

Mechanism Study on Surface Activation of Surfactant-Modified Polyvinyl Siloxane Impression Materials

Doug-Youn Lee,¹ Young-Il Oh,¹ Kyung-Ho Chung,² Kwang-Mahn Kim,¹ Kyoung-Nam Kim¹

¹Brain Korea 21 Project for Medical Science, Department and Research Institute of Dental Biomaterials and Bioengineering, College of Dentistry, Yonsei University, Seoul 120-752, Korea

²Department of Polymer Engineering, The University of Suwon, Suwon, Korea

Received 17 March 2003; accepted 4 November 2003

ABSTRACT: This study examined the mechanism on the surface activation of hydrophilic polyvinyl siloxane impression materials incorporated with nonionic surfactants. Hydrophilic polyvinyl siloxane impression materials were prepared with a polydimethylsiloxane composition and nonionic surfactants. The surfactants used were nonylphenoxy poly(ethyleneoxy) ethanol homologs of varying ethyleneoxy chain length. These homologs were designated NP4, NP6, and NP10 according to the mole number of ethyleneoxy group (hydrophilic group) of 4, 6, and 10, respectively. The incorporation of a nonionic surfactant into polyvinyl siloxanes enhanced their hydrophilicity and consequently led to the significant reduction in the contact angles. The higher the concentration of surfactant that was incorporated, the lower the contact angles that were observed. The contact angle was lowest when NP4 was incorporated, even though

NP4 is less hydrophilic than NP6 and NP10, which implies that the exposed surfactant concentration on the surface was highest when NP4 was used. Relatively lower surface energy of NP4 among three surfactants would induce spatial distribution of NP4 on the hydrophobic surface of polyvinyl siloxane and consequently resulted in higher surfactant concentration on the surface of the silicone impression material. The surfactant dispersion size also seemed to be relevant for the surface activation in these surfactant-modified silicone impression materials. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2395–2401, 2004

Key words: surface activation; polyvinyl siloxane impression materials; nonionic surfactants; contact angle; surface hydrophilicity

INTRODUCTION

The main purpose of a dental impression is to capture and reproduce hard and soft tissue detail with a dimensionally stable material as a mold to fabricate an accurate replica for definitive restorations. Polyvinyl siloxane impression materials are widely used for obtaining dimensionally accurate and stable models of oral structures, particularly in the production of inlays, crowns, and bridges. In contrast to earlier silicones, polyvinyl siloxane materials set by an addition polymerization reaction without the production of volatile byproducts, the loss of which can cause shrinkage.¹

Unfortunately, polyvinyl siloxane impression materials are essentially hydrophobic in nature and therefore are susceptible to poor wetting of moist oral tissue and poor wetting by aqueous slurries of gypsum-

based die materials (dental stone). The consequence is that set gypsum casts and dies may contain pits and voids.^{2,3}

Newer, so-called hydrophilic polyvinyl siloxane impression materials have been developed to provide improved impression making. Hydrophilic compounds have two major aims: (1) to enhance wetting and spreading on moist oral tissue, and (2) to ensure better wettability by water containing slurries of dental stone.¹

Clinically, the topical use of a surfactant has been demonstrated to improve wettability and significantly reduce the number of voids in silicone impressions. In previous studies investigating the relationship between the wettability and the gypsum castability of silicone materials, materials that exhibited the lowest contact angle with water produced dental casts and dies with the fewest voids.⁴ Cullen et al.⁵ also reported that voids in casts were larger when they were produced from materials with greater contact angles.

Some manufacturers claim that the wettability of their polyvinyl siloxane impression materials has been increased with the addition of new hydrophilic agents to the formulation. However, few have studied the mechanism of surface activation and wettability development of hydrophilic impression materials. Any change in surface hydrophilicity of the impression

Correspondence to: K.-N. Kim (kimkn@yumc.yonsei.ac.kr).

Contract grant sponsor: Brain Korea 21 Project for Medical Science, Yonsei University.

Contract grant sponsor: Medical Science and Engineering Research Program, Korea Science and Engineering Foundation; contract grant number: R13-2003-T3.

TABLE I
Nonionic Surfactants [Nonylphenoxy Poly(ethyleneoxy) Ethanol Homologs] Used in the Study

Surfactant	Code name	Formula	HLB ^a
Igepal® CO-430	NP4	C ₉ H ₁₉ C ₆ H ₄ O(CH ₂ CH ₂ O) ₄ H	8.8
Igepal® CO-530	NP6	C ₉ H ₁₉ C ₆ H ₄ O(CH ₂ CH ₂ O) ₆ H	10.8
Igepal® CO-660	NP10	C ₉ H ₁₉ C ₆ H ₄ O(CH ₂ CH ₂ O) ₁₀ H	13.2

^a HLB, hydrophilic–lipophilic balance (% of the hydrophilic group divided by 5).

materials can affect the accuracy of the impression as well as the quality of stone casts.

Various studies have focused on the wettability of elastomeric impression materials. It could be concluded that surface-activated silicone impression materials exhibit greater wettability than that of nonactivated materials.^{2,3,6–8} It has been observed that there is a strong negative correlation between mean contact angles and castability of die stone. Therefore, hydrophilic silicone impression materials cause less voids in stone casts than hydrophobic materials.

Norling and Reisbick⁹ added nonionic surfactants to polysulfide and silicone impression materials and noted significant reductions in contact angle values compared with untreated impression materials. They reported that the choice of surfactant is clearly critical for silicone modification. However, the mechanism of improved wettability resulting from surfactant additions was not clearly explained.

The objective of this study was to develop a better understanding of the contact angle development between a drop of water and the surface of each sample and the mechanism on the surface activation of hydrophilic polyvinyl siloxane impression materials incorporated with nonionic surfactants. The effect of nonionic surfactants on the surface properties of the polyvinyl siloxanes was investigated using contact angle methodology. For example, the surfactants, which are often found in silicone impression materials, can have a strong influence on the surface hydrophilicity.

The simple technique of contact angle measurement is often used to probe the surface energetics of polymers and could provide valuable information directly relevant to changes in surface properties as a result of a change in surfactant distribution.¹⁰ The interpretation of data depends entirely on the basic concept of the interfacial phenomenon. Thus, using the contact angle, information such as surface hydrophilicity and distribution of nonionic surfactants at the outermost surface can be deduced.

EXPERIMENTAL

Materials

The vinyl-terminated polysiloxane prepolymers, crosslinking agent, and Pt catalyst were purchased

from Bayer. The fillers (SiO₂, Al₂O₃, diatomite) were purchased from Sumitomo Chemical (Osaka, Japan). Three kinds of nonionic surfactants (Igepal® CO-430, Igepal® CO-530, and Igepal® CO-660) were purchased from Rhone-Poulenc Inc. (New Jersey) and used as received. These homologs were designated NP4, NP6, and NP10 according to the mole number of ethyleneoxy group (hydrophilic group) of 4, 6, and 10, respectively. Table I lists the nonylphenoxy poly(ethyleneoxy) ethanol homologs of varying ethyleneoxy chain length and the hydrophilic–lipophilic balance (HLB) of each surfactant.¹¹

Preparation of hydrophilic polyvinyl siloxane impression materials

Hydrophilic polyvinyl siloxane impression materials were prepared with a polydimethylsiloxane composition and nonionic surfactant. Table II shows the basic composition for hydrophilic polyvinyl siloxane impression materials. This study included polyvinyl siloxane impression materials prepared with and without inorganic fillers.

The base and catalyst pastes were prepared in glass vessel equipped with a stirrer at room temperature, respectively. The base paste contained the vinyl-terminated polydimethyl siloxanes and the crosslinking agent (polymethyl hydrogen siloxane), which is a moderately low molecular mass with silane terminal

TABLE II
Basic Composition of Hydrophilic Polyvinyl Siloxane Impression Materials Incorporated with Nonionic Surfactants

Composition	Base paste (wt %)	Accelerator paste (wt %)
Vinyl-terminated Polysiloxane prepolymers	56.3	63.2
Crosslinking agent	6.7	—
Pt catalyst	—	0.3
Nonionic surfactant ^a	—	0, 0.5, 1.5, 2.5
SiO ₂	37.0	—
Al ₂ O ₃	—	30.0
Diatomite	—	6.5

^a Nonylphenoxy poly(ethyleneoxy) ethanol homologs (NP4, NP6, and NP10).

groups. The accelerator paste contained the vinyl-terminated polydimethyl siloxanes, Pt catalyst, and non-ionic surfactant. One of a homologous series of non-ionic surfactants was incorporated into the polysiloxane prepolymers. An amount equal to 0.5, 1.5, and 2.5 wt % based on the accelerator paste was dispensed using an ultraprecision micrometer syringe. The base and accelerator pastes also contained fillers.

Once two pastes are mixed, an addition reaction occurs between the silane and the vinyl groups, which causes the setting of materials in 10 min. Pt catalyst was used to initiate the reaction.

Contact angle measurement

Rectangular specimens of each hydrophilic impression material were made from a highly polished stainless-steel mold (40 × 20 × 2 mm). The impression materials were injected and flat surfaces were obtained by pressing the mold against a glass plate. Measurements were performed on the surfaces cured against the glass plate immediately after setting of the materials. Care was taken not to contact the surfaces with any substance before the measurements.

Surface activation was evaluated by measuring advanced contact angles with a computer-aided Krüss G10-System (Krüss, Hamburg, Germany). Deionized water served as the wetting liquid. Contact angles were measured after 120 s from dropping of droplets. The average of the angles obtained from 10 different samples was reported.

Dispersion size of surfactant

Each surfactant (1.5%) was dispersed in polyvinyl siloxane prepolymers at 100 rpm of agitation speed for 30 min without addition of a catalyst and fillers. A drop of surfactant dispersion was placed on a slide glass and covered with a cover-glass on top. The dispersion size of nonionic surfactants in polyvinyl siloxane prepolymer was determined by optical microscope (Sony XC-711, Tokyo, Japan) at ×400 magnification.

SEM observation

Specimens of cured polyvinyl siloxane impression materials were immersed in ethyl alcohol for 24 h to extract the surfactants from the surface of cured samples. The surface images of surfactant-modified polyvinyl siloxane impression materials were observed by scanning electron microscopy (SEM, S4200; Hitachi, Osaka, Japan) after extraction of surfactant.

Statistical analysis

A one-way ANOVA was used to determine differences in the contact angles for all the polyvinyl silox-

ane impression materials. The results were considered significant at the 95% level. Differences among the means of the magnitude of the contact angles for the all polyvinyl siloxane impression materials were checked with a Kruskal–Wallis test and Tukey grouping. The results were considered significant at the 95% level.

RESULTS AND DISCUSSION

Wetting describes the relative affinity of a liquid for a solid. It is the degree to which a drop will spread on a solid surface, and can be quantified by observing the contact angle.¹² High angles (>90°) indicate poor wetting, whereas a 0° angle would indicate perfect wetting of the surface.

A serious problem in the use of silicone elastomeric impression materials is that their low surface energy renders them difficult to wet with gypsum slurries.⁹ Hydrophilic impression materials with contact angles much less than 90° are highly desirable because, when poured in gypsum, they are easily cast free of air bubbles and voids.¹³ When discussing the wetting characteristics of impression materials, it is important to distinguish between the ability of the material to flow around the soft and hard tissues of the mouth, and the ability of the material to be wet by a gypsum slurry.

Polyvinyl siloxanes are inherently hydrophobic. However, new hydrophilic polyvinyl siloxane impression materials have been recently introduced with manufacturer claims that they can better wet moist dental surfaces. These new formulations have intrinsic surfactants added. Typically these are nonionic surfactants of nonylphenoxy poly(ethyleneoxy) ethanol homologs.^{14,15} A surfactant modification that alters the surface chemistry of an impression material may change the hydrophilicity of the impression material.

The nonionic surfactants used in this study contain a silicone-loving group (nonylphenoxy group), which causes the surfactant to be dispersible in the silicone prepolymer. The surfactant also contains a poly(ethyleneoxy) group, which yields a cured hydrophilic silicone impression material. The hydrophilicity of nonionic surfactants (NP4, NP6, and NP10) depends on the mole number of the ethyleneoxy group (hydrophilic group) of 4, 6, and 10, respectively. NP4 surfactant has the lowest HLB value among the three nonionic surfactants, which indicates that NP4 is less hydrophilic than NP6 and NP10 (Table I).

The surface properties of a hydrophilic polyvinyl siloxane impression material are determined essentially by the surfactant concentration at the surface. This is the spatial distribution of surfactants in the outermost region of the material. This situation can best be understood by considering the outermost region of a material as in the "surface state," which

TABLE III
Contact Angle of Probe Liquid (Deionized Water) on
Surfactant-Modified Polyvinyl Siloxane Impression
Materials After 2 min

Sample	Surfactant type	Surfactant concentration (wt %)	Contact angle (°) [mean (\pm SD)]
S-0	—	0	104.9 (\pm 1.74)
S-NP4-0.5	NP4	0.5	74.9 (\pm 2.51)
S-NP4-1.5	NP4	1.5	35.8 (\pm 1.64)
S-NP4-2.5	NP4	2.5	33.9 (\pm 1.21)
S-NP6-0.5	NP6	0.5	77.3 (\pm 1.84)
S-NP6-1.5	NP6	1.5	40.9 (\pm 1.41)
S-NP6-2.5	NP6	2.5	35.8 (\pm 1.02)
S-NP10-0.5	NP10	0.5	83.2 (\pm 1.07)
S-NP10-1.5	NP10	1.5	68.3 (\pm 1.55)
S-NP10-2.5	NP10	2.5	59.8 (\pm 2.52)

could be quite different from the state of the bulk material.¹⁰

To determine the impact of surfactants on surface properties of silicone impression materials, particularly the hydrophilicity of surfaces, the contact angle between a drop of water and the surface of each sample was measured. The results are presented in Table III.

The incorporation of nonionic surfactant into polyvinyl siloxane impression materials enhanced their surface hydrophilicity. All types of nonionic surfactants used in this work reduced the contact angles. The contact angles were significantly reduced even at low surfactant concentration. The surfactant-modified polyvinyl siloxanes exhibited a contact angle of approximately 33–84°, whereas the unmodified product had a contact angle of 105°. The higher the concentration of surfactant that was incorporated, the lower the contact angles that were observed. Significant differ-

ences ($P < 0.05$) in contact angle were found statistically among the samples prepared with the same surfactant except for S-NP4-1.5 and S-NP4-2.5.

We found an interesting result that the lowest homolog, NP4, at all concentrations yielded contact angles that were smaller than those for NP6 and NP10, although NP4 is less hydrophilic than NP6 and NP10. This result was identical with the finding of Norling and Reisbick.⁹ Low contact angles resulted from the surface activation of the impression material. The surface concentration of surfactant (especially, hydrophilic moiety of surfactant) on the polysiloxane impression material is a crucial factor in determining the surface hydrophilicity. This implies that the exposed NP4 concentration on the polysiloxane surface was much higher because the hydrophilic group of NP4 was shorter than those of NP6 and NP10.

The exposed surfactant concentration on the hydrophobic surface depends on its surface energy. To evaluate the surface energy of nonionic surfactants indirectly, the contact angle of nonionic surfactants as a probe liquid on the surface of polyvinyl siloxane sample was measured. The contact angle between a solid substance and a liquid depends on the nature of the solid surface and the energy of the liquid surface, commonly called the surface tension.¹ Figure 1 shows the contact angles of nonionic surfactants on polyvinyl siloxane impression material (S-0) after 2 min. The NP4 surfactant showed contact angles that were smaller than those for NP6 and NP10. Significant differences in contact angle of surfactants were found statistically among the samples ($P < 0.05$). From the result, we can deduce that NP4 has the lowest surface energy among the three nonionic surfactants used in this study. This result is consistent with HLB values of the surfactants (Table I).

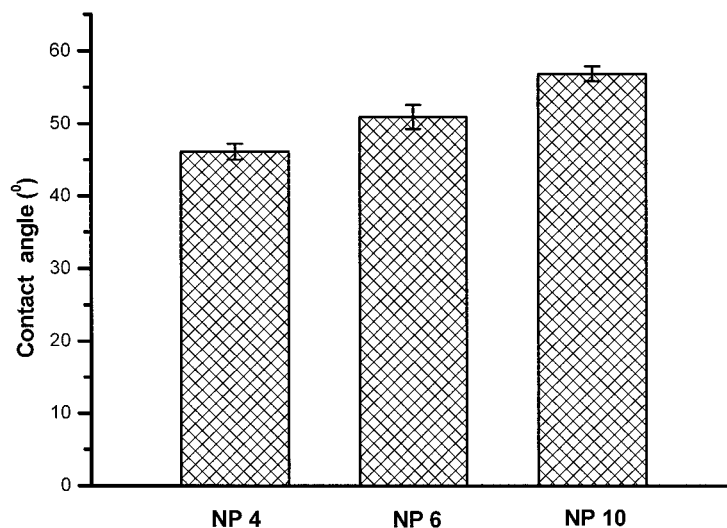


Figure 1 Contact angles of nonionic surfactants on polyvinyl siloxane impression material (S-0) after 2 min.

TABLE IV
Effect of Absence of Fillers on the Contact Angle of Deionized Water on Surfactant-Modified Polyvinyl Siloxane Impression Materials

Sample	Surfactant type	Surfactant concentration (wt %)	Fillers	Contact angle (°) [mean (\pm SD)]
S-NP4-1.5	NP4	1.5	Included	35.8 (\pm 1.64)
S-NP4-1.5-NF ^a	NP4	1.5	—	36.7 (\pm 0.82)
S-NP6-1.5	NP6	1.5	Included	40.9 (\pm 1.41)
S-NP6-1.5-NF ^a	NP6	1.5	—	42.5 (\pm 1.31)
S-NP10-1.5	NP10	1.5	Included	68.3 (\pm 1.55)
S-NP10-1.5-NF ^a	NP10	1.5	—	70.6 (\pm 0.93)

^a Prepared without fillers.

As a result, the relatively lower surface energy of NP4 would induce spatial distribution of NP4 on the hydrophobic surface of polyvinyl siloxane and consequently lead to higher surfactant concentration at the surface of the silicone impression material. The surface concentration of hydrophilic poly(ethyleneoxy) group must be higher when NP4 was used, which resulted from the high surface concentration of NP4 on the polysiloxane.

We also examined the effect of hydrophilic fillers on the contact angle of water on polyvinyl siloxane im-

pression materials. Table IV presents the contact angles of deionized water on surfactant-modified polyvinyl siloxane impression materials prepared with and without fillers. The fillers used to modify the silicone material were not effective in reducing the contact angles. This result suggested that the hydrophilic fillers were not exposed on the surface and consequently did not improve wettability.

Figure 2 shows the dispersion size of nonionic surfactants in polyvinyl siloxane prepolymers before setting. The dispersion size of NP4 surfactant was small-

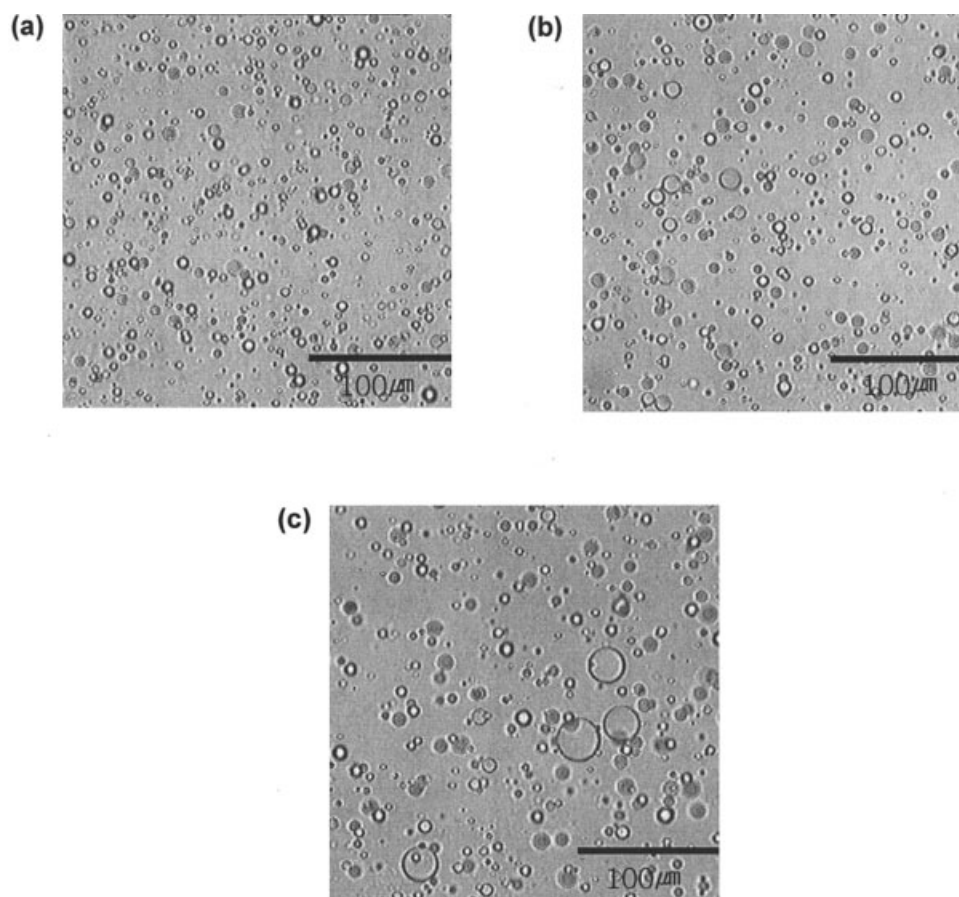


Figure 2 Dispersion size of nonionic surfactants in polyvinyl siloxane prepolymers: (a) NP4; (b) NP6; and (c) NP10.

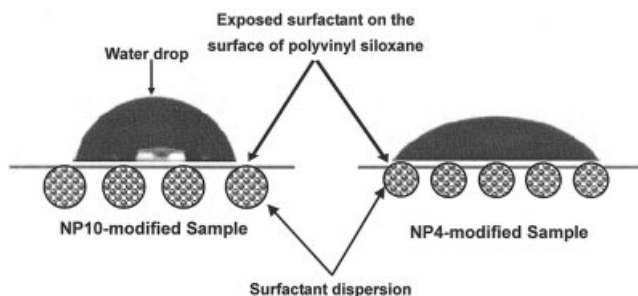


Figure 3 Schematic of contact angle development of deionized water on surfactant-modified polyvinyl siloxane impression materials. The exposed NP4 concentration on the surface was higher than that of NP10.

est among the three nonionic surfactants. The dispersion size of these surfactants in polyvinyl siloxane prepolymers is dependent on the HLB of each surfactant. The nonionic surfactants used in this study contained a silicone-loving group (nonylphenoxy group), which causes the surfactant to be dispersible in the silicone prepolymer. The more hydrophobic (silicone-loving) that a surfactant is, the smaller the dispersion size that is obtained.

When the same concentration of surfactants was incorporated, the surface area of dispersed surfactant would be affected by their dispersion size in silicone impression materials. The smaller dispersion size of surfactant would increase the concentration exposed on the surface of the silicone impression material.

Figure 3 shows a schematic of the surface concentration of nonionic surfactant on surfactant-modified polyvinyl siloxane impression materials. The NP4 surfactant, which has a relatively low surface energy, would be located to a greater extent on the hydrophobic surface of polyvinyl siloxane and would consequently lead to a higher NP4 concentration exposed on the surface of the silicone impression material. On the other hand, NP10 was expected to be buried in the hydrophobic surface of polyvinyl siloxane and accordingly was not effective in enhancing the wettability in spite of its highest hydrophilicity.

The surface images of surfactant-modified polyvinyl siloxane impression materials were observed by SEM after the extraction of surfactants using ethyl alcohol as a solvent. All surfactants used in this study were soluble in ethyl alcohol. Figure 4 shows SEM images of surfaces of cured surfactant-modified poly-

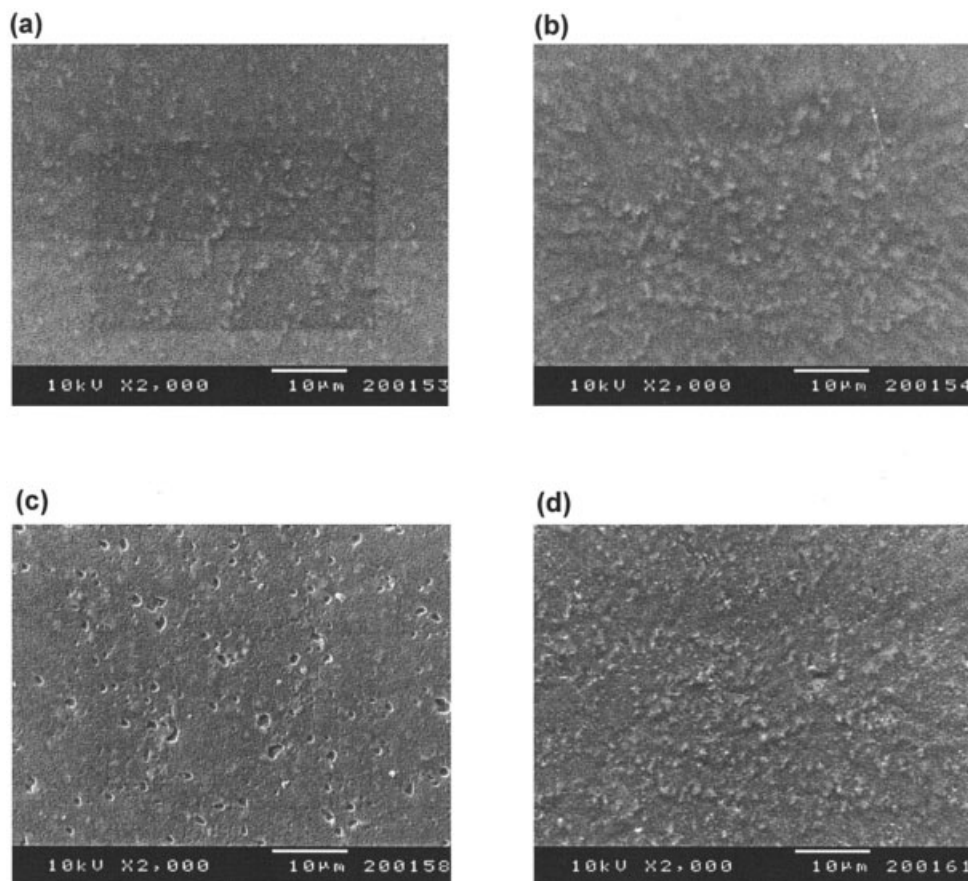


Figure 4 SEM images of surfaces of surfactant-modified polyvinyl siloxane impression materials after extraction of surfactant: (a) Control (S-0) before extraction; (b) S-0 after extraction; (c) S-NP4-1.5; and (d) S-NP10-1.5.

vinyl siloxane impression materials after extraction of surfactant. For control (S-0 prepared without a surfactant), the SEM image of surfaces of cured polyvinyl siloxane after extraction was not different from that observed before the extraction procedure. Many voids were observed on the surface of the S-NP4-1.5 sample after the surfactant extraction step. However, few voids caused by surfactant extraction were found on the surface of the S-NP10-1.5 sample. From this result, we can confirm that the exposed surfactant area on the surface was much larger when NP4 was used rather than NP10.

CONCLUSIONS

A serious problem in the use of silicone impression materials is that their low surface energy renders them difficult to wet with gypsum slurries. In this study, hydrophilic polyvinyl siloxane impression materials were prepared with a polydimethylsiloxane composition and nonionic surfactants (NP4, NP6, and NP10).

The incorporation of a nonionic surfactant into polyvinyl siloxane impression materials enhanced their surface hydrophilicity. All types of nonionic surfactants used in this work reduced the contact angles. The higher the concentration of surfactant that was incorporated, the lower the contact angles that were observed.

The surface properties of a hydrophilic polyvinyl siloxane impression material are determined essentially by the surfactant concentration at the surface. This is the spatial distribution of surfactants in the outermost region of the material, which is a crucial factor in determining the surface hydrophilicity. The relatively lower surface energy of NP4 among the three surfactants would improve the spatial distribu-

tion of NP4 on the hydrophobic surface of polyvinyl siloxane and consequently lead to higher surfactant concentration at the surface.

The surface concentration of surfactant on the silicone impression material was more critical than the inherent hydrophilicity of surfactant for the surface activation. Moreover, the surfactant dispersion size seems to be relevant for the surface activation in these surfactant-modified silicone impression materials.

This work was supported by the Brain Korea 21 Project for Medical Science, Yonsei University in 2002 and the Korea Health 21 R&D Project, Ministry of Health and Welfare, Republic of Korea (Grant HMP-99-E10-0003).

References

1. Kess, R. S.; Combe, E. C.; Sparks, B. S. *J Prosthet Dent* 2000, 84, 98.
2. Chong, Y. H.; Soh, G.; Setchell, D. J.; Wickens, J. L. *Dent Mater* 1990, 6, 162.
3. Pratten, D. H.; Craig, R. G. *J Prosthet Dent* 1989, 61, 197.
4. Milward, P. J.; Waters, M. G. *J Prosthet Dent* 2001, 86, 165.
5. Cullen, D. R.; Mikesell, J. W.; Sandrik, J. L. *J Prosthet Dent* 1991, 66, 261.
6. Vassilakos, N.; Pinheiro, Fernandes, C. *J Dent* 1993, 21, 297.
7. Panichuttra, R.; Jones, R. M.; Goodacre, C.; Munoz, C. A.; Moore, B. K. *Int J Prosthodont* 1991, 4, 240.
8. Boening, K. W.; Walter, M. H.; Schuette, U. *J Dent* 1998, 26, 447.
9. Norling, B. K.; Reisbick, M. H. *J Prosthet Dent* 1979, 42, 342.
10. Shin, J. S.; Lee, D. Y.; Ho, C. C.; Kim, J. H. *Langmuir* 2000, 16, 1882.
11. Ash, M.; Ash, I. *Handbook of Industrial Surfactants*; Gower Publishing: Vermont, 1993; p. 257.
12. O'Brien, W. J. *Dental Materials: Properties and Selection*; Quintessence Books: Chicago, 1989.
13. Pratten, D. H.; Covey, D. A.; Sheats, R. D. *J Prosthet Dent* 1990, 63, 223.
14. Chai, J. Y.; Yeung, T. *Int J Prosthodont* 1991, 4, 555.
15. Mandikos, M. N. *Aust Dent J* 1998, 43, 428.