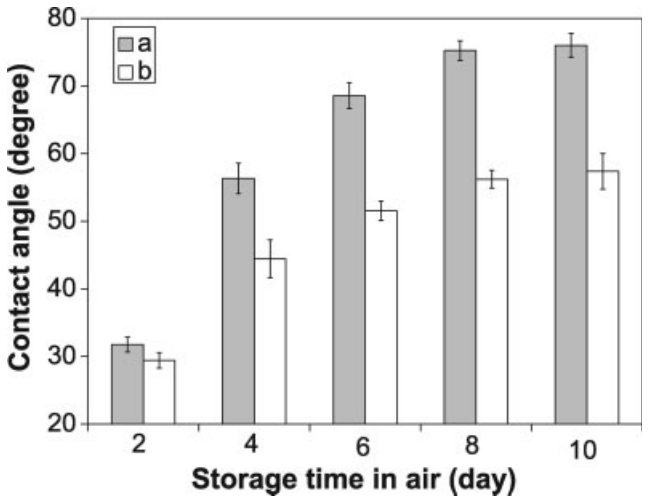

Figure 12 The effect of monomer concentration (HEMA/AAc) in graft on the contact angle of modified films, stored by dry method (stored in the air), ($n = 3$, mean ± standard deviation); (a) PDMS-*g*-HEMA3-AAc1, 1320 μg/cm^2 and (b) PDMS-*g*-HEMA1-AAc3, 1320 μg/cm^2.

equal monomers ratio [Fig. 10(c)], demonstrating that there has been some surface alteration as a result of the plasma graft copolymerization.

Contact angle and surface tension studies

The change in water contact angle of the control, oxygen plasma treated, and PDMS-*g*-HEMA-AAc films, which were stored in wet and dry conditions, was measured by a statistical contact angle measurement instrument (Fig. 11). The results revealed that the oxygen plasma treated and PDMS-*g*-HEMA-AAc films exhibited a gradual increase in contact angle with passage of time, when they were stored in air (dry method); whereas the increase rate in contact angles of the modified films, which were stored in water, was less than those stored in air.

To explain this phenomenon, according to the previous studies,[9,41–43] when the films were exposed to air, at a low-energy surface to minimize the surface energy, polar groups were buried away from the polymer–air interface. Meanwhile, the polar groups that came into contact with water at a high-energy surface remained at the polymer–water interface.

The change in contact angle of the grafted films with monomer ratios of 3 : 1 and 1 : 3 (HEMA-AAC) is shown in Figure 12. The values of contact angle were significantly different after storing for 10 days in the air at room temperature. As it is explained earlier, the hydroxyl groups of AAc and HEMA in copolymer were buried away from polymer–air interface and methyl groups of HEMA came into contact with that interface.[9,41–43] Therefore, the higher HEMA ratio in the graft, the more methyl groups appear on the surface, and consequently; the higher value of contact angle was obtained after storage in air.

Also the changes in surface tensions of the samples are shown in Table I. According to the results, grafting of hydrophilic monomers (HEMA and AAc) onto the surface of PDMS increased the surface tension from 22.04 ± 0.32 to 52.47 ± 1.21 mN/m ($n = 3$, P value < 0.005). On the other hand, γ_p (polar part of surface tension) significantly increased form 0.02 ± 0.00 to 32.49 ± 0.79 mN/m for untreated and PDMS-*g*-HEMA-AAc, respectively.[27]

Zeta potential

The results of zeta potential measurements are shown in Figure 13. Zeta potentials of grafted films are significantly different from those of plasma treated and control. Presences of two different functional groups (—COOH and —OH) on the surface of grafted samples lead to changes of zeta potentials. As it is known, dissociation of acidic groups on the surface gives rise to a negative charged surface. Conversely, a basic surface takes on a positive charge. In both cases, the magnitude of surface charge depends on the acidic or basic strength of the surface groups and on the pH of the solution.[37,44] On the other hand, hydroxyl groups of HEMA represent two different functions: an acidic function at moderate to high pH values and a basic function at low pH values.[45] In the former, the surface with these functional groups can be negatively charged, while in the latter, the surface can be positively charged. In Figure 13 at pH 1.8 most of the carboxylic groups of AAc are not dissociated and hydroxyl groups of HEMA represent their basic function, consequently the surface charge is positive, while at higher pH values (pH 12) both carboxylic groups of AAc and hydroxyl groups of HEMA are acidic groups and the surface charge with these functional groups is negative.

TABLE I
Surface Tension Measurements of Unmodified PDMS, Oxygen Plasma Treated PDMS, and PDMS-*g*-HEMA-AAc

	Total surface energy (γ)	Polar part (γ_p)	Disperse part (γ_d)
Untreated PDMS	22.04 ± 0.32	0.02 ± 0.00	22.02 ± 0.32
Oxygen plasma treated PDMS (3 min, 60 W)	28.39 ± 0.65	8.99 ± 0.27	19.40 ± 0.38
PDMS-*g*-HEMA-AAc	52.74 ± 1.21	32.49 ± 0.79	20.25 ± 0.42

$n = 3$, mean ± standard deviation, P value < 0.005 compared to untreated PDMS film.

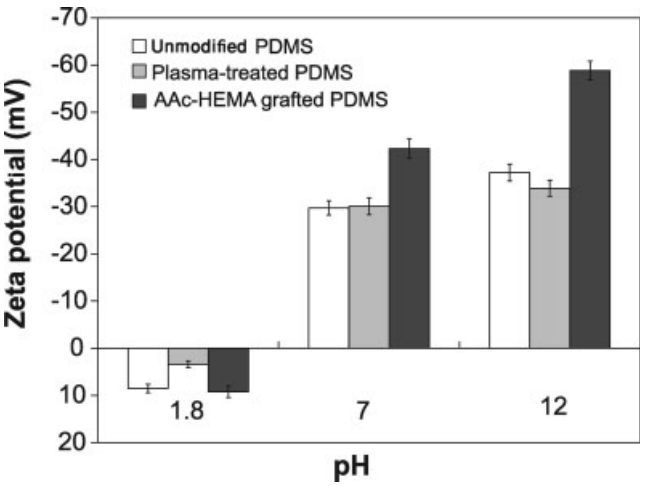

Figure 13 Zeta potential measurements of unmodified PDMS, oxygen plasma treated PDMS, and PDMS-*g*-HEMA-AAc. ($n = 3$, mean ± standard deviation, P value < 0.015 compared to unmodified PDMS film at each pH).

CONCLUSION

A two-step oxygen plasma treatment (TSPT) was successfully employed to simultaneously graft copolymerized HEMA/AAc mixture onto the chemically inert PDMS film. The presence of the graft was confirmed by appearance of two new characteristic bands of HEMA and AAc at 1720 and 1576 cm^{-1}, respectively. The changes in surface charge of the samples at pH 1.8, 7, and 12 were determined using zeta potential measurements of the surfaces. Also, surface tension measurements indicated that the values of γ and γ_p significantly increased after grafting of HEMA/AAc mixtures on the surfaces of PDMS films. Furthermore, the value of contact angle, depending on the grafting amount and monomers ratio considerably decreased. The morphology of the samples was also detected by both SEM and AFM. Additionally, using SEM cross-sectional micrographs, a consistent graft layer limited to the superficial region of the film was observed.

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