doi:10.1246/cl.2011.1297

Novel Method for Surface Modification of Silicone-containing Hydrogel Using Addition Reaction

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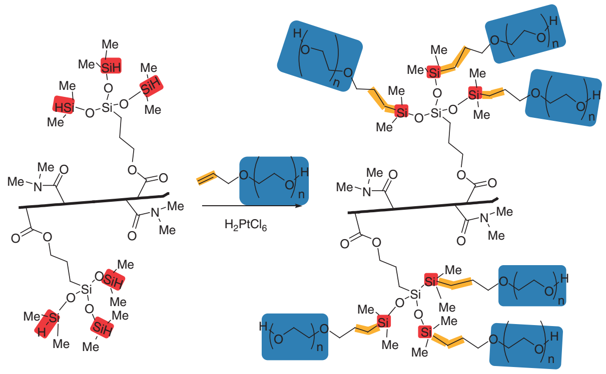
(Received August 25, 2011; CL-110718; E-mail: akashi@chem.eng.osaka-u.ac.jp)

We designed a novel surface modification method of shaped articles from silicone-containing hydrogel using hydrosilylation reaction between silicone component and poly(ethylene glycol) (PEG) chain in order to improve the surface wettability. For the introduction of –SiH group to hydrogel, in addition to copolymerization of –SiH-containing methacrylate, argon gas plasma treatment was found to be effective. Hydrosilylation reaction between shaped article and PEG easily proceeded in organic solvent, and the resultant hydrogel showed reduced contact angle after the hydration in water. FTIR-ATR measurement suggested the validity of our process design concept.

Silicone material has been attracting much interest due to its extremely high gas permeability, and it is widely used in the field of medical devices, such as artificial lungs[1,2] and silicone elastomer contact lenses.[3,4] Such applications have been achieved by the modification of the hydrophobic nature of silicone into hydrophilic character. Thus, the hydrophilicity is an important characteristic for medical use of siloxane compounds. In fact, hydrophilic material like hydrogel[5–9] is abundantly used. The compatibility between silicone material and hydrophilic component has been pursued, with multiblock copolymer synthesis from poly(dimethylsiloxane) and poly(ethylene glycol) (PEG)[10,11] or synthesis of novel silicone-containing monomers which bear both organosiloxanyl and hydrophilic groups.[12,13] We have recently reported a novel silicone monomer which enables provision of silicone hydrogel with a good balance among bulk properties.[14] On the other hand, the surface character improvement is also important.[15] For the improvement of wettability of silicone material or silicone-containing material, many efforts have been reported such as oxidative plasma discharge treatment,[3] low-temperature inert gas plasma processing,[16] plasma polymerization,[4,17] plasma-induced polymerization or graft polymerization,[18] combination of plasma polymerization and graft reaction.[19] However, there are still some points to be improved such as durability of wettability.[20] The combination of introducing reactive groups by plasma polymerization and subsequent reaction between PEG chain and the reactive group, is widely used.[19] However, as the reactive group exists only on the surface of plasma polymerized film, the density of the PEG chain might be insufficient, this resulting in unsatisfactory performance. Albertsson and co-workers reported Ar microwave plasma treatment and subsequent hydrosilylation grafting based on the assumption of –SiH group formation.[21] However, they used silicone elastomer instead of silicone hydrogel and made the speculation on –SiH formation indirectly from XPS data. Furthermore, they supplied hydrogen after microwave plasma treatment and used a fluorine-containing allyl compound leading to no change in contact angle.



Scheme 1. Introduction of PEG chain to overall hydrogel.

Our main concern is reducing the contact angle with PEG derivatives and to confirm the mechanism of hydrosilylation without special apparatus such as microwave plasma at 2.45 GHz or active gas such as hydrogen. Thus, we designed novel surface modification methods for direct introduction of PEG chain to siloxanyl groups by hydrosilylation. One is preparation of crosslinked copolymer from –SiH group bearing monomer and hydrophilic monomer followed by hydrosilylation. The scheme of this process is shown in Scheme 1. This was expected to allow the uniform introduction of PEG chain into all over the hydrogel.

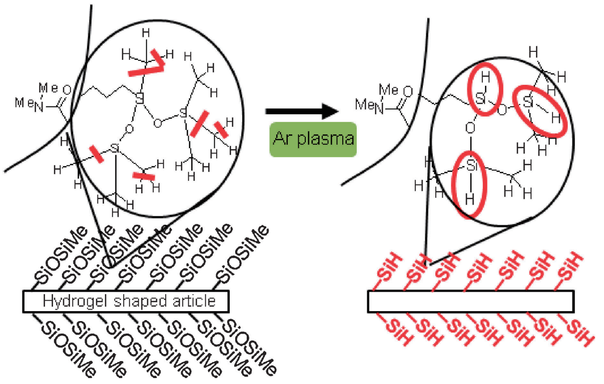
For this approach, –SiH-bearing silicone hydrogel was prepared from 3-methacryloyloxypropyltris(dimethylsiloxy)silane (TRIS-3H), 3-(2-methacryloyloxyethoxy)propyltris(trimethylsiloxy)silane (SiOEMA), *N*,*N*-dimethylacrylamide (DMA), and tri(ethylene glycol) dimethacrylate (3G), and hydrosilylation reaction between resultant gel and PEG monoallylether having two molecular weight (M_n), was carried out according to the method described in Supporting Information.[22] As shown in Table 1, it was found that the contact angle could be effectively reduced and that simultaneously water content increased. This increase of water content suggests the progress of hydrosilylation reaction between –SiH group and PEG monoallylether as it had survived the 120 °C, 30 min pretreatment in water before measurement.

The other approach is to restrict the place of hydrosilylation to only near the surface in hydrogel cross section. Our second concept could be achieved by using a dry process with conventional high-frequency (13.56 MHz) plasma treatment, in which diffusion of gas plasma into inside of the hydrogel is expected to be low because of the short processing time.

Table 1. Characteristics of hydrogels from overall hydrosilylation of silicone gel[a]

Entry	PEG M_n	Contact angle/°	Water content[b]/%
1	none	91	26
2	400	79	42
3	1500	66	43

[a] Gel composition: TRIS-3H/SiOEMA/DMA/3G = 10/55/35/1 (weight). [b] Water content was calculated from the following formula; $(W_w - W_d)/W_w \times 100$, where W_w and W_d show the wet weight and dry weight of hydrogel, respectively. Hydrogel sample was pretreated with 120 °C, 30 min in water before water content measurement.



Scheme 2. Expected scheme of Ar gas plasma treatment.

Table 2. Contact angle of silicone hydrogel[a] at each step of high-frequency Ar gas plasma and hydrosilylation process

None	After plasma	After immersion in PEG[b] solution	
		Without H_2PtCl_6	With H_2PtCl_6
87°	78°	75°	57°

[a] Silicone hydrogel composition: SiMAA2/FM0711/DMA/FM7711 = 31/31/38/2.6. [b] PEG M_n = 400.

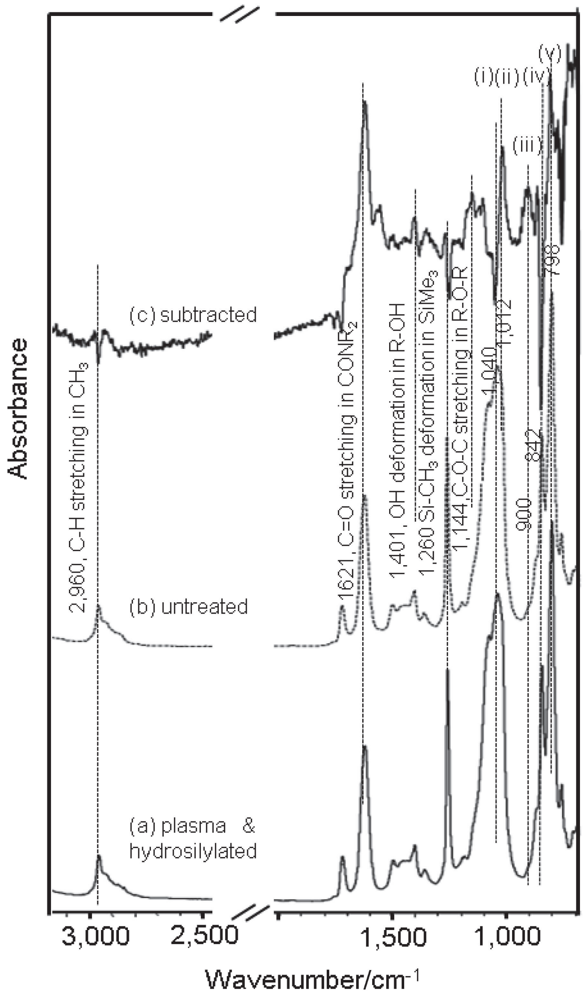


Figure 1. FTIR-ATR spectrum of (a) high frequency plasma treated and hydrosilylated hydrogel, (b) untreated hydrogel and (c) subtracted spectrum from (high frequency plasma treated and hydrosilylated silicone hydrogel – untreated). Composition is the same as that in Table 2. (i), (ii), (iii), (iv), and (v) show Si–O stretching in Si–O–Si (1040 cm^{-1}), C–O stretching in R–OH (1012 cm^{-1}), Si–H deformation in $SiHCH_3$ (900 cm^{-1}), $SiCH_3$ deformation in $SiMe_3$ (842 cm^{-1}), and $SiCH_3$ deformation in $SiMe_2$ (798 cm^{-1}) respectively.

Furthermore, Ar gas was selected for its nonoxidative action, scission of chemical bond, and recombination which could lead to the formation of –SiH groups on the surface. Thus, the combination of plasma treatment and hydrosilylation reaction is examined as the second method as shown in Scheme 2.

To confirm the effectiveness of this approach, silicone hydrogel bearing no –SiH groups was prepared from 3-(2-hydroxy-3-methacryloyloxy)propylmethylbis(trimethylsiloxy)silane (SiMAA2), methacryloyloxypropyl single end capped poly(dimethylsiloxane) (M_n = 1000, FM0711), DMA and methacryloyloxypropyl both end capped poly(dimethylsiloxane) (FM7711). After being dried and Ar gas plasma treated, hydrosilylation was carried out with and without hydrogen hexachloroplatinate(IV) hexahydrate as catalyst. The contact angles at each step of this process are shown in Table 2. It shows that Ar gas plasma treatment alone is insufficient, furthermore, the addition of hydrogen hexachloroplatinate(IV) hexahydrate has a great influence on the obtained contact angle. This suggests the formation of functional groups such as –SiH in silicone component which can undergo hydrosilylation reaction with PEG monoallylether. This –SiH group formation was also suggested by FTIR-ATR measurements shown in Figure 1. With regard to the plasma treatment and hydrosilylation, various changes of absorption band were observed. The decreases of intensity at 1260 (Si–CH_3 deformation in $SiMe_n$) and 842 cm^{-1} (Si–CH_3 deformation in $SiMe_3$) were recognized. The intensity of the peak around 1040 cm^{-1} (Si–O stretching in Si–O–Si group) also decreased, while the peak at 798 cm^{-1} increased which was assigned to Si–CH_3 deformation in $SiMe_2$ group. Also, the intensity change of the band at around 2960 cm^{-1} (C–H stretching in CH_3) suggests the scission of C–H bond. Furthermore, there exists a band at 900 cm^{-1} which is considered to correspond to –SiH bond (Si–H deformation).[23] So this is one proof of the formation of –SiH bond by high-frequency plasma treatment, and thus the expected scheme in

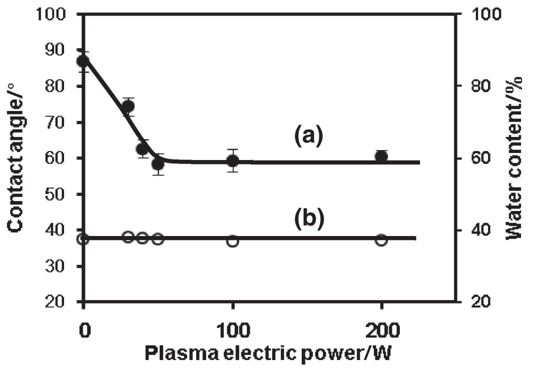


Figure 2. Relationship between plasma electrical power and contact angle and water content of high frequency plasma treated and hydrosilylated silicone hydrogel. (a) and (b) show contact angle and water content respectively.

Scheme 2 could be confirmed. This could be also supported by the results from XPS measurements which described the decomposition of some hydrocarbon and siloxane bonds under plasma bombardment.[16]

From FTIR-ATR spectra, the formation of PEG chain layer was confirmed by the existence of the band at around 1400 (O–H deformation in alcohol), around 1140 (C–O–C stretching in ether), and 1000 $\mathrm{cm^{-1}}$ (C–O stretching in alcohol).

Keeping the same hydrosilylation conditions as that in Table 2, the obtained relationships between the plasma treatment conditions and hydrogel properties were shown in Figure 2. It is noteworthy to point out that nevertheless the contact angle is greatly reduced, water content shows almost constant value. This suggests that introduction of PEG chain is restricted to near the hydrogel surface as expected in our process design concept.

In conclusion, novel surface modification methods of shaped articles from silicone-containing hydrogel were designed and carried out. The design concept of these methods was to introduce –SiH groups into silicone component and conduct hydrosilylation between this –SiH group and allyl group bearing PEG to improve contact angle of silicone hydrogel shaped articles. Both copolymerization of –SiH-group-bearing monomer and high-frequency Ar gas plasma treatment were effective for the hydrosilylation and contact angle reduction. From the effect of using hydrogen hexachloroplatinate(IV) hexahydrate to hydrosilylation reaction and FTIR-ATR spectra, the formation of –SiH group by Ar gas plasma was suggested. This finding may lead to development of novel application of plasma process combined with other chemical reactions.

This work was partly supported by Shorai Foundation for Science and Technology. The authors are grateful to Toray Industries Inc., for the permission to submit this manuscript.

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22 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

23 For example, FT-IR spectrum of tris(dimethylsilyloxy)-methylsilane: *The Aldrich Library of FT-IR Spectra*, 2nd ed., Sigma-Aldrich Co. LLC., Milwaukee, **1997**, Vol. 3, p. 4386C.