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Modification of Polysiloxane Networks for Biocompatibility

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The hydrophobic characteristics of polysiloxane networks somewhat limit their wide applications in biomedical fields in spite of their many promising properties. In this paper, several surface and bulk modifications to bimodal poly(dimethylsiloxane) (PDMS) networks are described to improve surface hydrophilicity as well as biocompatibility. Surface modification methods employed were ultraviolet/ozone-induced grafting hydrophilic monomer polymerization, plasma induced-surface grafting polymerization, and surface direct chemical bonding. Bulk modifications were carried out by using hydrophilic block copolymers and cross-linkers having hydrophilic dangling chains, which also conferred high surface hydrophilicity. The experimental results showed that the surface hydrophilicity was greatly improved, i.e., there were decreases from a static water contact angle of about 105° in pristine PDMS to about 20° in poly(ethylene oxide)/PDMS amphiphilic conetworks having linear dangling chains consisting of 6–9 units. The hydrophilic nature lasted at least 30 days, especially in the case of the application of the hydrophilic cross-linker in the networks. Some other properties including mechanical behavior, equilibrium water swelling content, surface characteristics, and morphology were also investigated.

Keywords Biocompatibility; hydrophilicity; polysiloxanes; surface modification

Introduction

Polysiloxanes, with repeat unit [-SiRR′-O-], have attracted great interest for use as the preferred material of choice to fabricate biomedical devices for many years because of their numerous attractive properties. These properties include (i) remarkably high gas permeability, (ii) good optical transparency, (iii) high flexibility and low risk or damage, (iv) non-toxicity and biocompatibility, (v) stability toward heat and chemicals, (vi) low curing temperature, (vii) moldability, and (viii) ease of sealing with other materials [1–14]. For these reasons, polysiloxanes have been widely used in microfluidic devices [1–3,5,14,15], microcontact printing technology [8,9], biocompatible devices [10,14], and drug delivery systems

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[11–13,16,17]. However, polysiloxanes have limited their uses in some applications, especially in those involving biocompatible devices, because their hydrophobic nature favors irreversible and undesirable adsorption/adhesion of nonpolar molecules, bimolecular species, and cells to their surfaces [5,18]. In addition, small hydrophobic molecules can actually be absorbed/imbibed into the bulk of the polysiloxanes because of the hydrophobicity [5]. This has led to recognition of the need for modifying the surface or bulk properties of these polymers to ameliorate such problems. Thus control of surface properties of the very important material, poly(dimethylsiloxane) (PDMS) is an indispensable prerequisite for its successful biomedical applications.

The modification of polymer surfaces is a topic of great theoretical and practical interest. In principle, doing this allows the production of polymer surfaces of desired composition and structures [19,20]. Obviously, increasing the hydrophilicity of any polymer surface improves its wettability and this, in turn, improves its biocompatibility [21,22]. There are many surface treatment procedures disclosed in the literature for making the surfaces of polysiloxanes more hydrophilic and more wettable, including changing the chemistry of the surface layer, coating the surface [23], and compounding the polymer with additives that subsequently diffuse to the surfaces [24–27]. The grafting of biocompatible polymer chains onto solid surfaces has been shown to be the most effective method to prevent adsorption and denaturation of proteins in contact with the surfaces. Such modifications of polysiloxanes can improve both surface and bulk biocompatibilities.

In this article, hydrophilic polymers that may be useful as biocompatible polymers to modify polysiloxanes are reviewed, and several bulk and surface modifications of bimodal polysiloxane networks in our group are reported. The bulk modification methods of polysiloxanes include the incorporation of the biocompatible polymers as main and/or side chains directly into polysiloxane networks. The surface modifications to make the surfaces more hydrophilic include chemical grafting, plasma polymerization and ultraviolet polymerization of biocompatible polymers such as poly(ethylene oxide) (PEO) or poly(ethylene glycol) (PEG), poly(N-isopropylacrylamide) (PIPAAm) and poly(acrylic acid) (PAA).

Experimental Section

Materials

Linear hydroxyl-terminated PDMS with average number-molecular weights, 22,600 $g \cdot mol^{-1}$, 18,000 $g \cdot mol^{-1}$ and 880 $g \cdot mol^{-1}$ (DMS-S31, DMS-S27 and DMS-S12) were purchased from Gelest Inc., Morrisville, PA. Hydroxyl-terminated linear siloxane copolymer (VDS-2513, Gelest Inc., PA) was composed of 25∼30 mol% vinylmethylsiloxane and 70∼75 mol% dimethylsiloxane. The cross-linkers were tetraethoxysilane (TEOS), N-(triethoxysilylpropyl)-O-polyethylene oxide urethane (brand name: SIT8192.0, designated here as S1), [methyoxy-(polyethyleneoxy) propyl]-trimethoxysilane (brand name: SIM6492.7, designated S2), and bis[(3-methyldimethoxysilyl)propyl]-polypropylene oxide (BMPPO). These cross-linkers and the catalyst, stannous-2-ethylhexanoate (SNB1100), were all purchased from Gelest Inc., Morrisville, PA. 2-[methoxy(polyethyleneoxy)propyl]-trichlorosilane (ClSiMPEO, molecular weight = 426–588 g/mol, SIM6492.66, was also purchased from Gelest Inc., PA. Alcohol, toluene, $NaIO_4$, benzyl alcohol and were purchased

from the Aldrich-Sigma Company, and were used directly without further purification. Deionized (DI) water was used in the measurements of static contact angles of the hydrogels. Hydroxyl-terminated linear PEO ($M_n = 800\,g/mol$, $300\,g/mol$), N-isopropylacrylamide (IPAAm), and acrylic acid (AA) were all purchased from Aldrich Co., MO.

Characterization

Contact angles were used to characterized the hydrophilicities of the surfaces of the hydrogels The tests were carried out at room temperature with ca. 1 μl deionized water, and angles were visually determined using a VS2000 digital camera with zoom capability. Measurements were taken from at least four areas on the surfaces for each sample.

FTIR spectroscopy measurements were carried out to identify the functional groups on the surfaces of the pristine hydrogel samples. This could be useful for analyzing the structures and reaction mechanism involved in the processing. The measurements were conducted using a Digilab Excalibur FTIR equipment in the mid-IR range (4000 to $500\,cm^{-1}$) at a resolution of $4\,cm^{-1}$, and sixteen scans per sample were analyzed using the Digilab Resolutions Software.

Values of the equilibrium water content (EWC) were obtained by immersing a $1\,cm \times 1\,cm \times 0.2\,cm$ piece of weighed hydrogel film in a large excess of distilled water at ambient temperature. The weights of the swollen samples were not recorded until they became constant. $EWC = (W_{ts} - W_{td})/W_{ts} \times 100\%$, where W_{ts} and W_{td} were the swollen and dry weights, respectively.

Biocompatible Polymers for Polysiloxanes Modification

Poly(ethylene glycol)

PEO or PEG is gaining wide recognition as a good choice for providing ''protein-friendly'' surfaces, due to their chains being hydrated, neutral, high mobile, flexible [28–30], and not interacting strongly with proteins or cells. As a result, there have been many attempts to create PEO surfaces through ''PEGylation'' for use in biomedical applications [7,31–35]. Experimental reports and theoretical considerations suggest that the brush-like PEG monolayers are best for preventing protein adsorption, since they provide maximum entropic repulsion between the proteins and surfaces. An alternative model for the cause of protein-surface repulsion is to attribute it to the rapid movement of the hydrated chains [36,37].

Poly(N-isopropylacrylamide)

PIPAAm has been suggested as a polymer for the recovery of cells from tissue culture substrates without the need for proteolytic enzymes to digest the matrix responsible for cell attachments [19,20,38]. This is because PIPAAm in water shows expanded chain conformations below the lower critical solution temperature (LCST) of 32°C and a collapsed, compact conformation at temperatures above the LCST. Recently PIPAAm has been extensively studied for controlled drug release applications as a biocompatible and hydrophilic polymer. Several methods have been suggested to produce PIPAAm-coated surfaces from electron beam and UV

grafting [39,40]. Irrespective of the surface modification methods, the surface characteristics of PIPAAm in solution were maintained when the polymer was grafted to a substrate surface [20,39,40].

Poly(acrylic acid)

PAA is a well known biocompatible polymer and has been used as a polyelectrolyte in various biomedical applications [41–43]. Moreover, the carboxylic groups present in its backbone allow it to be conjugated with bioactive molecules such as drugs [44,45]. PAA has also been suggested for use as biocompatible polymers to prepare PDMS-PAA interpenetrating networks [46] and for surface modifications of PDMS [47].

Modification of Polysiloxanes for Biocompatibility

Bulk Modifications

Hydrophilic Polymers in the Main Chains of the Networks. The introduction of biocompatible polymers into polysiloxanes to prepare interpenetrating networks (IPN) or amphiphilic conetworks (APCN) is a good approach to modify of the surface and bulk biocompatibility of polysiloxanes [28–30]. One feasible method developed in our group is to apply the hydrophilic functional cross-linker, BMPPO to end link the hydroxyl-terminated linear PDMS chains (DMS-S31) and hydroxyl-terminated linear PEO to prepare bimodal PDMS/PEO APCN hydrogels (see Fig. 1) The catalyst used was $(C_7H_{15}COO)_2Sn$. The surface hydrophilicity dropped from 105° (static water contact angle) in the pristine PDMS to 55° in the PDMS/PEO(1/6) APCN. The equilibrium water content (EWC) also greatly increased from about 0 vol% in pristine PDMS to nearly 60 vol% in PDMS/PEO(mol ratio 1/6) APCN [29].

Hydrophilic Polymers as Dangling Chains. The pristine PDMS was converted into silicone hydrogel by introducing hydrophilic side chains of sufficient lengths and amounts to overcome the hydrophobicity but sufficiently well dispersed to avoid

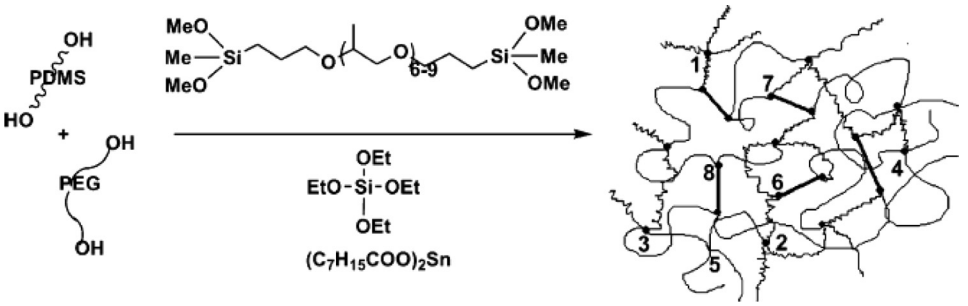

Figure 1. Preparation of PDMS-PEG amphiphilic conetworks by chain coupling of hydroxyl-terminated PEG and hydroxyl-terminated PDMS with BMPPO and tetraethoxysilane (TEOS). The dots indicate coupling sites between the polymer chains, the bold lines represent BMPPO, the thin smooth lines, PEG, and the wiggly lines, PDMS. (Reprinted with permission from reference 17).

disadvantages such as loss of the transparency required in some applications [48]. Specifically, polysiloxane hydrogels were successfully prepared by end linking a combination of long and short chains to give the bimodal distributions of network chain lengths that generally give unusually good mechanical properties. The end linkers were trialkoxysilanes $R_0Si(OR)_3$ having R_0 side chains that are hydrophilic of variable lengths and of sufficient hydrophilicity to produce the desired hydrogels. The first trialkoxysilane was N-(triethoxysilylpropyl)-O-polyethylene oxide urethane (S1) with 4–6 units of ethylene glycol, and the second was [methyoxy(polyethyleneoxy)propyl]-trimethoxysilane (S2) with 6–9 units of ethylene glycol, and they were used to end link hydroxyl-terminated PDMS chains in standard room-temperature condensation reactions (see Fig. 2). No discernible phase separation occurred in the resultant networks with the introduction of the hydrophilic side chains. These linear side chains increased the equilibrium water contents, from 0 to 11.2 wt% in the first series and from 0 to 29.8 wt% in the second. Longer hydrophilic chains clearly migrated to the surfaces of the resulting polysiloxanes hydrogels to give decreases of the static contact angles from 105° to 40° for the first series, and to 80° for the second. The longer hydrophilic chains were found to give larger decreases in the contact angles and larger equilibrium

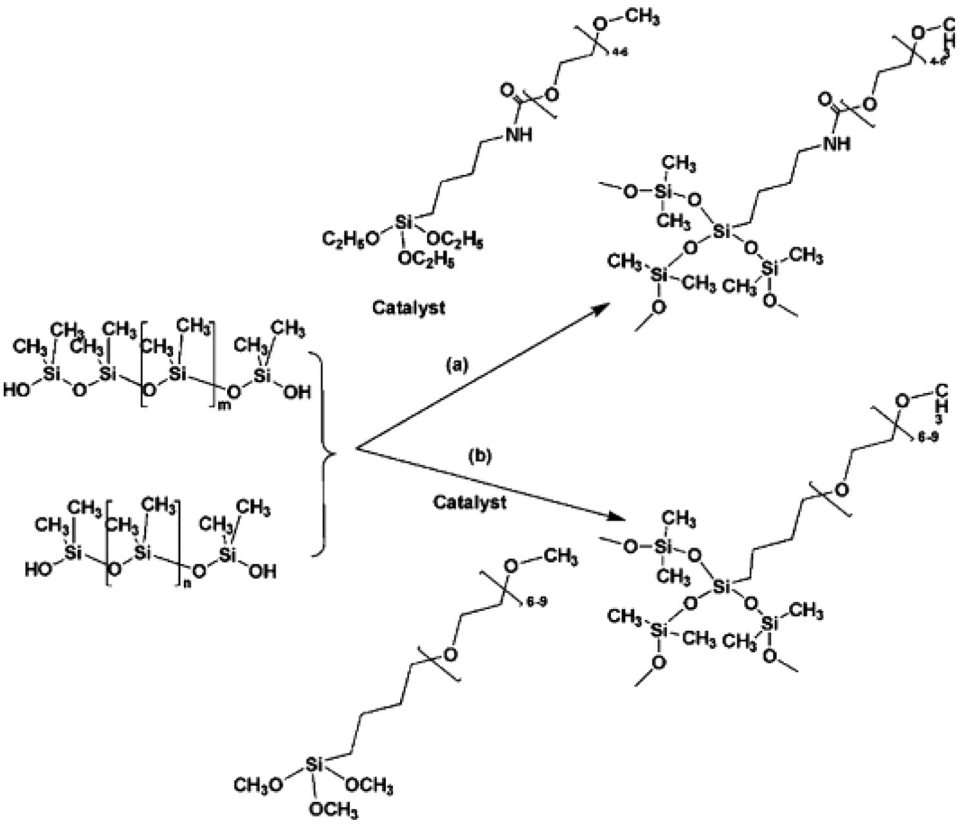

Figure 2. Scheme for the introduction of poly(ethylene glycol) into poly(dimethylsiloxane) networks using the cross-linker (a) N-(triethoxysilylpropyl)-O-polyethylene oxide urethane (S1) and (b) [methyoxy(polyethyleneoxy)propyl]-trimethoxysilane (S2).

water contents. The mechanical properties demonstrated that the Young's moduli of the hydrogels did not change upon introduction of the S1 hydrophilic cross-linker, but did decrease from the presence of the S2. The tensile strength and elongation at break were relatively insensitive to the amounts of either of the hydrophilic groups [28].

Surface Modifications

All the surface modifications were based on the substrate polydimethylsiloxane-poly(vinylmethylsiloxane) (PDMS-PVMS) bimodal networks [28,29]. The details of the preparation are described as follows: The linear hydroxyl-terminated PDMS (DMS-S27) had a number average molecular weight corresponding to $M_n \sim 18{,}000\,g/mol$. Hydroxyl-terminated linear siloxane copolymer (VDS-2513) was composed of 25∼30 mol% vinylmethylsiloxane and 70 ∼ 75 mol% dimethyl-siloxane. TEOS was used as the tetrafunctional cross-linker, and stannous-2-ethyl-hexanoate (SNB1100) was used as the catalyst.

A series of bimodal silicone networks with various vinyl groups were prepared by employing different mol ratios of PDMS-PVMS to PDMS (0:100, 5:95, 10:90, 15:85, 20:80), corresponding to the short chains and long chains, respectively. The short chains and long chains were tetrafunctionally end linked in the undiluted state with the stoichiometrically-required amounts of TEOS and the catalyst, stannous-2-ethylhexanoate (0.6 wt%) (Fig. 3). The reactions were run in Teflon^{TM} molds at room temperature for three days for completion of the cross linking. The resulting network sheets were extracted with toluene for three days, then deswelled with methanol, and finally dried under vacuum. The number of vinyl groups depended on the molar concentration of PDMS-PVDS used to prepare the samples. It could be determined by FTIR, NMR, titration, etc.

Chemical Grafting. The native PDMS and PVMS-PDMS network films were first pretreated by exposure to UV light (185 nm and 254 nm) in a UVO cleaner (model 42-220, Jetlight, USA) for 30 min with ozone flow in ambient atmosphere to oxidize the surface. The films were then immersed in a 2 mM solution of 2-[methoxy(polyethyleneoxy)propyl]-trichlorosilane (ClSiMPEO) immediately after UV treatments in a glove-box filled with N_2 for 24 hrs. The samples were then thoroughly washed in water and dried in a stream of N_2.

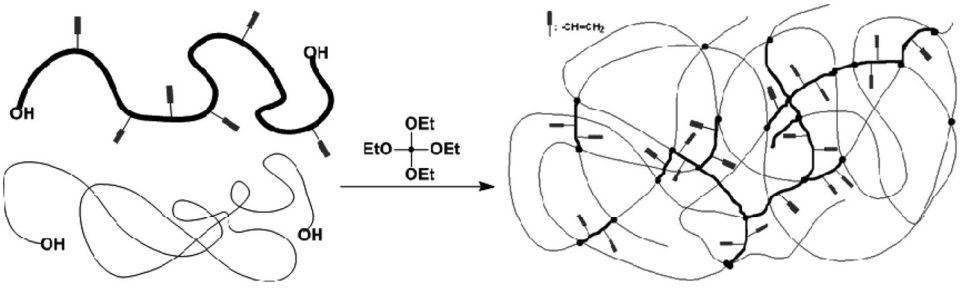

Figure 3. Scheme for the preparation of bimodal PVMS-PDMS networks. Bold lines: short linear PVMS-PDMS; thin lines: long linear PDMS; side groups are vinyls in PVMS-PDMS; dots: cross links.

The grafting of ClSiMPEO onto the oxidized PDMS and PVMS-PDMS networks (as shown in Fig. 4) was first confirmed by the FTIR spectra in Figure 5, which demonstrated the surface characteristics of the untreated pristine PDMS, the treated PDMS and PVMS-PDMS. The peaks near 2855 cm^{-1} are the fingerprints of aliphatic carbon atoms involved with the symmetric and asymmetric stretching vibrations of CH_2 in the ClSiMPEO (see Table 1). This spectral change clearly indicated that the SiCl groups of the ClSiMPEO molecules were strongly reacting with SiOH groups at the polysiloxanes surfaces, and therefore, the hydrophilic PEO was seen to be covalently bonded onto the surfaces. The absorption bands at 1270 and 800 cm^{-1}, which were attributed to the $SiCH_3$ groups, were not altered by the surface treatment because the $SiCH_3$ groups were mostly irradiated by UV/ozone oxidation. The peak near 2855 cm^{-1} almost remained constant with increase of vinyl groups in the PVMS-PDMS. This indicated that the vinyl groups, as was found for the CH_3 groups in the networks, possibly formed SiOH groups under UV/ozone treatment. Therefore the formation the hydrophilic layers of linear PEO on the surfaces Figure 4 (1st Step) did occur in the process of PDMS-PVMS being treated with UV/ozone. UV treatment of PVMS-PDMS in ambient atmosphere for 30 min reduced the contact angle of native PVMS-PDMS (105°) only slightly (to 102°). PDMS networks treated with reactive oxygen (irradiated by plasma or UV/ozone) resembles glass surfaces in their chemical properties due to the creation of silanol groups on the surface. The 30 min UV/ozone treatments significantly enhanced the hydrophilicity of the PVMS-PDMS surface, but since cracks occurred in the PDMS, these surfaces were not stable because the broken chains and hydroxyl groups diffused or sank into the matrix. This suggests that UV treatment may not be suitable for long-term hydrophilicity improvements. Therefore, the covalent bonding of

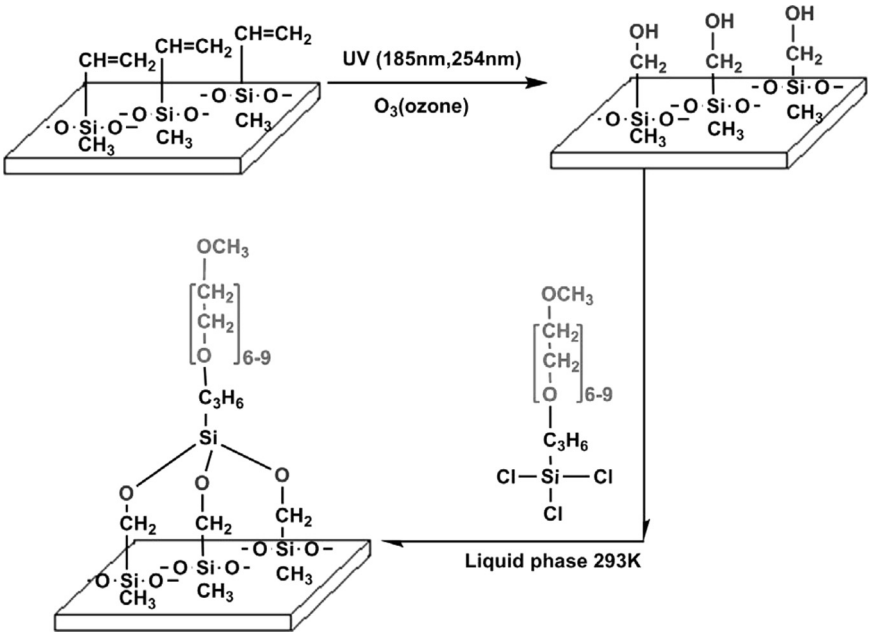

Figure 4. Scheme for the ClSiMPEO chemical-bonding onto the surfaces of the pristine PDMS and PDMS-PVMS networks.

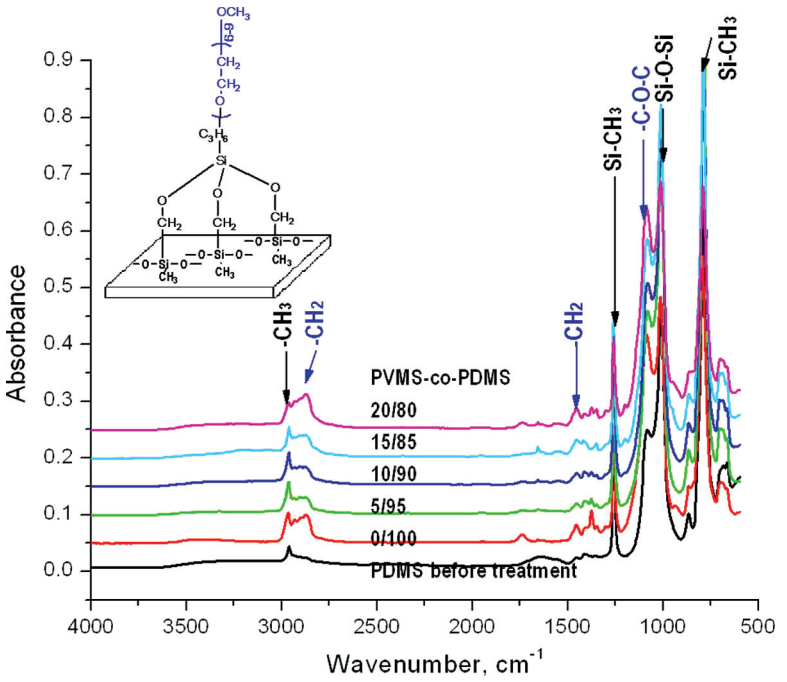

Figure 5. FTIR spectra of PVMS-PDMS networks surface treated with PEO-silane.

hydrophilic chains was proposed to react with the silanol groups to form a thin hydrophilic layer. Figure 4 (2nd Step) shows the covalent attachment of PEO onto PDMS. ClSiMPEO likely coupled to the silanol groups on the oxidized PDMS-PVMS surface [49,50].

The ClSiMPEO treatment of the pristine PDMS, exhibited a contact angle of 65.5°, which was lower than that of the pristine PDMS and PVMS-PDMS networks (105°). This is shown in Figure 6. The contact angles decreased to near 20° when the contact time was 360 sec. The contact angles of ClSiMPEO treated PVMS-PDMS networks was almost the same (near 62°) with increase in content of vinyl groups in the PVMS-PDMS networks (Table 1). With the ClSiMPEO as a silane coupling agent, the ethoxy groups were hydrophobic and the ClSiMPEO treatment provided the hydrophilic surface. The absorbance of water by the PEO in the surface layers changed the water contact angles to lower values. It is noteworthy that the surface

Table 1. The static contact angles of PDMS, PVMS-PDMS after surface treatments

PVMS/PDMS	Static contact angle, degrees
0/100	65.5 ± 2.0
5/95	60.6 ± 3.4
10/90	61.2 ± 2.7
15/85	63.2 ± 3.6
20/80	62.5 ± 2.7

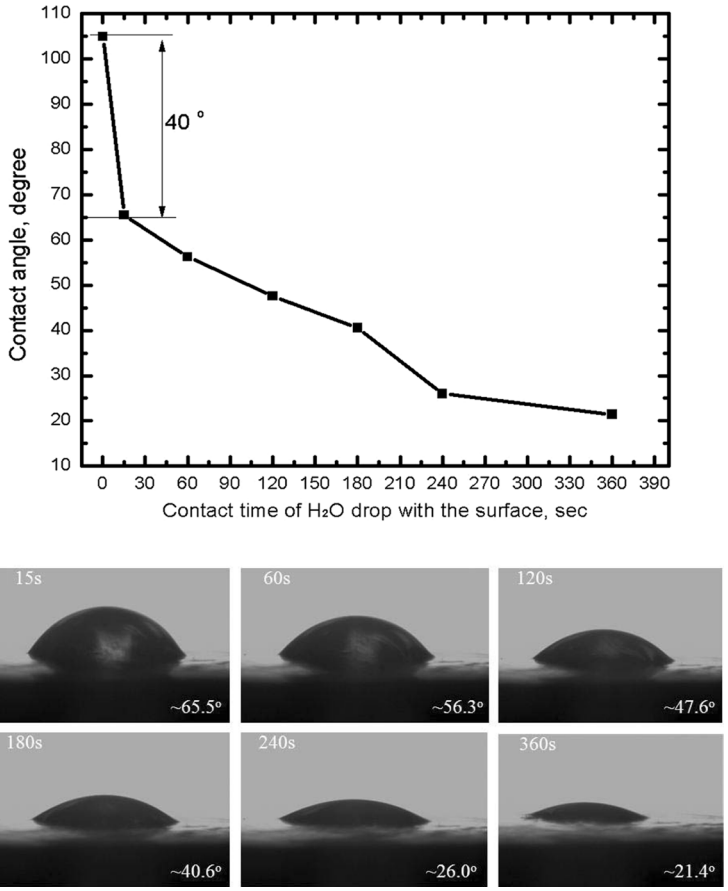

Figure 6. Water contact angles and their change with time for the pristine PDMS networks treated by ClSiMPEO.

of polysiloxane networks could be controlled by this ClSiMPEO coupling agent, specifically changing it from hydrophobic to hydrophilic.

Grafting by Ultraviolet Polymerization. The native PDMS and PDMS-PVMS films were first immersed in an aqueous solution containing $NaIO_4$ (0.5 mM), benzyl alcohol (0.5 wt%), and IPAAm at the concentrations and ratios. After immersion, the films were placed in a custom-built irradiator (in a reaction chamber containing a medium-pressure 450 W mercury-vapor lamp housed in a Pyrex immersion well that was cooled with water) for various times from 30 min to 4 hrs. The distance between the sample and the irradiation lamp was 5 cm. Uniform UV exposures were obtained by rotating the films (10 rpm) for various times under the UV source. The samples were then washed in distilled water at 80°C under constant stirring for 24 h to remove adsorbed monomer and polymer. The films were then vacuum-dried (0.01 atm, 23°C). The graft density was defined as the difference in the film weight before and after grafting divided by the total surface area of the film. For these measurements of the graft density, the samples were approximately $1.0 \times 1.0 \times 0.2\,cm^3$.

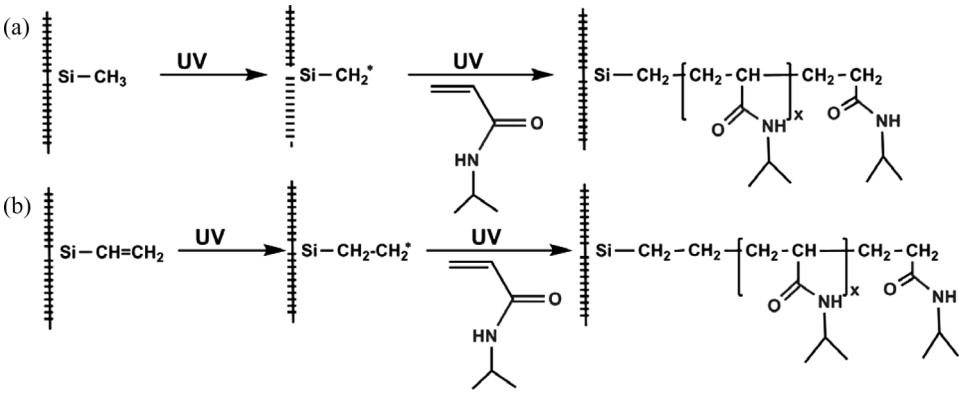

Figure 7. Scheme for the ultraviolet polymerization of PIPAAm onto the surface of PDMS (a) and PVMS-PDMS networks (b).

The surface composition of the PIPAAm-grafted PDMS and PVMS-PDMS networks together with the pristine polysiloxane (see Fig. 7) were tested with FTIR, with the results shown in Figure 8 and Table 2. The surface of the pristine PDMS contained only CH_3 groups (2960 cm^{-1} and 1240 cm^{-1}, 785–815 cm^{-1}) and Si-O groups (1015 cm^{-1}) (Fig. 8a). The surface of PVMD-PDMS contained CH_3 groups (2960 cm^{-1} and 1240 cm^{-1}, 785–815 cm^{-1}), Si-O group (1015 cm^{-1}) and CH_2=CH- (1599 cm^{-1}) (Fig. 8b). No traces of contaminants or extraneous groups were detected [19,40,51].

After PIPAAm grafting, the surface compositions were close to the composition expected for the polymers, PIPAAm and PDMS, with the appearance of peaks at 1370, 1640 and 3310 cm^{-1}. The grafted PIPAAm amounts on the surfaces could be estimated from the FTIR measurements. The results also clearly showed the increases in the relative intensity of the PIPAAm specific peak with increasing UV exposure time. From a surface chemistry point of view, it must be noted that

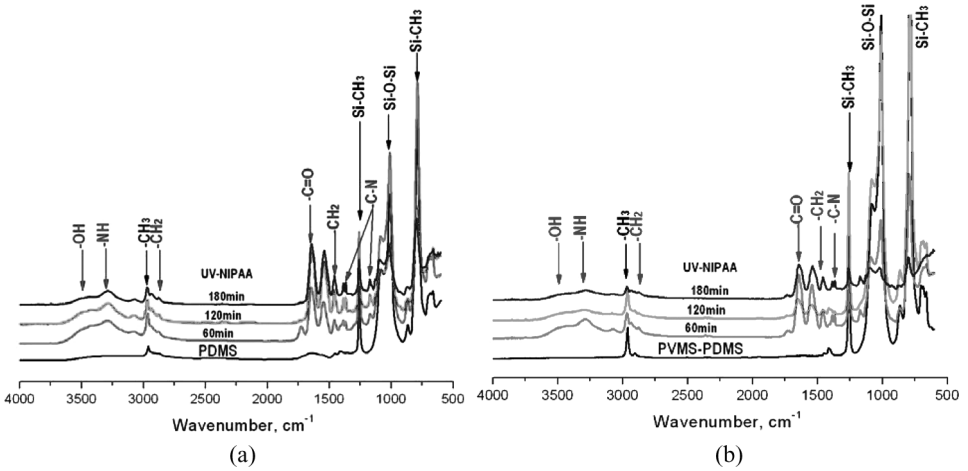

Figure 8. FTIR spectra of the surface of (a) PDMS and (b) PDMS-PVMS after the UV polymerization (IPAA).

Table 2. Absorption band assignments for the FTIR spectra

IR region (cm^{-1})	Assignment
614	Si-CH=CH_2
785–815	-CH_3 rocking and Si-C stretching in Si-CH_3
1015	Si-O-Si asymmetric stretching (doublet)
825–865	Si-O stretching in Si-OH
1025–1150	In-phase and out-of-phase wagging vibrations of -(CH_2)- in Si-(CH_2)$_2$-Si and Si-CH_2-Si
1055–1090	Asymmetric Si-O-Si stretching in [-(CH_2)$_2$Si-O]
1245–1270	Symmetric -CH_3 stretching in Si-CH_3
1370	C-N and N-H
1400–1450	Asymmetric -CH_3
1599	C=C stretching in CH_2 = CH-
1640–1650	C=O
2855	-CH_2- in PEO
2912	C-H symmetric stretching in sp^3 CH_3
2964–2967	C-H asymmetric stretching in sp^3 and -CH_3 in Si-CH_3
3020	=CH_2 symmetric stretching in CH_2=CH-
3060	=CH_2 asymmetric stretching in CH_2=CH-
3050–3700	-OH stretching in Si-OH, possibly also in C-OH (3610–3640 cm^{-1})
3310	N-H stretching

Note. See references [16,17,48].

in the present case no direct evidence exists that the polymerized acrylate was, indeed, covalently grafted to the substrate surface. A strong physical interaction or entanglement between the UV-treated PDMS surface and the PIPAAm chains could explain the observed results as well. Meanwhile, it is important to note that the PIPAAm surface coating could successfully withstand overnight extraction in water.

The CA results of native PDMS and PDMS-PVMS networks after UV treatment for 1, 2 and 3 h, respectively (Fig. 9), indicated that the contact angles were decreased significantly compared with that of pure PDMS (contact angle of 105°).

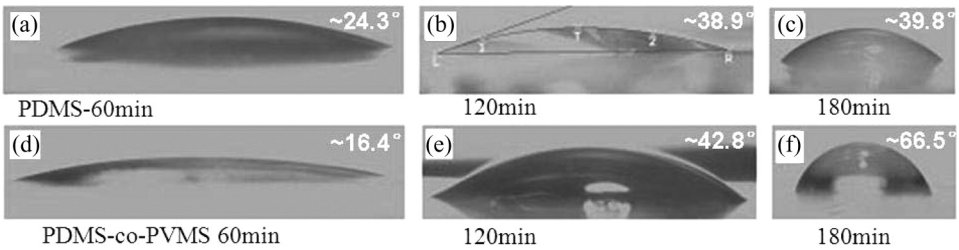

Figure 9. Contact angles (CA) for the bimodal networks treated by PIPAA. (a) pristine PDMS, 1 h; (b) pristine PDMS, 2 h; (c) pristine PDMS, 3 h; (d) PDMS-PVMS, 1 h; (e) PDMS-PVMS, 2 h; and (f) PDMS-PVMS, 3 h.

However, the CA of pristine PDMS increased with increase in duration of the UV treatment. The same was true for the PDMS-PVMS. The FTIR results in Figure 8 also indicated that the PIPAA was grafted onto the surface of the pristine PDMS and the PDMS-PVMS. The surface hydrophilicity greatly depended on the thickness and amount of the grafted hydrophilic material on the surface. There should be an optimal content of grafted PIPAAm to exhibit the balance of transparency, protein deposition, and wettability properties.

Plasma Polymerization. There are also non-polymeric plasma treatments and corona treatments for chemical surface modifications. They include etching or the selective destruction of parts of a surface layer. Surface modification techniques also include the introduction of functional groups onto a surface layer, for example the introduction of oxygenated functions (hydroxyl, carboxyl, etc.) at the surface of organic polymeric materials for the purpose of increasing hydrophilicity, thereby promoting increased wettability. Such techniques may employ flame treatments, corona treatments, or plasma treatments, and plasma treatments have been increasingly studied for the modification of surfaces [23]. The plasma gas can include many species, such as free radicals and energetic electrons and ions. Depending on the gas or vapor used in the plasma and the process conditions, the effects of non-polymeric or non-depositing plasma treatment include surface etching or ablation, oxidation, the formation of reactive groups, and combinations thereof.

Polysiloxanes have been subjected to plasma surface treatment to improve their surface properties, e.g., surfaces have been rendered more hydrophilic, deposit resistant, scratch resistant, etc. Many references disclosed plasma surface treatments include subjecting contact lens surfaces to plasmas comprising an inert gas or oxygen [52–54]. Here, we discuss the introduction of functional groups absent in the parent polymer using plasma polymerization onto a surface to promote the hydrophilicity.

The pristine PDMS and PDMS-PVMS bimodal networks were first activated by the oxygen present in the reactor in an oxygen plasma, which led to a partial oxidation of the topmost layer. This pretreatment also led to better adhesion of the deposited film. Plasmas contained acrylic acid (AA) as the monomer for polymerization. Polyethylene oxide (PEO), hydroxyl terminated, $M_n \sim 300\,g/mol$, was subsequently used to deposit a PAA coating on the pretreated PDMS and PDMS-PVMS networks. The plasma treatments of the PDMS-PVMS bimodal networks were carried out in a plasma reactor at 0.2 mbar at 60 W for 15 min. The samples were immediately immersed into a PEO water solution for further treatment. The vinyl groups in the PVMS-PDMS networks here were used as the original points for homo- or block polymerization, although the plasma treatment also oxidized the pristine PDMS networks through irradiation to generate radical groups to initiate polymerization of the PAA. The plasma polymerization was carried out to deposit the hydrophilic PAA polymer on to the surface of the PDMS-PVMS (see Fig. 10).

Figure 11 shows the contact angle results for (i) the pristine PDMS, native PDMS-PVMS bimodal networks, (ii) PDMS and PDMS-PVMS with deposited PAA after air plasma treatment, and (iii) PDMS and PDMS-PVMS further treated by PEO. The CA of PDMS and PDMS-PVMS remained about 105° with increase in the density of vinyl groups. The results demonstrated that vinyl groups did not affect the hydrophobicity of the polysiloxane networks. The experimental results also indicated that the CA is greatly decreased from 105° in PDMS to 70° in PDMS

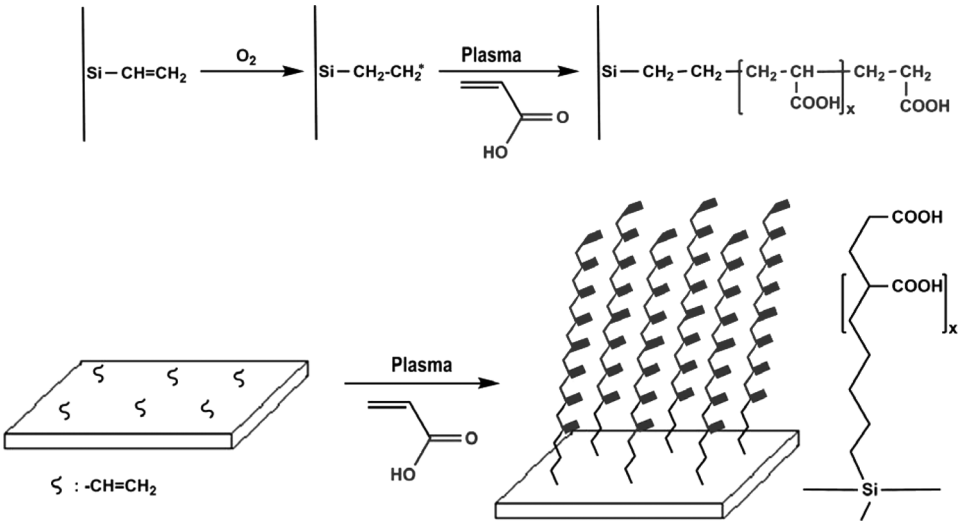

Figure 10. Scheme for the plasma polymerization of acrylic acid on the surface of bimodal PDMS.

after the PAA plasma polymerization. The CA value decreased even more in PDMS-PVMS after PAA polymerization compared with those of the corresponding samples before plasma treatment. The CA obviously decreased greatly with increasing treatment time after the AA plasma procedure. Especially, the CA decreased significantly with increasing number of vinyl groups from 100/0 to 85/15 in the PDMS-PVMS samples, but only slightly when the PDMS/PVMS molar ratio was less than 85/15. Further PEO treatment of the PDMS-PVMS after AA plasma polymerization slightly decreased the CA. The experimental results obviously

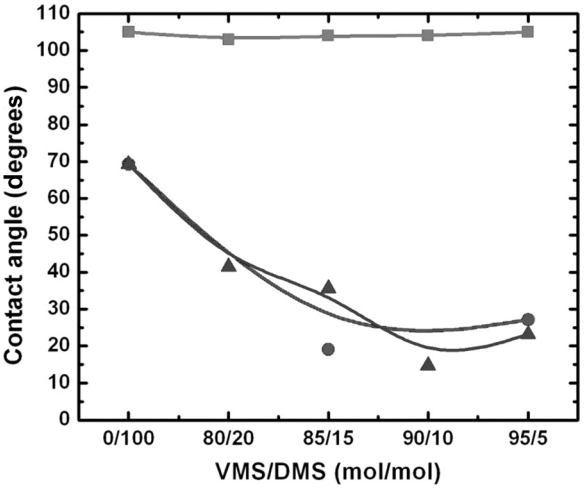

Figure 11. Contact angles for PDMS-PVMS bimodal networks. -■-: native PDMS-PVMS; -●-: PDMS-PVMS deposited with PAA after oxygen plasma treatment; -▲-: PDMS-PVMS further treated by PEO after deposition of PAA.

indicated that the PAA plasma polymerization on the surface of PDMS-PVMS improved the surface wettabilities, and the vinyl groups might be the grafting points for the PAA polymerizations on the surfaces of the PDMS-PVMS networks. The higher density of the vinyl groups, the lower CA, and therefore the better the wettability. The wettability improvements were strongly related to the vinyl density, and further PEO treatment had only a slight effect on the wettability. However, the immersion in PEO made the surface hydrophilically stable for up to 30 days and even longer, thus preventing rearrangements or hydrophobicity recoveries [55].

Conclusions

In this paper, several surface and bulk modifications to the bimodal PDMS networks employed in our research group were described for improving surface hydrophilicity and biocompatibility as expected. Surface modifications including ultraviolet/ozone-induced graft hydrophilic monomer polymerization, plasma induced-surface grafting polymerization, and surface direct chemical bonding. Bulk modifications were carried out by applying amphiphilic block copolymers and cross-linkers with hydrophilic dangling chains to get high surface hydrophilicities. The results showed that the surface hydrophilicity was greatly improved, i.e., decreased from static contact angle about 105° of pristine PDMS to about 20° in the PDMS-PEG amphiphilic conetworks, and the hydrophilic stability up to 30 days or even longer, especially in the case of the application of the hydrophilic cross-linker in the networks. The mechanical properties, swelling equilibrium water content and the surface characteristics as well as the morphology were also investigated and described.

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