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표면개질과 보강제를 이용한 의료용 접착제의 기계적 특성 향상

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Improvement of Mechanical Properties of Bone Cement by Surface Modification and Reinforcement

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요 약 : 저온 플라스마 공정을 이용하여 X-ray 비투과성 분말의 표면을 개질시키고, 소량의 운모, Kevlar 섬유, 유리 섬유, 탄소 섬유, 잘게 간 탄소 섬유 등을 보강제로 사용하여 의료용 아크릴 접착제의 기계적 특성을 향상시키고자 하였다. X-ray 비투과성 분말은 접착제가 굳은 후 인장강도와 피로강도를 저하시키는 요인이 되었으나 HMDSO/AA 플라스마로 표면을 개질시켜 접착제 기질과의 적합성을 높인 후에는 보강제 역할을 하였다. 잘게 간 탄소 섬유는 표면개질을 시켜 접착제 기질과의 적합성을 좋게 할 경우에 접착제의 피로강도를 크게 향상시켰다.

Abstract : Improvement of mechanical properties of acrylic bone cement was tried by surface modification of radiopaque powder using a low temperature plasma process and by reinforcement with small amount of mica flake, Kevlar fiber, glass fiber, carbon fiber, or milled carbon fiber. Radiopaque powder which caused the reduction of tensile strength and fatigue strength of cured bone cement became a reinforcing material after it was surface-modified with HMDSO/AA plasma to be compatible with the matrix. Fatigue strength could be greatly improved by milled carbon fiber, but only after it was surface-modified to be compatible with the matrix.

Keywords : *bone cement, plasma, surface modification, reinforcement.*

INTRODUCTION

Acrylic bone cement is a medical glue used for the firm fixation of orthopaedic implants such as partial or total hip prostheses or for the stabilization of pathogenic fractures. It serves as an interfacial bonding between an implant and a natural bone. It also eliminates high contact-stress points which cause earlier failure of the implant and smoothly transfers applied loads during body movements from the implant to the bone.

The bone cement is primarily made of poly (methylmethacylate)(PMMA) powder and methylmethacrylate(MMA) liquid monomer.[1] The PMMA powder and the liquid monomer are

mixed together with initiator and promoter before the surgical application. Upon mixing, the monomer starts to polymerize and the mixture is self-cured in the cavity between an implant and a natural bone after being injected into a body. In clinical applications, small amount of radiopaque powder(powder which is not transparent to X-ray) such as ZrO_2 or $BaSO_4$ is mixed together for postoperative X-ray follow-ups.

The bone cement has been used with a relatively high success rate since the pioneering work of Charnley in the late 1950s.[2, 3] However, there are still a number of problems encountered. The bone cement often shows premature failure and breaks in one out of three patients within three to four years or in 57% of patients after five years, depending on age and weight.[4, 5] The failures can also cause important long-term complications not to mention resurgery. For instance, wear particles from the fractured bone cement can lead to the release of bone-resorbing factors, which results in deteriorative osteolysis.[6, 7] Therefore, development of a high-performance bone cement is of prime importance for successful joint replacement surgeries.

Several approaches have been tried to improve the performance of the bone cement.[8~17] Among them, reinforcement with fillers has attracted special attention since the failures are closely related to the poor mechanical properties, especially fatigue property, of the bone cement, whether they were initiated by crack formation in the bone cement or by debonding of the bone cement from the implant or from the bone. Consequently, addition of various kinds of fillers such as polymeric and metallic fibers and rubbers has been tried. However, the results were not so good as expected, which can be explained by the poor compatibility between MMA or PMMA and the fillers.

This study deals with the improvement of mechanical properties, especially fatigue strength, of the acrylic bone cement. The improvement of mechanical properties is approached in two steps. In the first step, radiopaque powder is surface-modified by the low temperature process to improve its compatibility with MMA or PMMA. In the second step, fillers are added for the reinforcement after being surface-modified.

EXPERIMENTAL

Materials. PMMA powder(IF850, M.W. of 90,000 particle size of 300-400μm and MMA(purified by distillation) was purchased from LG chemical and LG MMA, respectively and used as received. Benzoylperoxide(BPO) which was used as an initiator for the polymerization of MMA was purchased from Fluoka. N,N-Dimethyl-p-toluidine(DMPT) which was used as a promoter was purchased from Aldrich. Radiopaque powders, ZrO_2 and $BaSO_4$, were purchased from Aldrich.

Fillers for the reinforcement were mica flake (Mica Supplies), glass fiber(LG Owens Corning), Kevlar 29 fiber(DuPont), carbon fiber (Toray), and milled carbon fiber(Zoltec). Long fibers, glass fiber, Kevlar, and carbon fiber, were cut into a small size of approximately 2 mm so that these fillers do not interfere with the flow of bone cement when it is injected into the cavity in clinical applications.

Plasma Treatments. Two kinds of R. F. (radio frequency, 13.56 MHz) plasma reactors were used in this study. Long fibers were treat-

ed in a custom-made barrel-type multi-purpose reactor and cut into a small size after the treatment. Radiopaque powders, mica flakes, and milled carbon fibers were treated in a custom-made powder treatment reactor which is shown in Figure 1. During plasma treatment, the baffled glass chamber in the powder treatment reactor rotates in 30 r.p.m. so that all the powders are uniformly treated. Those reactors are evacuated to less than 6.65 Pa before the introduction of monomer or gas for plasma treatment.

Monomers and gas for plasma treatment were hexamethyldisiloxane(HMDSO), acrylic acid(AA), MMA and oxygen. They were purchased from Aldrich, Junsei Chemical, LG MMA, and Dae Chang Gas, respectively.

Sample Preparation and Tests. Bone cement was formulated by mixing 2 part of PMMA powder which contains small amount of BPO with 1 part of MMA liquid monomer which contains small amount of DMPT at room temperature. In this mixture, radioapque powders were added as much as 20 wt% of PMMA powder. The mixture was stirred for 2 minutes and kept until it reached a dough-state. Then, the mixture was poured into a molder to make test samples of dog-bone shape(150 mm long and 5 mm thick).

Mechanical properties of cured bone cements were evaluated by measuring ultimate tensile strength, fatigue strength, and impact strength. Ultimate tensile strength was measured using an Instron(AGS-500D, Shimadzu, Japan) with a head speed of 10 mm/min. Fatigue strength was determined by measuring the total number of fatigue cycles to fracture using a custom-made fatigue tester(Figure 2) in which samples rotate at 60 r.p.m. with a weight of 533 g attached 80 mm away from the breaking point (fully reversed tension-compression fatigue at ±9.6 MPa and 1 Hz).

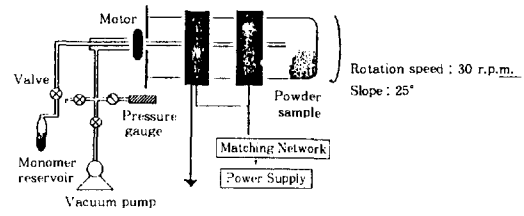

Fig. 1. Schematic diagram of the powder treatment plasma reactor; reactor volume:1,400cm^3.

RESULTS AND DISCUSSION

Effects of BPO and DMPT Amounts on Mechanical Properties of Bone Cement. Amounts of an initiator and a promoter added for the polymerization of MMA at room temperature influence the curing time(characterized by dough time) and the mechanical properties of bone cement. Since there has been no agreement on their proper amounts,[18, 19] effects of their amounts were investigated by varying their amounts from 0.5 wt% to 3.0 wt% of MMA for BPO(initiator) and from 0.7 wt% to 2.0 wt% for DMPT(promoter) to fix the formulation before any further study.

Dough time depended highly on the DMPT amount but not much on the BPO amount. The dough time and the DMPT amount were inversely proportional, as shown in Figure 3. Considering handling time during clinical applications, bone cements which contain more than 1.0 wt% of DMPT seem to have too short dough time. And, the best tensile strength and fatigue strength of cured bone cement were obtained with a bone cement which contained 1.0 wt% of

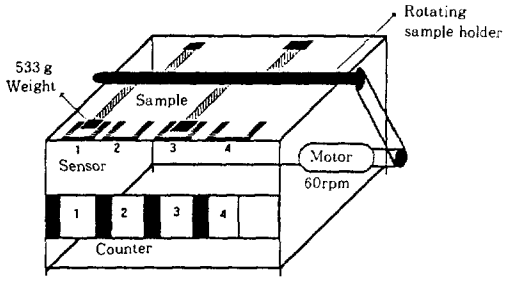

Fig. 2. Schematic diagram of the fatigue tester.

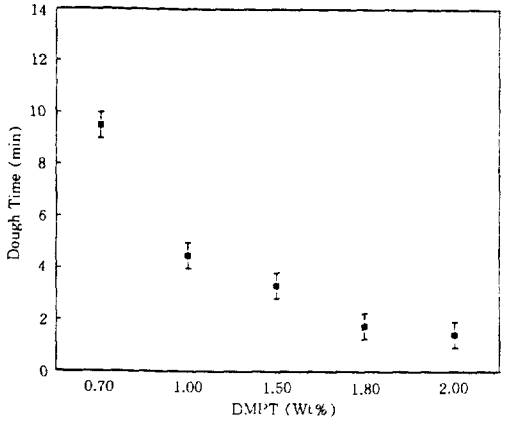

Fig. 3. Effect of DMPT amount on the dough time of bone cement.

DMPT and 2.0 wt% of BPO although there were no large differences. Therefore, these percentages were fixed as the amount of DMPT and BPO in further study.

Besides the mechanical properties, an important thing to be considered for the clinical application of bone cement is temperature-rise during the curing of bone cement. If temperature rises too high, tissues can be damaged.

The temperature-rise was monitored with a model shown in Figure 4 for our bone cement and commercial bone cement(Simplex P) for comparison. In both cases, the maximum temperature was 42 ℃. A conservative guideline used by authorities for tissue damage temperature is around 56 ℃.[20] The temperature reached the maximum at 13 minutes after the mixing in case of our bone cement while temperature reached the maximum at 20 minutes after the mixing in case of commercial bone cement.

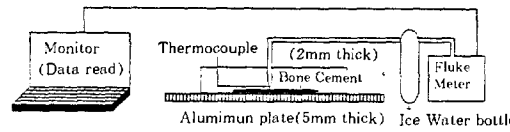

Fig. 4. Schematic diagram of the apparatus for temperature measurement during the curing of bone cement.

Effects of Surface Modifications of Radiopaque Powder on Mechanical Properties of Bone Cement. One of the major reasons why bone cement has poor mechanical properties is that radiopaque powder such as ZrO_2 or $BaSO_4$ which is added for postoperative X-ray follow-ups causes the reduction of mechanical strengths of cured bone cement. This is shown in Table 1. ZrO_2 reduced the ultimate tensile strength of PMMA by 17.3% and the fatigue strength by 12.2%. $BaSO_4$ reduced the ultimate tensile strength by 25.7% and the fatigue strength by 39%.

This is not a matter of bulk properties of the radiopaque powders but an interfacial problem between the radiopaque powder and the matrix of bone cement. The radiopaque powders are inorganic materials which have quite different chemical structures from that of organic MMA or PMMA. The dissimilarity causes poor compatibility of the radiopaque powders with MMA or PMMA, which results in poor dispersion in MMA and poor adhesion with PMMA of the radiopaque powders, and thus poor mechanical properties of cured bone cement. This means that mechanical properties of bone cement can

Table 1. Ultimate Tensile Strengths and Fatigue Strengths of Various Bone Cements

Type of Sample	Plasma Treatment	UTS (MPa)[a]	Fatigue Cycles[b]
PMMA+MMA	none	39.3	385135
PMMA+MMA+ZrO_2	none	32.5	338196
PMMA+MMA+$BaSO_4$	none	29.2	235069
PMMA+MMA+ZrO_2	AA[c]	40.7	406765
PMMA+MMA+ZrO_2	MMA[c]	40.6	418920
PMMA+MMA+ZrO_2	HMDSO[c]/AA[d]	42.9	420365
PMMA+MMA+ZrO_2	HMDSO/O[e]	37.9	373679
PMMA+MMA+$BaSO_4$	HMDSO/AA	35.0	324186
PMMA+MMA+$BaSO_4$	HMDSO/AA	27.3	402738

[a] ultimate tensile strength, average values of 2 to 3 samples.
[b] total number of fatigue cycles to fracture, average values of 3 to 4 samples.
[c] plasma condition; 30W, 66.5 Pa, 30 minutes.
[d] plasma condition; 5W, 133 Pa, 15 minutes.
[e] plasma condition; 20W, 266 Pa, 5 minutes.

be improved if the compatibility is improved.

To improve the compatibility, the radiopaque powders were surface-modified by the low temperature plasma process. An ultrathin film which has similar chemical structure to that of MMA or PMMA was deposited onto the radiopaque powders using MMA or AA as a monomer for plasma polymerization. The chemical structure of a plasma polymerized AA film analyzed by Electron Spectroscopy for Chemical Analysis(ESCA) is shown in Figure 5. The film was deposited onto a polyethylene film at the same plasma condition. It has a high content of -COO- groups. For some samples, the modification was done in double step; deposition of an HMDSO plasma film followed by the deposition of an AA plasma film or O_2 plasma treatment. Purpose of the HMDSO plasma film deposition is to improve adhesion of the AA plasma film.

The surface modification improved the compatibility of the radiopaque powders with MMA or PMMA. Surface-modified radiopaque powders showed much better dispersion in MMA, as

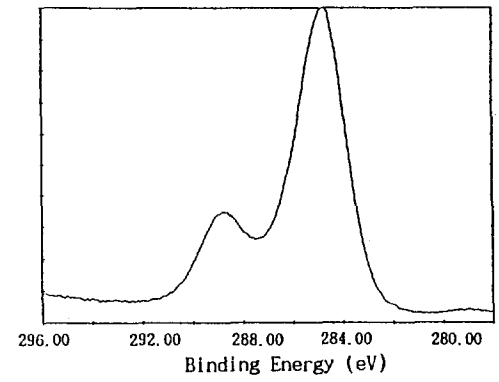

Fig. 5. ESCA C1s spectrum of a plasma polymerized AA film.

shown in Figure 6. When dropped into a cylinder which contained MMA liquid, the surface-modified powders dispersed from the top to the bottom of the cylinder changing the color of the liquid white while most of the unmodified powders sank to the bottom in a short time. The surface-modified powders also showed more uniform distribution than unmodified powders in cured bone cement. This is shown in Figure 7, SEM pictures of fractured surfaces of cured bone cement after fatigue test.

Mechanical properties of cured bone cement could greatly be improved owing to the improved compatibility. Ultimate tensile strengths and fatigue strengths of various bone cements which contain surface-modified radiopaque powder are listed in Table 1. There are large increases both in tensile strength and in fatigue strength. Some samples showed even higher strengths than the sample without radiopaque powder. This means that even the radiopaque powders can be used as a reinforcing material if it is properly surface-modified.

Based on mechanical properties of cured bone cement, ZrO_2 was better than $BaSO_4$ as a

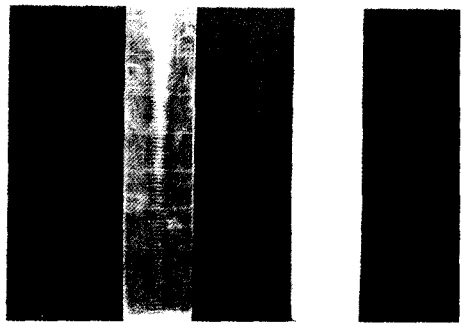

Fig. 6. Dispersion states of unmodified ZrO_2(left-hand) and surface-modified ZrO_2(righ-hand, white color) in MMA.

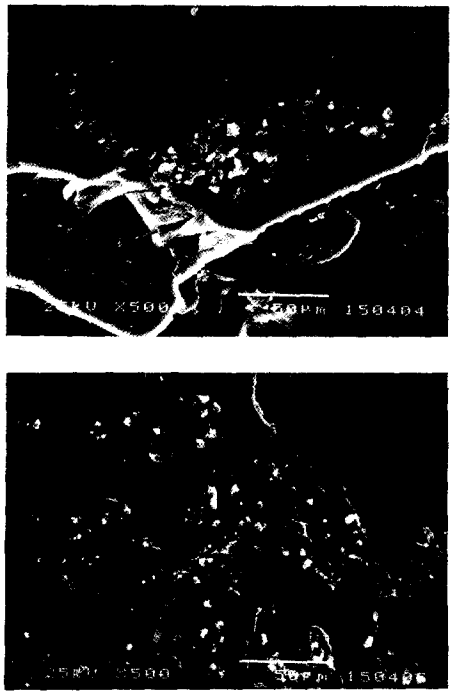

Fig. 7. SEM pictures of fractured surfaces after fatigue test of cured bone cement containing unmodified ZrO_2(above) and surface-modified ZrO_2 (below).

radiopaque material for bone cement and the best plasma treatment for surface modification was HMDSO plasma treatment followed by AA plasma treatment. Therefore, only ZrO_2 was used as a radiopaque material in further study and it was treated with HMDSO/AA plasma when surface modification is necessary.

Effects of Reinforcing Materials on Mechanical Properties of Bone Cement. To increase the mechanical strengths of cured bone cement further reinforcement with small amount of mica flake, short Kevlar 29 fiber, short glass fiber, short carbon fiber, or milled carbon fiber was tried. These materials are commonly used materials for the reinforcement of Bone Cement, except for mica.[20] Mica flake and milled carbon were relatively easy to mix and 2 wt% was added. However, the others were so difficult to mix that only approximately 0.3 wt% was added. Short fibers(2 mm) were entangled each other in a small volume of MMA in which PMMA and radiopaque powder are mixed together.

Table 2 shows effects of these reinforcing materials on mechanical properties of cured bone cement. None of them increased any mechanical strength. Rather, they severely reduced the mechanical strengths. An interesting observation here is that reductions of the mechanical strengths are higher for all of them when they mixed together with surface-modified radiopaque powder than when they were mixed with unmodified radiopaque powder.

Reinforcing materials were surface-modified by a low temperature plasma process to be compatible with MMA or PMMA. Even after the surface modification, however, not much improvements were observed for mica flake, Kevlar fiber, glass fiber, and carbon fiber. Mica flake increased the fatigue strength a little bit but reduced the tensile strength significantly. This seems to be due to the multi-layer struc-

Table 2. Ultimate Tensile Strengths and Fatigue Strengths of Various Bone Cements Filled with Reinforcing Materials

Reinforcing Material	Radiopaque Powder	UTS(MPa)[a]	Fatigue Cycles[b]
None	ZrO_2	32.5	338196
None	plasma treated ZrO_2[c]	42.9	420365
Mica	ZrO_2	26.5	369554
Mica	plasma treated ZrO_2	24.3	–
Plasma treated mica[c]	plasma treated ZrO_2[c]	33.2	437150
Kevlar fiber	ZrO_2	30.7	298066
Kevlar fiber	plasma treated ZrO_2	28.1	–
Plasma treated Kevlar fiber[d]	plasma treated ZrO_2	42.4	411862
Glass fiber	ZrO_2	28.0	223870
Glass fiber	plasma treated ZrO_2	26.0	–
Plasma treated glass fiber[c]	plasma treated ZrO_2[c]	33.2	282558
Carbon fiber	ZrO_2	30.2	211890
Carbon fiber	plasma treated ZrO_2	27.8	–
Plasma treated carbon fiber[c]	plasma treated ZrO_2[c]	44.2	374802
Milled carbon fiber	ZrO_2	29.6	416182
Milled carbon fiber	plasma treated ZrO_2[c]	26.3	–
Plasma treated milled carbon fiber[c]	plasma treated ZrO_2[c]	42.1	863822

[a] Ultimate tensile strength, average values of 2 to 3 samples.
[b] Total number of fatigue cycles to fracture, average values of 3 to 4 samples.
[c] Plasma condition; HMDSO(30W, 66.5 Pa, 30 minutes)/AA(5W, 133 Pa, 15 minutes).
[d] Plasma condition; O_2(20W, 266 Pa, 5 minutes)/AA(5W, 133 Pa, 5 minutes).
* Amount of mica or milled carbon; 2wt%, amount of others; approximately 0.3 wt%.

ture of mica. Adhesion strength between layers of mica is not so strong that the tensile strength may be reduced but certain amount of fatigue energy can be absorbed by the delamination of layers in fatigue test. Kevlar fiber reduced the fatigue strength a little bit. Glass fiber reduced both strengths. Carbon fiber increased the tensile strength but reduced the fatigue strength. These were due to mixing problem. Although they were cut into a small size, they were too long to completely avoid the entangling problem even after the surface modification. This fact is supported by the results obtained with milled carbon fiber which is approximately 150 μm long.

Surface-modified milled carbon fiber was easy to mix. It increased the fatigue strength remarkably with no change of the tensile strength. Total number of fatigue cycles to fracture was doubled from 420365 to 863822. It may be explained with SEM pictures of fractured surfaces. Figure 8 shows the fractured surface after tensile test and Figure 9 after fatigue test. In both pictures, it is shown that some surface-modified fibers are partially covered with PMMA matrix while all unmodified fibers have bare surfaces. This indicates that adhesion of PMMA to surface-modified fibers is stronger than adhesion to unmodified fibers. Therefore, both tensile strength and fatigue strength with surface-modified fibers are higher than with unmodified fibers. If fibers had really strong adhesion with PMMA, all the fibers would have been totally covered with PMMA

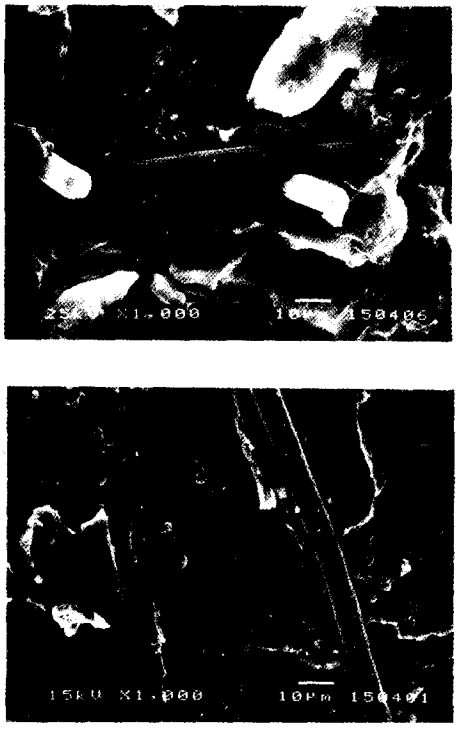

Fig. 8. SEM pictures of fractured surfaces after tensile test of cured bone cement containing unmodified milled carbon fiber(above) and surface-modified milled carbon fiber(below).

Fig. 9. SEM pictures of fractured surfaces after fatigue test of cured bone cement containing unmodified milled carbon fiber(above) and surface −modified milled carbon fiber(below).

with further increased tensile strength. As far as fatigue strength is concerned, however, very strong adhesion is not always necessary. If adhesion is too strong, cracks propagate through the matrix without debonding. In this case, absorbed energy may be smaller than the absorbed energy by debonding.

As a whole, improvement of the tensile strength by 29.5% and the fatigue strength by 155% of bone cement was achieved by surface modification and reinforcement. Bone cement developed in this study is expected to have much longer life-time compared to commercial bone cements. For comparison, ultimate tensile strength and total number of fatigue cycles to fracture of commercial bone (Simplex P) measured in this study was 27.2 MPa and 205,000 and tensile strengths of commercial bone cements in the literature range from 21.9 MPa to 33.9 MPa.[21, 22]

CONCLUSIONS

From this study, followings can be concluded:

1. Mechanical properties which are of prime importance in the performance of bone cement depend on the amounts of initiator and a promoter and the compatibility of radiopaque powder with the matrix.

2. The proper amount of an initiator(BPO)

and a promoter(DMPT) is 2.0 wt% and 1.0 wt % of MMA, respectively.

3. Radiopaque powder in bone cement gives a negative effect on the mechanical properties of cured bone cement. If it is surface-modified to be compatible with MMA or PMMA, however, it rather improves the mechanical properties to a large extent.

4. A low temperature process is an adequate process for such modification.

5. Fatigue strength can greatly be improved by small amount of reinforcing material. To achieve this, however, the reinforcing material should be easy to mix with other components in MMA and compatible with MMA or PMMA.

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