*The Korean Journal of Ceramics*, 5[3] 265-269 (1999)

# Apatite Formation on Polyethylene Modified with Silanols by Grafting of Vinyltrimethoxysilane and Subsequent Hydrolysis

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(Received September 23, 1998)

Polyethylene was modified with silanol groups on its surface by photografting of vinyltrimethoxysilane in vapor phase by using benzophenon as a polymerization initiator and by hydrolyzing the methoxysilane groups into the silanol groups with HCl solution. The modified polyethylene formed a dense and homogeneous apatite layer on its surface in a solution with ion concentrations 1.5 times those of human blood plasma within 21 days. This kind of biomimetic process could provide techniques for fabricating apatite-polymer composites with three dimensional structure analogous to the natural bone.

***Key words :*** Polyethylene, Photografting, Silanol (Si-OH) groups, Simulated body fluid (SBF), Apatite, Apatite-polymer composite

## I. Introduction

An artificial bone substitute material is highly recommended to possess mechanical properties analogous to bone, i.e., a fairly high fracture toughness (2-12 MPa) and a fairly low elastic modulus (7-30 GPa) as well as bioactivity. The bone is a composite in which inorganic apatite crystallites are deposited on organic collagen fibers to be built up into a three dimensional structure. This composite structure of bone is responsible for its unique mechanical properties and bioactivity. An apatite-organic polymer composite with three dimensional structure analogous to that of bone is therefore believed to be truly useful for bone substitutes.

The present authors early proposed a potentially probable biomimetic process to fabricate such apatite-organic polymer composites as follows.[1] An organic polymer is set in contact with particles of a CaO, $SiO_2$-based glass soaked in a simulated body fluid (first treatment): silicate ions containing silanol groups are released from the glass to be adsorbed on the surface of polymer, and then the silanol groups induce apatite nucleation at the surface. The polymer is next soaked in another solution highly supersaturated with respect to the apatite (second treatment): the apatite nuclei formed at the first treatment grow on the surface of polymer *in situ* to form an apatite layer. This process provides a dense and uniform bonelike apatite layer with desired thickness on any kinds of organic polymers.[2] Adhesion of the apatite layer to the polymer substrate could be appreciably improved by a surface treatment, e.g., a glow discharge treatment, prior to the apatite nucleation on their surfaces.[3-6]

A technical problem of the above biomimetic process is that it produces apatite layer only on the surface of polymer faced to the nucleation agent of apatite, i.e., the CaO, $SiO_2$-based glass, in the first treatment. If a solution or vapor phase could be used to form Si-OH groups onto a polymer, such techniques might be much more probable to prepare an apatite-polymer composite with three dimensional structure analogous to the natural bone. On the other hand, so-called photografting techniques to form specific functional groups from its monomer precusors onto polymer are being actively researched in the field of polymer industry.[7-10] The purpose of the present study is to attempt an advanced biomimetic process for the apatite formation on a polymer through such techniques. Surface of polyethylene was modified with silanol groups by photografting vinyltrimethoxysilane in vapor phase and subsequently hydrolyzing it into Si-OH groups with HCl solution. Apatite formation on the polyethylene thus modified was investigated in a solution highly supersaturated with respect to the apatite.

## II. Experimental Procedure

Low density (Mw=34,000) polyethylene (PE; Sumitomo Chem. Ind., Japan) was hot-pressed at 170°C to be cut into substrates $10 \times 10 \times 1\ mm^3$ in size. The PE substrates were abraded with No. 400 diamond paste, ultasonically washed with acetone and ethanol, and dried at 40°C for 24 h.

Photografting on the PE substrates was performed by

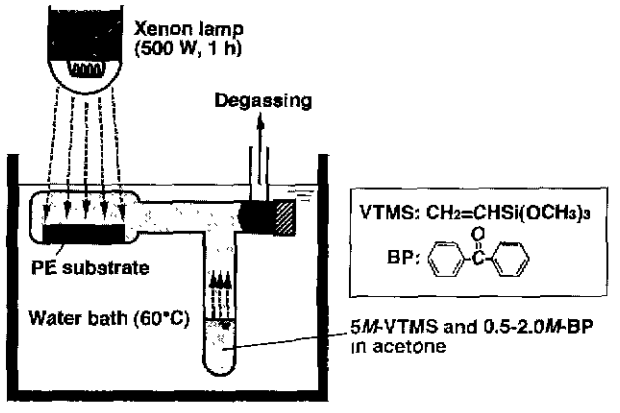



**Fig. 1.** Materials and method for vapor phase photografting of VTMS onto PE substrate by using BP as a polymerization initiator.

using silane coupling agent of vinyltrimethoxysilane (VTMS: Chisso Co., Japan) as the monomer, benzophenon (BP; Nacalai Tesque Ltd., Japan) as photoinitiator and dehydrated acetone (Wako Pure Chemical Ind. Co., Japan) as solvent. The substrate was placed with 5M-VTMS and 0.5-2.0M-BP acetone solution in a Pyrex® glass reaction chamber as shown in Fig. 1. The reaction chamber was priorly frozen in liquid $N_2$ to be degassed, and kept at 80°C for 15 min to vaporize the solution. The surface of substrate was then irradiated for photopolymerization of the vapor phase with xenon lamp at 500 W for 1 h. The substrate was soaked in dehydrated acetone for 3 h, and dried for 24 h *in vacuo*.

The PE substrates after the above VTMS grafting were subsequently subjected to surface hydrolysis by soaking in 1.0M-HCl solution at 60°C for 5 days, washed with distilled water, and dried at 40°C for 24 h.

The PE substrates after the VTMS grafting and subsequent hydrolysis were soaked in solution (1.5SBF) with ion concentrations ($Na^+$ 213.0, $K^+$ 7.5, $Mg^{2+}$ 2.3, $Ca^{2+}$ 3.8, $Cl^-$ 223.0, $HCO^{3-}$ 6.3, $HPO_4^{2-}$ 1.5, $SO_4^{2-}$ 0.75 mM) 1.5 times those of human blood plasma at 36.5°C for various periods. The 1.5SBF was prepared by dissolving reagent-grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4$ $3H_2O$, $MgCl_2$ $6H_2O$, $CaCl_2$ and $Na_2SO_4$ into distilled water, and buffered at pH 7.40 with tris-hydroxymethylaminomethane ($(CH_2OH)_3CNH_3$) and hydrochloric acid at 36.5°C.

The surface of PE substrate after the VTMS grafting and subsequent hydrolysis was analyzed by Fourier transform infrared attenuated total reflection spectroscopy (FT-IR ATR; FT-IR 2000, Perkin-Elmer Ltd., England) and X-ray photoelectron spectroscopy (XPS; Model MT5500, ULVAC-PHI Co., Japan). The surface of PE substrate after soaking in 1.5SBF was analyzed by scanning electron microscopy (SEM; Model S2500CX, Hitachi Co., Japan), thin-film X-ray diffraction (TF-XRD; Model 2651A1, Rigaku Co., Japan) and Fourier transform infrared reflection spectroscopy (FT-IR; Perkin-Elmer Ltd., England).

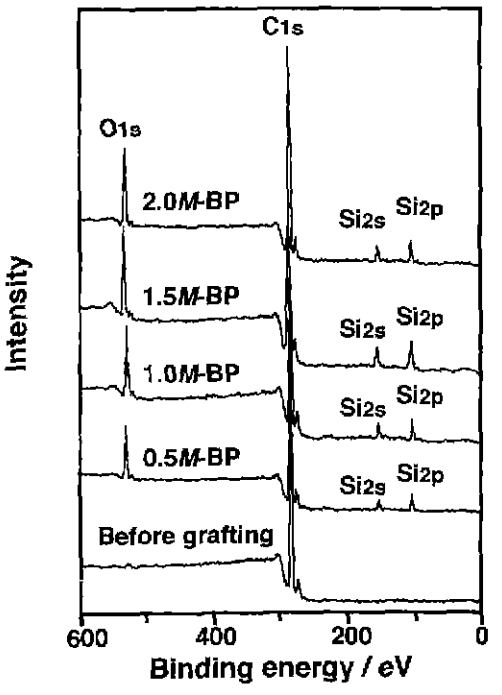



**Fig. 2.** XPS spectra of the surfaces of PE substrates before and after VTMS grafting in the presence of BP with various concentrations.

## III. Results and Discussion

Fig. 2 shows XPS spectra of the surfaces of PE substrates before and after VTMS grafting in the presence of BP with various concentrations. Revelations of peaks due to $Si_{2s}$, $Si_{2p}$ and $O_{1s}$ after the photografting indicate that the VTMS was successfully grafted on the surface of PE

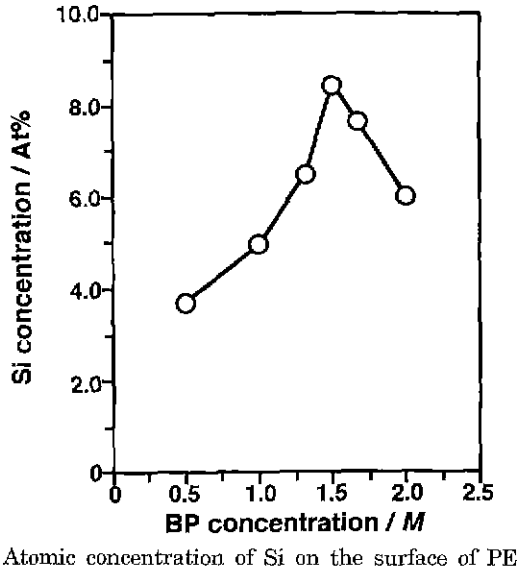



**Fig. 3.** Atomic concentration of Si on the surface of PE substrate after VTMS photografting as a function of BP concentration.

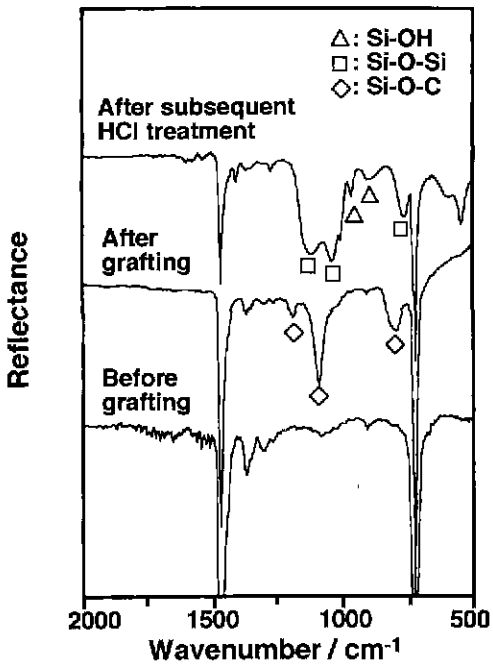



**Fig. 4.** FT-IR ATR spectra of the surfaces of PE substrates before and after VTMS grafting in the presence of 1.5M-BP and subsequent 1.0M-HCl treatment.

substrate.

Fig. 3 shows atomic concentration of Si on the surface of PE substrate after VTMS photografting as a function of BP concentration. The Si concentrations were calculated from the $Si_{2s}$ and $Si_{2p}$ XPS spectra shown in Fig. 2. The Si concentration was shown to appreciably increase with photoinitiator BP concentration and be maximized at 1.5M-BP.

Fig. 4 shows FT-IR ATR spectra of the surfaces of PE substrates before and after VTMS grafting in the presence of 1.5M-BP and subsequent 1.0M-HCl treatment. IR peaks appeared after the VTMS grafting were ascribed to Si-O-C bonds which were assumed to be due to methoxysilyl ($Si\text{-}OCH_3$) groups on the substrate. They were disappeared to change into those ascribed to siloxane (Si-O-Si) and silanol (Si-OH) bonds by the subsequent HCl treatment.

Fig. 5 shows SEM photographs of the surfaces of PE substrates which were soaked in 1.5SBF for various periods after VTMS grafting in the presence of 1.5M-BP and subsequent 1.0M-HCl treatment. Some spherulites were observed to be formed on the substrate after soaking in SBF for 5 d. Further increase in the soaking time made the spherulites gradually grow into uniform and dense surface layer.

Fig. 6 shows TF-XRD patterns and FT-IR reflection spectra of the surfaces of PE substrates which were soaked in 1.5SBF for various periods after VTMS grafting in the presence of 1.5M-BP and subsequent 1.0M-HCl treatment. All the XRD and IR peaks appeared after the soaking in 1.5SBF were ascribed to crystalline apatite, indicating that the surface layer observed in Fig. 5 is an apatite layer.

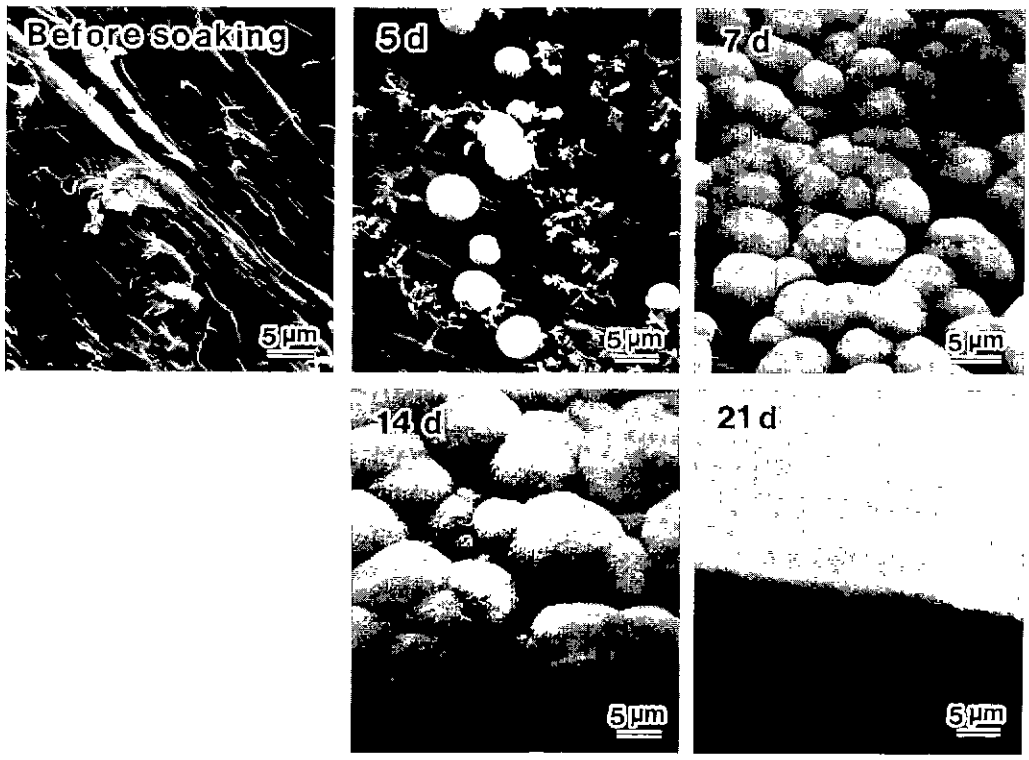



**Fig. 5.** SEM photographs of the surfaces of PE substrates which were soaked in 1.5SBF for various periods after VTMS grafting in the presence of 1.5M-BP and subsequent 1.0M-HCl treatment.

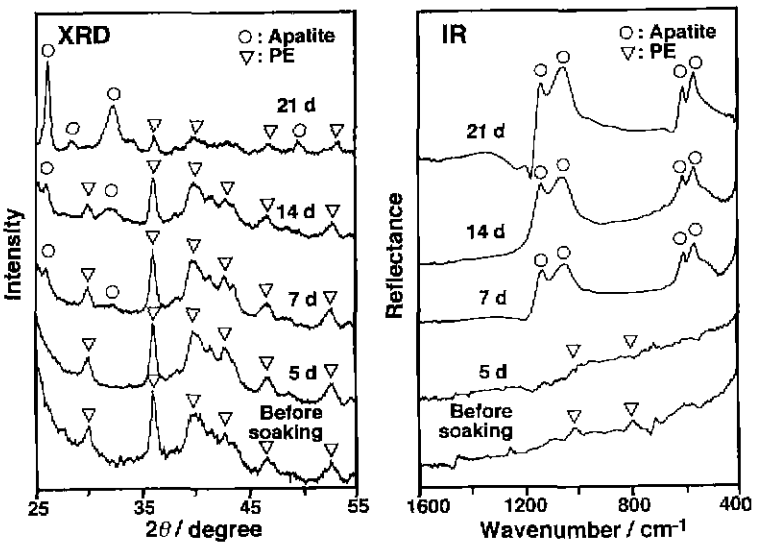
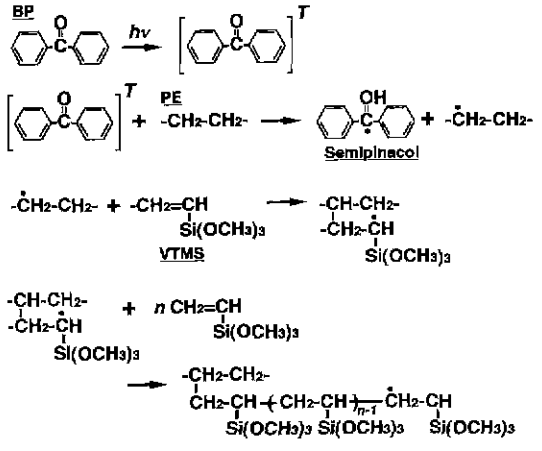
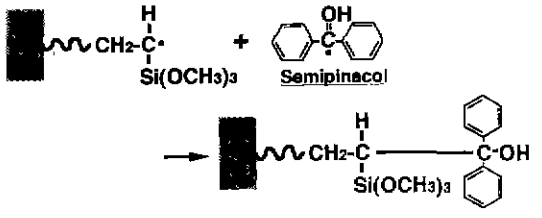



**Fig. 6.** TF-XRD patterns and FT-IR reflection spectra of the surfaces of PE substrates which were soaked in 1.5SBF for various periods after VTMS grafting in the presence of 1.5M-BP and subsequent 1.0M-HCl treatment.

*It is apparent from the above results that Si-OH groups* able to induce apatite formation are successfully formed on the surface of PE by photografting of VTMS and subsequent hydrolysis. The photopolymerization of VTMS on the surface of PE is assumed to proceed via (1) ultraviolet absorption of BP (2) to abstract hydrogen from PE to generate radicals on both the PE and BP, (3) grafting of the VTMS to the radical on PE to generate radical on VTMS, and (4) propagation reaction to consecutively polymerize VTMS on the radical.[7]




(5) The propagation reaction (4) is terminated by bonding *of the semipinacol free radical of BP in reaction (2) to* a radical on VTMS.[9]




The photopolymerized amount of VTMS onto PE was shown to be maximized at 1.5M-BP (Fig. 3). It is speculated that the reaction (2) or (5) is dominant respectively below or above this BP concentration. The Si-$OCH_3$ groups in thus grafted chain on PE are almost perfectly hydrolyzed to form Si-O-Si and Si-OH bonds by the subsequent HCl treatment (Fig. 4).

The PE substrate modified in this way successfully forms an apatite layer on its surface in 1.5SBF (Figs. 5 and 6). The apatite formation is assumed to be initiated by apatite nucleation induced by the Si-OH groups which are formed on the PE substrate via the above method. Since the body fluid, therefore SBF with ion concentrations nearly equal to those of the body fluid, is metastably supersaturated with respect to the apatite, 1.5SBF is much more highly supersaturated with respect to the apatite.[11,12] Therefore, once the apatite nuclei are formed, they spontaneously grow by consuming calcium and phosphate ions from the 1.5SBF with soaking period. The growth of apatite nuclei eventually results in a extremely dense and uniform apatite surface layer on PE substrate (Fig. 6).

Significant merit of the above kind of surface modification of polymer is that such method allows very uniform formation of Si-OH groups even on the surfaces of polymer bulks or fabrics with complex shapes, thereby inducing a uniform apatite formation just according to the surface shape. *This types of surface modification of a polymer* and subsequent apatite formation on its surface is therefore believed to provide an apatite-polymer composites with mechanical properties analogous to natural bone and thus truly useful for bone substitutes. It should be noted, however, that the apatite formed in 1.5SBF is a lit-

tle different from the bone apatite in its structure and composition.[17] In order to obtain the apatite identical to the bone apatite, apatite must be formed in the SBF with equal concentrations to those of human blood plasma. Some surface modification is further needed for depositing the bonelike apatite on the polymer surfaces.

## IV. Conclusions

Polyethylene substrate successfully formed a dense and uniform apatite layer on its surface, when it is priorly modified with silanol groups on its surface by photografting vinyltrimethoxysilane and hydrolyzing the methoxysilane groups into the silanol groups with HCl solution. Since this kind of process could be applied even to polymers with complex shapes, it is believed to provide an apatite-polymer composites with three dimensional structure analogous to natural bone.

## Acknowledgments

This study was supported by Grant-in-Aid for Scientific Research, the Ministry of Education, Science, Sports and Culture, Japan.

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