

Surface and Chemical Properties of Surface-Modified UHMWPE Powder and Mechanical and Thermal Properties of Its Impregnated PMMA Bone Cement V. Effect of Silane Coupling Agent on the Surface Modification of UHMWPE Powder

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Received October 28, 2004; Revised March 3, 2005

Abstract: Conventional poly(methyl methacrylate) (PMMA) bone cement has been widely used as an useful biopolymeric material to fix bone using artificial prostheses. However, many patients had to be reoperated, due to the poor mechanical and thermal properties of conventional PMMA bone cement, which are derived from the presence of unreacted MMA liquid, the shrinkage and bubble formation that occur during the curing process of the bone cement, and the high curing temperature (above 100 °C) which has to be used. In the present study, a composite PMMA bone cement was prepared by impregnating conventional PMMA bone cement with ultra high molecular weight polyethylene (UHMWPE) powder, in order to improve its mechanical and thermal properties. The UHMWPE powder has poor adhesion with other biopolymeric materials due to the inertness of the powder surface. Therefore, the surface of the UHMWPE powder was modified with two kinds of silane coupling agent containing amino groups (3-amino propyltriethoxysilane (TSL 8331[®]) and *N*-(2-aminoethyl)-3-(amino propyltrimethoxysilane) (TSL 8340[®])), in order to improve its bonding strength with the conventional PMMA bone cement. The tensile strengths of the composite PMMA bone cements containing 3 wt% of the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®] were similar or a little higher than that of the conventional PMMA bone cement. However, no significant difference in the tensile strengths between the conventional PMMA bone cement and the composite PMMA bone cements could be found. However, the curing temperatures of the composite PMMA bone cements were significantly decreased.

Keywords : PMMA bone cement, UHMWPE powder, silane coupling agent.

Introduction

Conventional poly(methyl methacrylate) (PMMA) bone cement, which is useful for the fixation of bone and artificial prosthesis, consists of the two parts of PMMA powder and methyl methacrylate (MMA) liquid. Generally, the PMMA powder part is composed of PMMA powder, barium sulfate as radiopaque agent, and benzoyl peroxide (BPO) as radical initiator and the MMA liquid part is composed of MMA monomer, *N,N*-dimethyl-*p*-toluidine as aid

initiation of radical polymerization, and hydroquinone.

However, the longevity of the bone cement was decreased because of the aseptic loosening resulting from several disadvantages; (1) thermal cellular necrosis due to the high curing temperature of the bone cement,¹⁻³ (2) chemical cellular necrosis due to unreacted MMA liquid,⁴⁻¹⁰ and (3) poor mechanical strengths due to the formation of many of the microscopic bubbles or shrinkages during the curing process of the bone cement.¹¹⁻¹⁹ To improve these disadvantages, the several composite PMMA bone cements impregnated with organic or inorganic biomaterials have been prepared by using hydroxyapatite,²⁰ calcium phosphate,^{21,22} carbon fibers,^{23,24} graphite,²⁵ aramid,^{26,27} bone particles,^{28,29} titanium,³⁰

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PMMA fibers,^{31,32} and ultra high molecular weight polyethylene (UHMWPE) fiber.³³

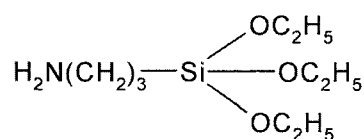
In the present study, we proposed development on the composite PMMA bone cement impregnated with UHMWPE powder for the improvement of the poor mechanical and thermal properties of conventional PMMA bone cement. UHMWPE has many of the excellent characteristics such as good dynamic and static strengths, modulus of elasticity as similar as bone tissue, high energy absorption, and degradation or wear resistance *in vivo*.³⁴

But, the surface inertness of UHMWPE powder induced weak bonding force with another polymeric biomaterial. In our previous studies, the surface of UHMWPE powder was modified by means of MMA/xylene solution,³ MMA/PMMA mixture,³⁶ BPO/hydroquinone system,³⁷ and MMA/*N,N*-dimethyl-*p*-toluidine solution.³⁸ From the results of our previous studies, we observed that the tensile strengths of the 3 wt% of UHMWPE powders surface-modified by the four methods impregnated composite PMMA bone cements were slightly improved and the curing temperatures of the composite PMMA bone cements were slightly decreased.

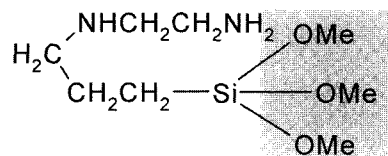
In this study, two kinds of silane coupling agent with amino group were used for the surface modification of UHMWPE powder. Silane coupling agent, which is composed of hydrophobic and hydrophilic nature, has been widely known as an additive to achieve strong link with PMMA bone cement and inorganic fillers when inorganic filler was added between PMMA bone cement and artificial prosthesis.^{38-39,42} The aims of this study are (1) to observe the surface morphology of the UHMWPE powder surface-modified with various ratios of 3-amino propyltriethoxysilane (TSL 8331[®]) and *N*-(2-aminoethyl)-3-(amino propyltrimethoxysilane) (TSL 8340[®]), (2) to measure the tensile strengths and the curing temperatures of 3 wt% of the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®] impregnated composite PMMA bone cements, (3) to analyze the changes of the chemical composition of the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®], and (4) to propose the improved adhesion mechanism between the UHMWPE powder surface-modified with the two kinds of silane coupling agent and conventional PMMA bone cement.

Experimental

Materials. UHMWPE (Hostalen Gur 4113, molecular weight: 3,800,000 g/mol) powder was purchased from Ticona GmbH (Germany). As shown in Figure 1, TSL 8331[®] and TSL 8340[®] with amino group were kindly obtained from Dongyang Silicon Chem. Co. Ltd. (Korea) for the surface modification of UHMWPE powder. Conventional PMMA bone cement (Vertex[®]) was purchased from Dentimex Co. (Netherlands). All chemicals and organic sol-



3-aminopropyltriethoxysilane (TSL 8331)



N-(2-aminoethyl)-3-(aminopropyltrimethoxysilane) (TSL 8340)

Ethoxy group

Methoxy group

Amino group

Figure 1. Chemical structure of TSL 8331[®] and TSL 8340[®].

Table I. Content of TSL 8331[®] and TSL 8340[®] with Amino Group for the Surface Modification of UHMWPE Powder

Ethanol/ Acetone (vol%)	Distilled Water (vol%)	Acetic Acid (pH)	TSL 8331 [®] /TSL 8340 [®] (vol%)
95/95	5	4.5 ~ 5.5	0.5 / 0.5
95/95	5	4.5 ~ 5.5	1 / 1
95/95	5	4.5 ~ 5.5	2.5 / 2.5
95/95	5	4.5 ~ 5.5	5 / 5

vents were used as HPLC grade.

Surface Modification of UHMWPE Powder. Table I illustrates the surface modification of UHMWPE powder with various ratios of TSL 8331[®] and TSL 8340[®]. Simple dipping method was adopted for the surface modification of UHMWPE powder. This method is to modify the surface of UHMWPE powders as impregnating the powders to the 5 (pH) of solution added with drops of acetic acid. The solution is composed of 95 vol% of ethanol and/or acetone, 5 vol% of distilled water, and various amounts of silane coupling agent. Silanol group, including oxygen-hydrogen (O-H) bond, was generated by means of hydrolysis³⁹ when were continuously stirred for 50~60 min after adding various ratios of TSL 8331[®] (1, 2, 5, and 10 mL) and TSL 8340[®] (1, 2, 5, and 10 mL) to the solution, respectively. At the same time, 1 g of UHMWPE powder was added to the two mixtures. Then, it was dried and kept in vacuo before use.

Specimen Fabrication for the Measurement of Tensile Strength. 3 wt% of the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®] was uniformly mixed with 3 g of PMMA powder and 1.5 mL of

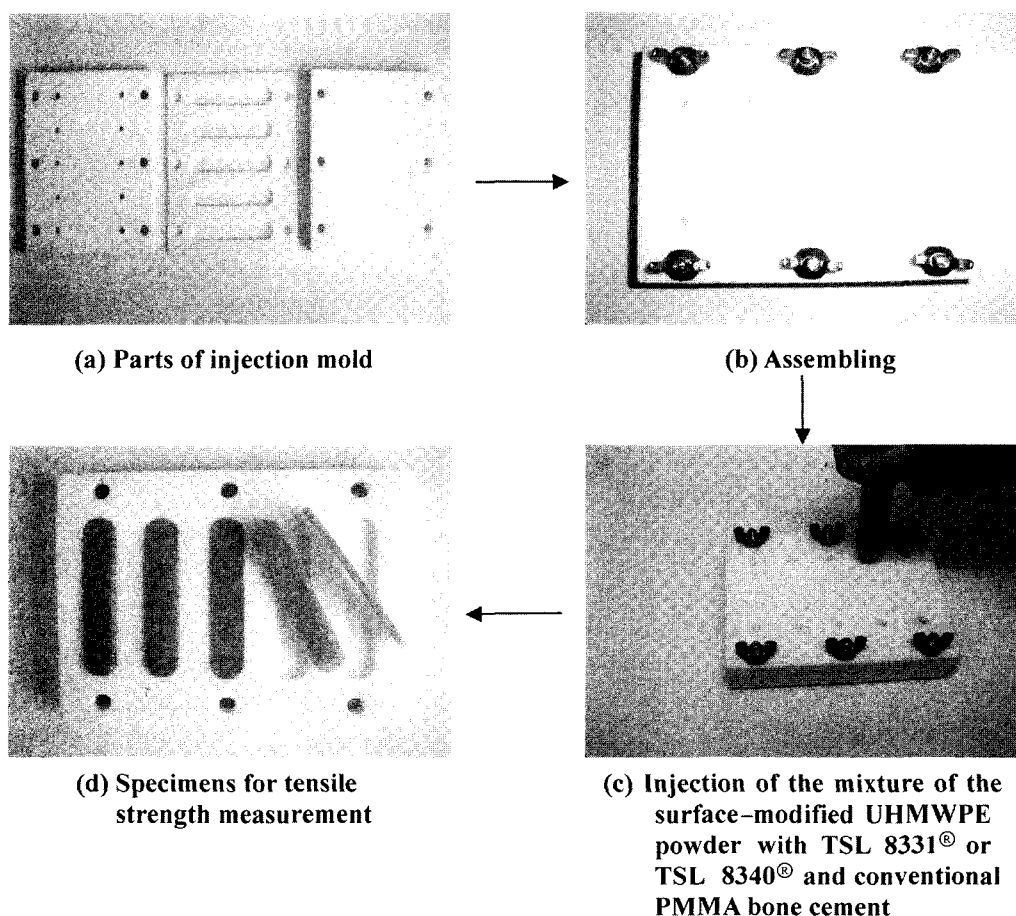


Figure 2. Fabrication method of specimen for tensile strength measurement.

MMA liquid of conventional PMMA bone cement. As shown in Figure 2, the specimen for tensile strength measurement was fabricated by injecting the mixture of 3 wt% of the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®] and 3 g of PMMA powder, and 1.5 mL of MMA liquid into the hole of 64 mm × 12 mm × 2.2 mm size using Teflon mold.

Surface Observation. Scanning electron microscope (SEM, Hitachi, S-2250N, Japan) was used for the surface observation of virgin UHMWPE powder and the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®]. Platinum was coated on the surface-modified UHMWPE powders under argon gas using plasma sputter (K575 Emitech, Japan) after putting them on metal board and their surface were observed.

Analysis of the Changes of Chemical Composition. The changes of the chemical composition of the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®] were analyzed by means of Fourier transform infrared-attenuated total reflectance (FTIR-ATR, Digi-Lab FTS 80, Bio-Rad, USA). The film for FTIR-ATR characterization was fabricated under 140 °C and 200 kg/cm² (Carver WMV50, USA).

Student's t-Test. This method was used for the calculation of the significant difference on tensile strengths of conventional PMMA bone cement and 3 wt% of the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®] impregnated composite PMMA bone cements. It signified when the *p* value is below than 0.05.

Measurement of Tensile Strength. The tensile strengths of 3 wt% of the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®] impregnated composite PMMA bone cements were measured by means of universal transverse mercator (UTM, United STM-10, USA) and compared with those of conventional PMMA bone cement as well as 3 wt% of no surface-modified UHMWPE powder impregnated composite PMMA bone cement. The test speed for tensile strength measurement was 5 mm/min and the cross area of the fabricated specimen was 2 mm × 12 mm.

Measurement of Curing Temperature. The curing temperatures of 3 wt% of the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®] impregnated composite PMMA bone cements were measured by means of digital thermometer (TES 1300 Thermometer, Taiwan).

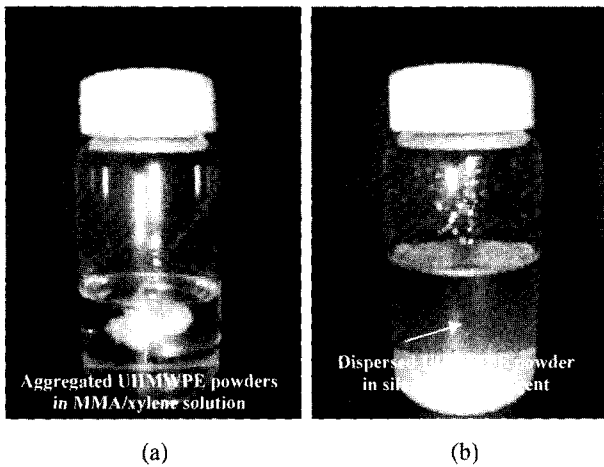


Figure 3. Aggregation phenomenon of UHMWPE powders with (a) TSL 8340[®] and (b) MMA/xylene solution.

Results and Discussion

Surface Morphology of Virgin and the Surface-Modified UHMWPE Powder. As shown in Figure 3(a), in our previous study, UHMWPE powders were surface-modified

by means of MMA/xylene solution, they had a difficulty in precoating MMA to the surface of UHMWPE powder because UHMWPE powders were aggregated in the near or below of their melting point.³⁵ But, in our present study, it could confirm that TSL 8331[®] and TSL 8340[®] prevent UHMWPE powders from aggregating and the powders were uniformly surface-modified, as shown in Figure 3(b). UHMWPE powder characterizes white color having a variety of diameters from 63 to 250 μm . At low magnification, it only characterizes a particle with rounded shape. But, at high magnification, the complicated form revealed from the powder surface. The shape of UHMWPE powder is an intricate hierarchy. It consisted of three kinds of characteristic such as fibril, nodules, and three dimensional networks. Nodules which are less than 1 μm of diameter connected with very thin fibrils and three dimensional networks are formed by means of the aggregation of many of the nodules and fibriles.³⁴ As shown in Figure 4(a), the surface of virgin UHMWPE powder exists in microscopic porous structure. This is generated by means of hydrodynamic shear field during polymerization reaction. In particular, when UHMWPE powder was surface-modified by means of the mixture of 5 vol% of TSL 8340[®], 95 vol% of acetone, and 5 vol% of distilled water, the surface revealed roughness, as

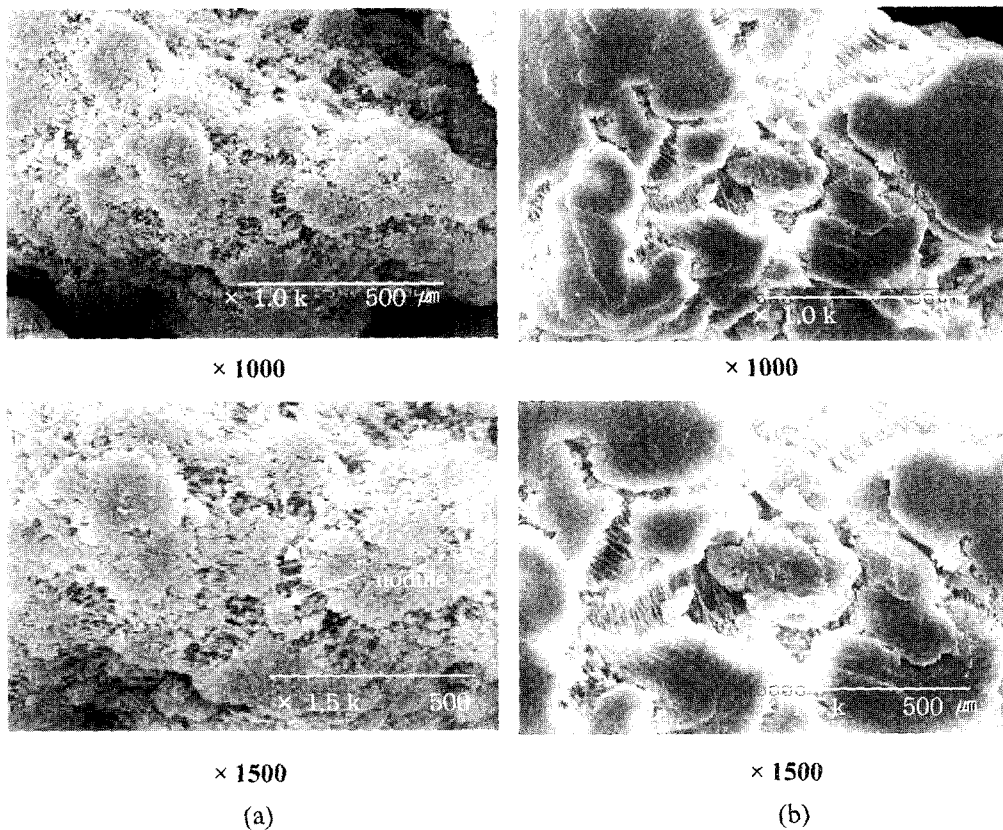
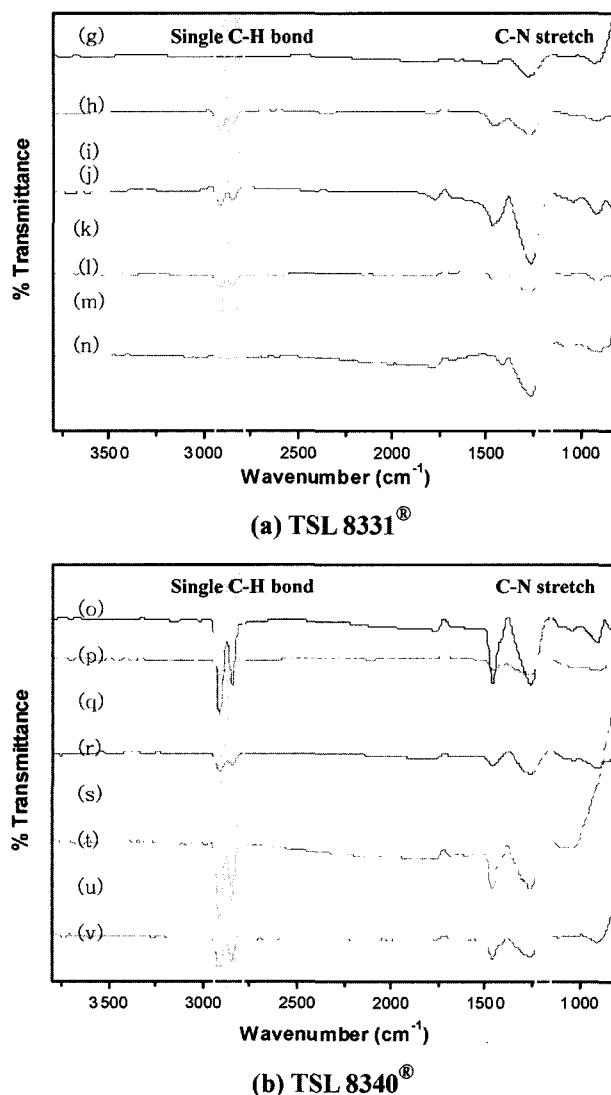


Figure 4. SEM microphotographs of (a) the surface morphology of virgin UHMWPE powder and (b) the UHMWPE powder surface-modified with TSL 8340[®] under acetone.

shown in Figure 4(b). It could be expected that the surface of UHMWPE powder might accelerate the physical coating with TSL 8340[®]. Also, the hydrophilic nature of the best surface-coated UHMWPE powder with TSL 8340[®] might increase the inducement of molecular interaction with PMMA bone cement.

Changes of the Chemical Composition of the Surface-Modified UHMWPE Powder with TSL 8331[®] and TSL 8340[®]. FTIR-ATR characterization was analyzed to confirm how to link between UHMWPE powder and two kinds of silane coupling agent. Figure 5(a) and (b) are the FTIR-ATR characterization of the UHMWPE powder surface-modified with TSL 8331[®] and TSL 8340[®], respectively. Carbon-hydrogen (C-H, 3000 cm⁻¹) bond is the main characteristic of UHMWPE powder and TSL 8331[®] and TSL 8340[®] with amino group represent carbene-nitrogen (C-N, 1000-1350 cm⁻¹) stretch bond.⁴⁰ The existence of the peak of C-N stretch might be indicated that TSL 8331[®] and TSL 8340[®] were surface-precoated on UHMWPE powder. But, it was confirmed that the formation of chemical reaction as well as silanol group did not produce between the interface of the powder and TSL 8331[®] and TSL 8340[®]. It was expected that the surface of UHMWPE powder is roughed by means of ethanol and acetone, hence, mechanical interlocking is only formed by means of soaking TSL 8331[®] and TSL 8340[®] into the expanded surface of UHMWPE powder between the powder. But, the amino group of TSL 8331[®] and TSL 8340[®] might produce strong chemical bonding with conventional PMMA bone cement. Figure 6 is the presumptive picture representing interface bonding between conventional PMMA bone cement, the two kinds of silane coupling agent, and UHMWPE powder. The hydrophobic surface of UHMWPE powder might be connected with the hydrophobic part of TSL 8331[®] and TSL 8340[®] by means of hydrophobic force and covalent bond might be produced among the two kinds of silane coupling agent with amino group and conventional PMMA bone cement.

Tensile Strength Measurement. As shown in Table II and Figure 7, the tensile strengths of 3 wt% of the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®] impregnated composite PMMA bone cements revealed more similar than that of conventional PMMA bone cement. In particular, it was confirmed that the tensile strength of 3 wt% of the UHMWPE powder surface-modified with the mixture of 95 vol% of acetone, 5 vol% of distilled water, and 5 vol% of TSL 8340[®] impregnated composite PMMA bone cement significantly revealed higher than that of conventional PMMA bone cement. Also, the tensile strengths of 3 wt% of the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®] mixed with acetone impregnated PMMA bone cements were much higher than those of ethanol. Pluedemann proposed the hydrolyzation mechanism of silane coupling agent. The methoxy (-OCH₃) group of TSL 8340[®] or



- (g) 95 vol% ethanol and 0.5 vol% TSL 8331[®] (o) 95 vol% ethanol and 0.5 vol% TSL 8340[®]
 (h) 95 vol% ethanol and 1 vol% TSL 8331[®] (p) 95 vol% ethanol and 1 vol% TSL 8340[®]
 (i) 95 vol% ethanol and 2.5 vol% TSL 8331[®] (q) 95 vol% ethanol and 2.5 vol% TSL 8340[®]
 (j) 95 vol% ethanol and 5 vol% TSL 8331[®] (r) 95 vol% ethanol and 5 vol% TSL 8340[®]
 (k) 95 vol% acetone and 0.5 vol% TSL 8331[®] (s) 95 vol% acetone and 0.5 vol% TSL 8340[®]
 (l) 95 vol% acetone and 1 vol% TSL 8331[®] (t) 95 vol% acetone and 1 vol% TSL 8340[®]
 (m) 95 vol% acetone and 2.5 vol% TSL 8331[®] (u) 95 vol% acetone and 2.5 vol% TSL 8340[®]
 (n) 95 vol% acetone and 5 vol% TSL 8331[®] (v) 95 vol% acetone and 5 vol% TSL 8340[®]

Figure 5. FTIR-ATR scanning of the UHMWPE powder surface-modified with (a) TSL 8331[®] and (b) TSL 8340[®].

the ethoxy (-OC₂H₅) group of TSL 8331[®] are hydrolyzed to silanol group (SiOH) by means of moisture in many solvents. According to this mechanism, the existence of water is important to produce the silanol of silane coupling agent. Because of the fact, the formation of silanol is carried out under the mixture of organic solvent and water.³⁹ From our

Table II. Tensile Strengths of 3 wt% of the UHMWPE Powder Surface-Modified with Various Ratios of TSL 8331[®] and TSL 8340[®] Impregnated Composite PMMA Bone Cements

Content of TSL 8331 [®] / TSL 8340 [®] (vol%)	TSL 8331 [®] (ethanol/acetone)	<i>P</i> value ^a (ethanol/acetone)	TSL 8340 [®] (ethanol/acetone)	<i>P</i> value (ethanol/acetone)
S1	44.5±1.78	.	44.5±1.78	.
S2	33.8±2.5	0.09	33.8±2.5	0.09
0.5	44.97±2.56/ 47.93±0.41	0.004*/0.024*	43.14±1.52/ 46.28±1.32	0.01*/0.013*
1	45.05±0.73/ 47.24±2.23	0.004*/0.019*	45.15±0.79/ 46.64±1.82	0.005*/0.015*
2.5	47.8±2.15/ 48.16±2.7	0.002*/0.025*	46.18±2.57/ 48.63±1.6	0.012*/0.028*
5	43.67±2.4/ 46.6±1.7	0.006*/0.015*	45±1/ 49.05±2.27	0.004*/0.031*

^aSignificant difference, *p*<0.05 compared than standard (S2).

S1: conventional PMMA bone cement. S2: 3 wt% of unmodified UHMWPE powder impregnated composite PMMA bone cement.

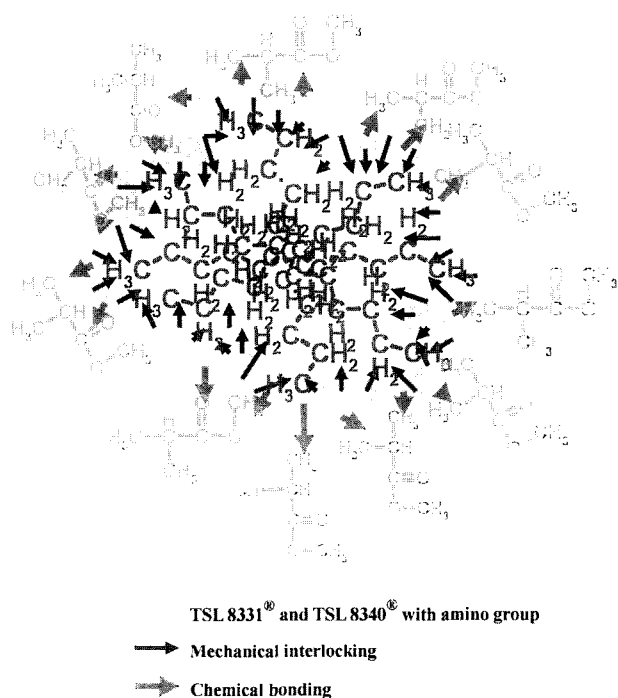
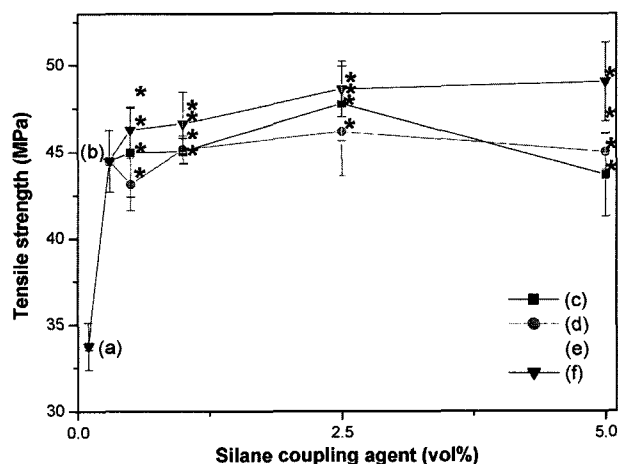


Figure 6. Expected interfacial bonding mechanism of the UHMWPE powder surface-modified with (a) TSL 8331[®] and (b) TSL 8340[®].

present study, Le Chatelier's principle⁴¹ was applied to explain that the formation of silanol group is more active under acetone than under ethanol. TSL 8331[®] and TSL 8340[®] are hydrolyzed with water. So, silanol groups such as silanol, silandiol, and silantriol are produced, as shown in Figure 8. But, the reversible reaction of silane coupling agent with ethanol is prevented from the formation of silanol group. It could indicate that the silanol group is again irreversed as the ethoxy group. But, the amount of silanol



(a) 3 wt% of no surface-modified UHMWPE powder impregnated PMMA bone cement
 (b) conventional PMMA bone cement
 (c) TSL 8331[®] (ethanol)
 (d) TSL 8340[®] (ethanol)
 (e) TSL 8331[®] (acetone)
 (f) TSL 8340[®] (acetone)

Figure 7. Tensile strengths of 3 wt% of the UHMWPE powder surface-modified with TSL 8331[®] and TSL 8340[®] with amino group impregnated composite PMMA bone cement.

group is much higher under acetone than under ethanol because the irreversible reaction of silanol coupling agent do not happen. So, from the produced silanol group, strong mechanical interlocking can be generated between silane coupling agent and UHMWPE powder. After all, the more the amount of silanol group is increased, the more the adhesion of UHMWPE powder with silane coupling agent is improved. Also, amino group accelerates silane absorption for the purpose of the good adhesion of conventional PMMA bone cement with UHMWPE powder and the tensile strength of the UHMWPE powder surface-modified

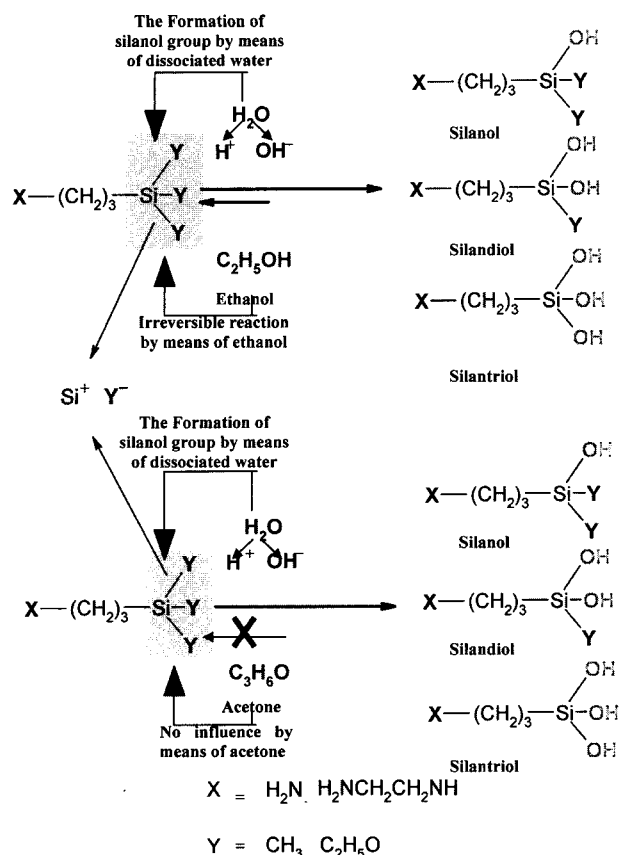
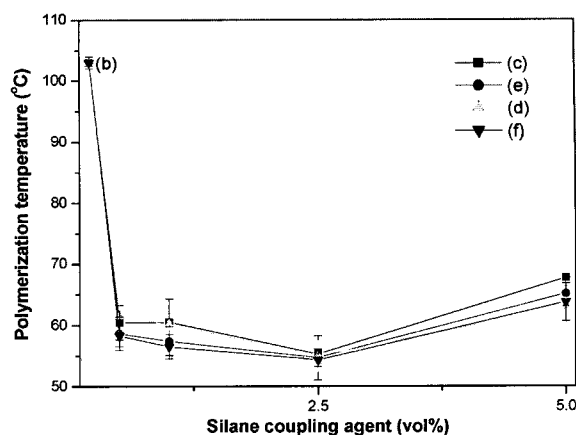


Figure 8. Expected mechanism of the silanol formation of TSL 8331[®] and TSL 8340[®].

with silane coupling agent with amino group impregnated composite PMMA bone cement is improved.⁴² It was confirmed that the type of solvent and the existence of the amino group of silane coupling agent play an important factor in the improvement of the tensile strength of the composite PMMA bone cement.

Curing Temperature Measurement. Another problem of conventional PMMA bone cement is thermal cellular necrosis resulting from high curing temperature (above 100 °C). As shown in Table III and Figure 9, the curing temperatures of 3 wt% of the UHMWPE powder surface-modified with various ratios of TSL 8331[®] and TSL 8340[®] impregnated composite PMMA bone cements were much lower



(b) conventional PMMA bone cement
(c) TSL 8331[®] (ethanol)
(d) TSL 8340[®] (ethanol)
(e) TSL 8331[®] (acetone)
(f) TSL 8340[®] (acetone)

Figure 9. Curing temperatures of 3 wt% of the UHMWPE powder surface-modified with TSL 8331[®] and TSL 8340[®] with amino group impregnated composite PMMA bone cement.

than that of conventional PMMA bone cement. However, the content of TSL 8331[®] and TSL 8340[®] has not a comprehensive influence on the reduction of the curing temperature of the composite PMMA bone cements. It could be expected that UHMWPE powders only acted as heat sink pool resulting in lowering curing temperatures of the composite PMMA bone cements.

Conclusions

Conventional PMMA bone cement has been extensively introduced as a hopeful biopolymeric material to many patients suffering from hip joint damage. But, it induced short longevity due to a lot of problems such as thermal cellular necrosis resulted from high curing temperature, chemical cellular necrosis from unreacted MMA liquid, and the formation of shrinkage or bubble from sharp polymerization velocity. In the present study, the UHMWPE powder surface-modified with TSL 8331[®] and TSL 8340[®] with amino group was introduced to overcome these disadvantages. The

Table III. Curing Temperatures of 3 wt% of the UHMWPE Powder Surface-Modified with Various Ratios of TSL 8331[®] and TSL 8340[®] Impregnated Composite PMMA Bone Cements

Content of TSL 8331 [®] / TSL 8340 [®] (vol%)	TSL 8331 [®] (ethanol)	TSL 8331 [®] (acetone)	TSL 8340 [®] (ethanol)	TSL 8340 [®] (acetone)
S1	103±1	103±1	103±1	103±1
0.5	60.5±2.8	58.7±2.7	61.5±2.4	58.3±1.7
1	60.5±3.8	57.4±2.3	60.2±0.5	56.5±2
2.5	55.3±0.8	54.7±3.6	55±2.6	54.3±1.1
5	67.7±0.1	65.1±2.1	63±3.3	63.7±3.1

curing temperatures (58.7-66.7 °C) of 3 wt% of the UHMWPE powder surface-modified with TSL 8331® and TSL 8340® impregnated composite PMMA bone cements were much lower than that (above 100 °C) of conventional PMMA bone cement. But, the tensile strengths of the composite PMMA bone cements were similar to that of conventional PMMA bone cement. Studies such as the confirmation of silanol group formation of the surface-precoated UHMWPE powder with silane coupling agent through diffuse reflectance (DRIFT) measurement and fatigue test for the aging effect of the hybrid composites are in progress.

Acknowledgements. This work was supported by Nano Science Core Fundamental Laboratory of KMOST (2004-01352).

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