JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **11** (2000) 593–600

Radiation-induced grafting of methylmethacrylate onto ultrahigh molecular weight polyethylene and its adhesive characteristics

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The surface of ultrahigh molecular weight polyethylene (UHMWPE) was modified by radiation-grafting methylmethacrylate (MMA) in the presence of sulfuric acid and metallic salt to increase bonding strength with polymethylmethacrylate. The effect of the addition of metallic salts and sulfuric acid on the radiation grafting reaction was investigated when MMA was grafted to the irradiated UHMWPE. The adhesive characteristics with the grafting yield were investigated using conventional acrylic bone cement based on poly(methyl methacrylate) [PMMA]. The results showed that the inclusion of an $FeSO_4 \cdot 7H_2O$ and sulfuric acid in MMA grafting solutions was extremely beneficial and led to a most unusual synergistic effect, while $CuSO_4 \cdot 5H_2O$ led to a detrimental effect. The tensile bonding strength between UHMWPE and PMMA sheet increased remarkably with an increased grafting yield on UHMWPE surfaces.

1. Introduction

As early as 1890 Gluck reported on the fixation of total prostheses made of ivory using a bone cement consisting of colophonium with the addition of plaster [1]. Acrylate bone cements were first introduced into the medical field in 1932 as tooth filling materials. It was not until 1960 that cold-polymerizing acrylates were used clinically by Charnley to fix hip joint prostheses [2, 3]. Conventional acrylic bone cements are usually based on PMMA [4]. The bone cements are generally obtained by free radical polymerization of MMA monomer mixed with a solid phase containing beads of PMMA. The polymerization is initiated in the presence of benzoyl peroxide which is incorporated in the solid polymer phase. N,N-dimethyl-p-toluidine is constituted in the liquid phase which acts as an activator for the reaction [4]. Despite the advances in the improvement of bone cement, clinical experience showed that the bone cement, and above all the relevant handling technique, required improvement in order to achieve stable anchoring of the implant in its seat in the bone, so as to ensure long-term anchorage of the implant [5–10].

The superiority of UHMWPE to most other polymers because of its mechanical properties, resistance to chemicals and to abrasion, has called for its use in a variety of applications such as implantable prosthetic devices, particularly acetabular cups [11–14]. UHMWPE has a number of mechanical and chemical properties which make it highly suitable for orthopaedic implants [15]. However, it is difficult to adhere UHMWPE to human bone, organic and inorganic materials because UHMWPE is inactive chemically. Especially, the bonding strength of PMMA adhesives to UHMWPE is extremely low. Accordingly, the bonding of PMMA bone cement to UHMWPE depends on the mechanical interlocking. The grafting of MMA onto UHMWPE can be used to improve the adhesive properties of UHMWPE with PMMA bone cement [16]. The grafting method needs free radicals or peroxides to modify the surface of polymers. The grafting polymerization can be carried out by ionization radiation [17, 18], UV [19, 20], plasma [21], ion beam [22] or chemical initiator. Among these techniques, the radiation method is one of useful methods because of uniform and rapid creation of active radical sites. The methods of achieving grafting reaction using radiation include (1) simultaneous irradiation of the backbone polymer in the presence of the monomer [17], (2) preirradiation of the backbone polymer in vacuum or nitrogen gas and subsequent monomer grafting by trapped radicals [23], and (3) preirradiation of the backbone polymer in the presence of air or oxygen and subsequent monomer grafting by polymeric peroxides such as diperoxides and hydroperoxides [24]. When UHMWPE is subjected to ionizing radiation in air, trapped radicals or peroxy radicals are generally formed. The trapped radicals formed by irradiation in air are converted gradually to peroxides and hydroperoxide species which may result in undesirable homopolymerization initiated by the mobile $\cdot$OH radical formed in the thermal decomposition reaction. It is possible to obviate this problem by using a reducing agent, e.g. metallic salt, to decompose the peroxy species. We [24] performed effectively graft polymerization using an Fe^{2+} ion as a reducing agent to decompose the hydroperoxides, thereby converting hydroxyl radicals to the inactive hydroxide ion, which can prevent an undesirable homopolymerization.

In this study, the grafting reaction was carried out in the presence of sulfuric acid and metallic salt by means of a preirradiation method in which the substrate polymer of UHMWPE was preirradiated with γ-rays in air. The effect of the addition of metallic salts and sulfuric acid on the radiation grafting reaction was investigated when MMA was grafted to irradiated UHMWPE. The adhesive characteristics of the grafted UHMWPE were investigated.

2. Experimental

2.1. Materials

Commercial UHMWPE with a thickness of 1.0 mm (MW 5.5×10^6, 0.94 g/cm^3, Saxin Co., Ltd) was used as a substrate for graft polymerization. UHMWPE was cut into 1.5×5.0 cm pieces and ultrasonically cleaned twice in methanol for 1 h each time, and dried in a vacuum oven. MMA (Junsei Chemical Co. Ltd), $FeSO_4 \cdot 7H_2O$ (Merck AG) and $CuSO_4 \cdot 5H_2O$ (Waco Pure Chemical Co. Ltd) were used without further treatment as supplied. Other chemicals were reagent grade.

2.2. Irradiation

The γ-ray irradiations from Co-60 sources (Korea Atomic Energy Research Institute, AECL type C-188) were carried out at an exposure rate of 4.87 kGy/h in the presence of air to a total dose of 10 to 30 kGy.

2.3. Grafting procedure

The irradiated UHMWPE sheets were stored in a refrigerator kept at $-130\,^{\circ}$C immediately after irradiation until the grafting reaction was carried out. The grafting experiments were conducted in a glass ampoule having a cock, methanol and additives being added first, followed by monomer to a total volume of 50 ml. The preirradiated UHMWPE was immersed in the monomer solution, purged by bubbling nitrogen gas for degassing and then sealed in a glass ampoule. The grafting reaction was carried out by placing the ampoules in a water bath set at the relevant temperature. This graft copolymerization was initiated by radicals on the UHMWPE. After the grafting copolymerization reaction, the grafted UHMWPE was taken out of the monomer solution in a glass ampoule and extracted by hot acetone in a Soxhlet extractor over 24 h to remove the unreacted remaining monomers or MMA homopolymers. Then the grafted UHMWPE was dried in a vacuum oven at $60\,^{\circ}$C for 24 h after it was ultrasonically cleaned several times in acetone for 1 h each time. The degree of grafting was determined by the following:

$$\text{Degree of grafting (mg/cm}^2\text{)} = \frac{W_g - W_0}{\text{Surface area}} \qquad (1)$$

where W_g and W_0 are weights of the grafted and ungrafted UHMWPE, respectively. The grafted UHMWPE was verified by Fourier transform infrared spectroscopy in the attenuated total reflectance mode (FTIR-ATR) and electron spectroscopy for chemical analysis (ESCA). A Nicolet model 205 FT-IR spectrometer (USA) with a nominal 45 degree attenuated total reflectance was used to examine the grafting onto UHMWPE induced by irradiation. ESCA for examining the grafting onto UHMWPE sheet by irradiation was carried out with a V. G. Scientific Escalab MK II spectrometer using MgKα X-ray radiation at 1253.6 eV operating at 10^{-9} mbar and photoelectron take-off angles of 60 degrees. The control and UHMWPE samples were cut to form 6 mm disks, and then introduced to the UHV spectrometer chamber. MgKα radiation was used with the analyzer operating at a constant band pass energy of 20 eV. The spectrometer was calibrated by assuming the binding energy of the Au $4f_{7/2}$ line to be 83.9 eV with respect to the Fermi level. Survey scans (0 to 1200 eV) were recorded for each sample to obtain a qualitative elemental analysis. Following spectra acquisition, peak identification and quantification were achieved using V. G. Scientific Escalab package software. High-resolution spectra for the carbon-1s and oxygen-1s were also obtained and computer curve-fitted employing a Gaussian model, using the same package software, to obtain the best binding energy values. To take into account some shift caused by charging of the sample surface, all spectra were adjusted taking the carbon-1s peak at 284.6 eV as reference for the adventitious carbon contamination.

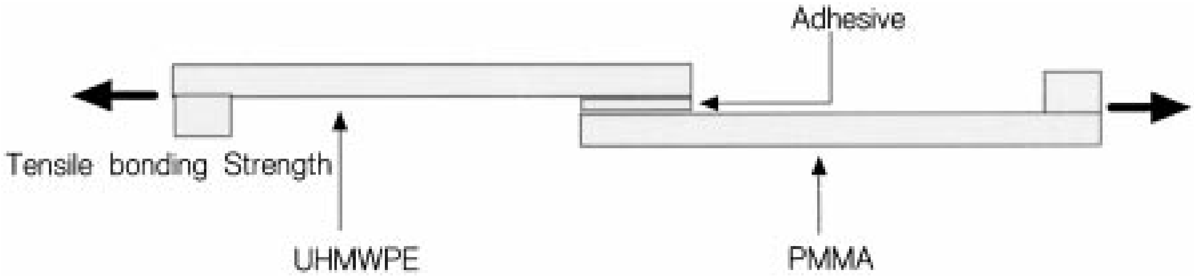
A scanning electron microscope (SEM, JSM-840A, JEOL Co., Japan) was used to observe the surface topography of MMA-grafted UHMWPE and control.

2.4. Contact angle measurement

The control and MMA-grafted UHMWPE surfaces with the various grafting yield were characterized by water contact angle measurements using an optical contact angle goniometer (Erma Optical Ltd., Japan). The water contact angle for each UHMWPE sample was measured by a sessile drop method five times at room temperature. Drops of purified water (3 µl) were deposited onto the control and MMA-grafted UHMWPE surface, and the direct microscopic measurement of the contact angles for UHMWPE stored at room temperature during the 3 min after deposition was performed with a goniometer.

2.5. Measurement of tensile bonding strength

The tensile bonding strength of control and MMA-grafted UHMWPE samples with the various grafting yields was measured using a universal testing machine. Tensilon CFT-200 equipped with pneumatic grips at room temperature. The specimens of UHMWPE for testing bonding strength with dimensions $15 \times 50 \times 3$ mm. As shown in Scheme 1, the control or MMA-grafted UHMWPE and PMMA sheets with the same dimensions were overlapped on both ends to an area of 2.25 cm^2 in room temperature, the area being coated beforehand with adhesives, SULFIX$^{\text{TM}}$-60 Bone Cement (Allopro, Switzerland), consisting of polymer powder



Scheme 1 Scheme for measurement of tensile bonding strength between UHMWPE and PMMA sheets.

containing PMMA, polymethyl-butylmethacrylate, zirconium dioxide and benzoyl peroxide and of monomer fluid containing MMA, butylmethacrylate, N,N-dimethyl-p-toluidine and 2-[4-(dimethylamino)phenyl]ethanol as promotors. After mixing of 2.5 : 1 ratio of polymer powder to monomer fluid, and then it was filled in the syringe. After standing for 1 min, the bone cement adhesives were coated on spaces overlapped between control or MMA-grafted UHMWPE and PMMA sheets. The coating was adjusted to the infinite thickness of 0.7 mm by using the spacer. The tensile bonding strength of control and of MMA-grafted UHMWPE samples to PMMA sheets was measured after aging for 1 h at room temperature. The measurements were at a crosshead speed of 0.508 mm/min ($0.02\,\text{min}^{-1}$) and at a gauge length of 70 mm. Specimen load was sensed by a 500 kg capacity Instron Type-A load cell. This cell was mechanically calibrated by precision standard weights prior to testing each set of samples. A calibration check was also performed at the conclusion of each test set. The tensile bonding strength of control and MMA-grafted UHMWPE samples was measured five times for each sample.

3. Results and discussion

The grafting technique can be used to modify the surface of UHMWPE for the purpose of adhesive improvement. The grafting technique needs free radicals or peroxides to modify the surface of polymers. When UHMWPE are subjected to ionizing radiation in air, trapped radicals or peroxy radicals are generally formed. The yield of free radicals and peroxy radicals is different depending on the presence of oxygen when UHMWPE is irradiated. In our previous paper, Nho and Jin explained that the schematic mechanism of UHMWPE during irradiation in air is as follows [24]:

$$\mathrm{PH} \xrightarrow{\gamma} \mathrm{P}\cdot + \mathrm{H}\cdot \tag{2}$$

$$\mathrm{P}\cdot + \mathrm{O_2} \rightarrow \mathrm{POO}\cdot \tag{3}$$

$$\mathrm{POO}\cdot + \mathrm{PH} \rightarrow \mathrm{POOH} + \mathrm{P}\cdot \tag{4}$$

$$\mathrm{POO}\cdot + \mathrm{P}\cdot \rightarrow \mathrm{POOP} \tag{5}$$

$$\mathrm{POO}\cdot + \cdot\mathrm{OOP} \rightarrow \mathrm{POOP} + \mathrm{O_2} \tag{6}$$

$$\mathrm{P}\cdot + \mathrm{P}\cdot \rightarrow \mathrm{P\text{-}P} \tag{7}$$

Where P and P$\cdot$ represent the UHMWPE chain and UHMWPE radicals produced by irradiation, respectively. Irradiation in air leads to the formation of hydroperoxide species which may result in undesirable homopolymerization initiated by the mobile $\cdot$OH radical formed in the thermal decomposition reaction. It is possible to obviate this problem by using a reducing agent, e.g. metallic salt, to decompose the peroxy species. Nho and Jin [24] performed effective graft polymerization using a metallic salt as a reducing agent to decompose the hydroperoxides, thereby converting hydroxyl radicals to the inactive hydroxide ion, which can prevent an undesirable homopolymerization. In the paper, they reported that the $\mathrm{Fe^{2+}}$, $\mathrm{Fe^{3+}}$ and $\mathrm{Cu^{2+}}$ metallic compounds were effective inhibitors of the homopolymerization of acrylic acid or methacrylic acid onto polyethylene [24], where the radical termination occurs by an electron transfer process from a propagating polymer to a *d*-orbital of the cation [25]. They explained that the reaction of $\mathrm{Fe^{2+}}$ with hydroperoxide which occurs during irradiation is as follows:

$$\mathrm{POOH} + \mathrm{Fe^{2+}} \rightarrow \mathrm{PO}\cdot + \mathrm{Fe^{3+}} + \mathrm{OH^-} \tag{8}$$

Metallic salt plays an important role in decomposing the hydroperoxides by a redox reaction, as shown in reaction (8). In addition, the deactivation process of the grafting chain radical growth is as follows, this reaction leads to a reduction in the grafting reaction.

$$\mathrm{PO}\cdot + \mathrm{Fe^{2+}} \rightarrow \mathrm{PO^-} + \mathrm{Fe^{3+}} \tag{9}$$

Fig. 1 shows the effect of monomer concentration in the methanol on the grafting yields at various irradiation doses of 10, 20 and 30 kGy. As shown in Fig. 1, in the case of 30 kGy irradiated sample, the grafting yield was much higher than that of 20 kGy, while the grafting yield was remarlablely low at 10 kGy. The maximum peak occurred at around 60% monomer concentration, in which appearance of such maxima can be explained by means of a Trommsdorff effect with methanol as a solvent [26].

The effect of reaction time on the grafting of MMA onto UHMWPE in the presence of various additives is shown in Fig. 2. With the addition of sulfuric acid, the grafting yield increased with an increased reaction time. When $\mathrm{FeSO_4 \cdot 7H_2O}$ was added to the grafting solution, the grafting yield was much larger than $\mathrm{CuSO_4 \cdot 5H_2O}$. The grafting yield was remarkably low when additive was not used. With the addition of both sulfuric acid and $\mathrm{FeSO_4 \cdot 7H_2O}$, the grafting yield was rapidly increased with an increased reaction time. On the other hand, in the case where both $\mathrm{CuSO_4 \cdot 5H_2O}$ and sulfuric acid are added in the grafting solution, the grafting yield was much lower, compared with the addition of $\mathrm{CuSO_4 \cdot 5H_2O}$. The grafting yield was much higher in the case of $\mathrm{FeSO_4 \cdot 7H_2O}$ than $\mathrm{CuSO_4 \cdot 5H_2O}$, because

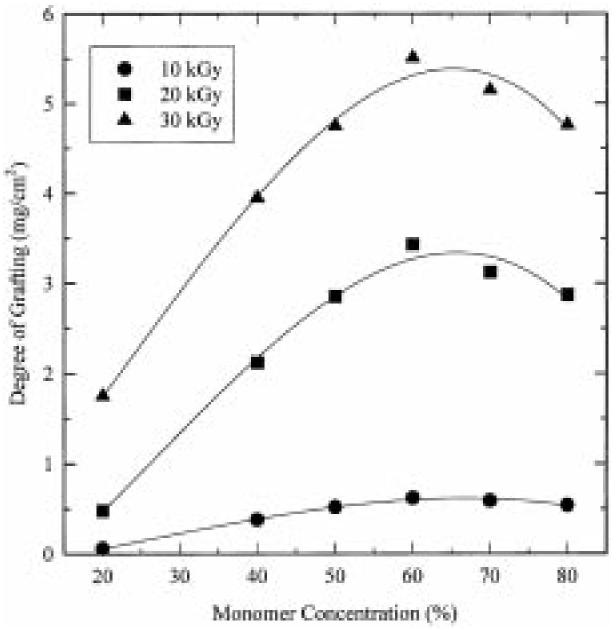


Figure 1 Effect of monomer concentration on the grafting of MMA onto irradiated UHMWPE in methanol solution containing 0.05 M H_2SO_4 and 1.5×10^{-4} M $FeSO_4 \cdot 7H_2O$ at 50 °C for 3 h.

Fe^{2+} converts to Fe^{3+} by oxidation to dissociate hydroxides. However, it should be noted it is impossible to oxidize Cu^{2+}.

$FeSO_4 \cdot 7H_2O$ has a synergistic effect on grafting, as shown in reaction (8), in the presence of sulfuric acid. From the result it was assumed that sulfuric acid accelerated the decomposition of hydroperoxide in the presence of a metallic salt such as Fe^{2+} to form radicals that can initiate the grafting reaction as shown in reaction (8). By the addition of sulfuric acid to the grafting solution, the OH^- accumulated in reaction (8) can be consumed by a reaction with H^+, which dissociates from sulfuric acid. Therefore, reaction (8) can progress in the presence of acid by the principle of Le Chartelier. Garnett *et al.* [27] published that for a typical system such as the grafting of styrene in the monomer solution to polyethylene initiated by either cobalt-60 or UV, inclusion of mineral acid in the monomer solution leads to an increase in the concentration of monomer in the grafting monomer solution absorbed within the backbone polymer when compared with original bulk grafting monomer solution. This partitioning of monomer within the backbone polymer leads to the observed grafting enhancement. It is considered that in this grafting system, the increasing grafting yield by acid is also closely related to the partitioning effect.

The reaction time in the grafting yield is one of the important factors controlling the grafting. Fig. 3 shows the effect of reaction time on the grafting of MMA onto UHMWPE which was irradiated at 10, 20 and 30 kGy. The grafting yield increased in proportion to reaction time. Fig. 4 shows the effect of reaction time and temperature on the grafting of MMA onto UHMWPE which was irradiated at 10 kGy. As shown in Fig. 4, the grafting yield at 70 °C was much higher than that at 50 °C, while the grafting yield was remarkably low at 30 °C. Most grafting reactions at particularly low reaction temperatures can be attributable to only trapped radicals. On the other hand, it is possible that the reactive sites for the grafting reaction on the backbone polymer can be generated by the decomposition of hydroperoxide species in the presence of cationic salt and/or acid at high temperatures, as well as trapped radicals. Therefore, high temperature is of advantage to the radiation grafting reaction.

Based on the data in Fig. 4, logarithmic plots of the grafting rate against the reciprocal grafting temperature are shown in Fig. 5. The increase in grafting rate with grafting temperature follows the Arrhenius relationship, as shown in Equation 10:

$$\text{Log } K = \log A - \frac{E_a}{2.3RT} \qquad (10)$$

where K is the grafting reaction rate, A is a temperature-

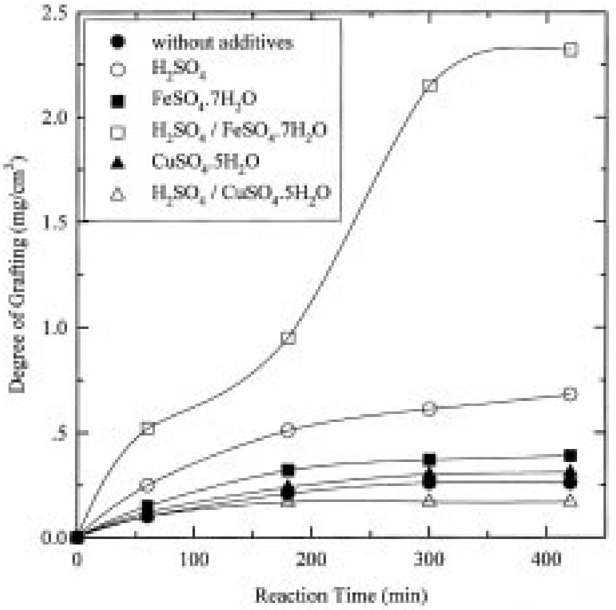


Figure 2 Effect of reaction time on the grafting of MMA onto 10 kGy preirradiated UHMWPE in 60v% MMA methanol solution containing 0.1 M H_2SO_4 and 1.5×10^{-4} M salts at 70 °C.

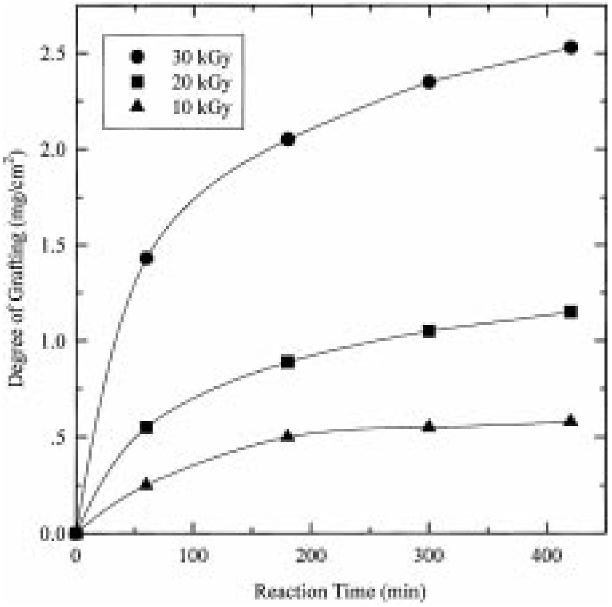


Figure 3 Effect of reaction time on the grafting of MMA onto preirradiated UHMWPE in 60v% MMA methanol solution containing 0.05 M H_2SO_4 and 1.5×10^{-4} M $FeSO_4 \cdot 7H_2O$ at 30 °C.

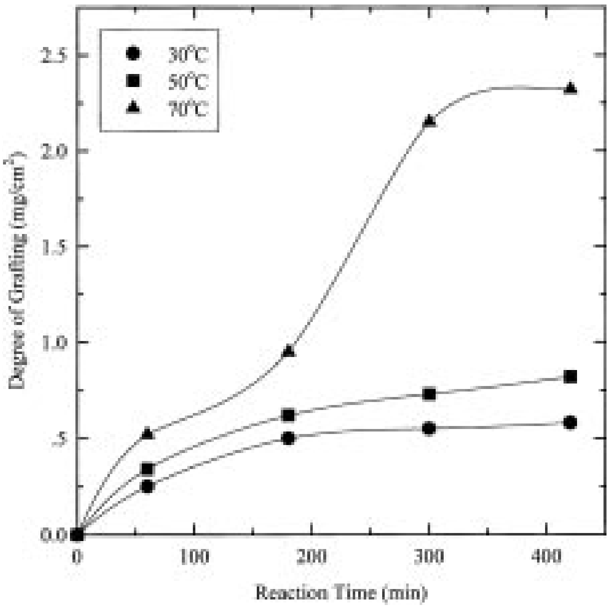


Figure 4 Effect of reaction time on the grafting of MMA onto 10 kGy preirradiated UHMWPE in 60v% MMA methanol solution containing 0.05 M H_2SO_4 and 1.5×10^{-4} M $FeSO_4 \cdot 7H_2O$.

independent constant, E_a is the activation energy, R is the Boltzmann's constant, and T is absolute temperature. Based on the slopes of the Arrhenius plots, the activation energy of grafting was 20 kcal/mol. This value is apparently too high for a reaction between free radicals and vinyl monomer to take place. Therefore, the high apparent activation energy may mainly be due to a monomer diffusion process.

By heating the irradiated UHMWPE in MMA methanol solution, the grafting of MMA to UHMWPE initiated by peroxyradicals proceeds. However, undesirable homopolymerization initiated by the $\cdot$OH radical formed in the thermodecomposition reaction takes place simultaneously. It leads not only to a lower grafting yield but also an enhancement of homopolymerization, and the homopolymers anchored on the UHMWPE are difficult to remove. To prevent homopolymerization, Nho and Jin reported a method of using a reducing agent to decompose the peroxy species by converting $\cdot$OH to inactive ions [24]. In the paper, the grafting reaction was severely limited in the absence of metallic salt because of homopolymer formation during the grafting reaction. Therefore, in this study, the effect of metallic salt concentration on the grafting yield was examined. Fig. 6 shows the effect of $FeSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ concentration on the grafting yield in the presence or absence of sulfuric acid. For the $FeSO_4 \cdot 7H_2O$, the grafting yield increased with an increased concentration of $FeSO_4 \cdot 7H_2O$ until 1.5×10^{-4} M salt, and then decreased with an increased concentration of $FeSO_4 \cdot 7H_2O$ without regard to any additional sulfuric acid. The excessive addition of $FeSO \cdot 7H_2O$ can suppress the grafting reaction by Equation 9. In the presence of sulfuric acid, however, the grafting yield was much higher than in the absence of sulfuric acid. In the case where $CuSO_4 \cdot 5H_2O$ was added into the grafting solution in the absence of sulfuric acid, the grafting yield increased with an increased $CuSO_4 \cdot 5H_2O$ concentration until 1.5×10^{-4} M salt, and then decreased with further addition. However, for $CuSO_4 \cdot 5H_2O$ in the presence of sulfuric acid, the grafting yield was rapidly decreased with increasing concentration of $CuSO_4 \cdot 5H_2O$.

The effect of sulfuric acid concentration on the grafting yield is shown in Fig. 7. As shown in Fig. 7, in the presence of $FeSO_4 \cdot 7H_2O$, the grafting yield increased rapidly with the inclusion of sulfuric acid up to 0.1 M, and then slightly decreased. Without $FeSO_4 \cdot 7H_2O$, the grafting yield also increased rapidly with the addition of sulfuric acid, and then slightly decreased, the maxima peak occurring at 0.1 M sulfuric acid. When $CuSO_4 \cdot 5H_2O$ was used as an additive, however, the grafting yield decreased slightly with

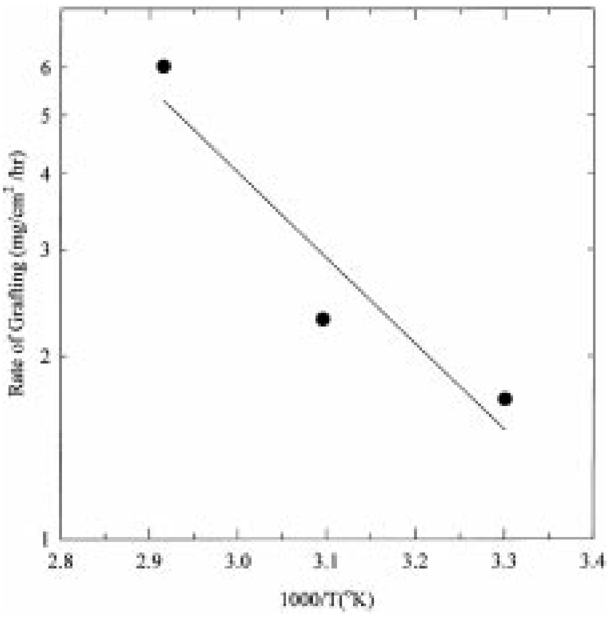


Figure 5 Logarithmic plots of grafting rate vs reciprocal of grafting temperature. Grafting conditions are the same as in Fig. 4.

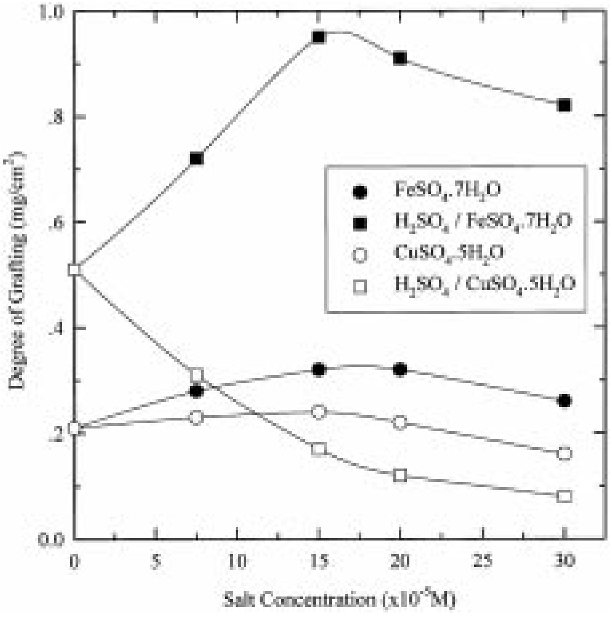


Figure 6 Effect of salt concentration on the grafting of MMA onto 10 kGy preirradiated UHMWPE in 60v% MMA methanol solution containing 0.1 M H_2SO_4 at 70 °C for 3 h.

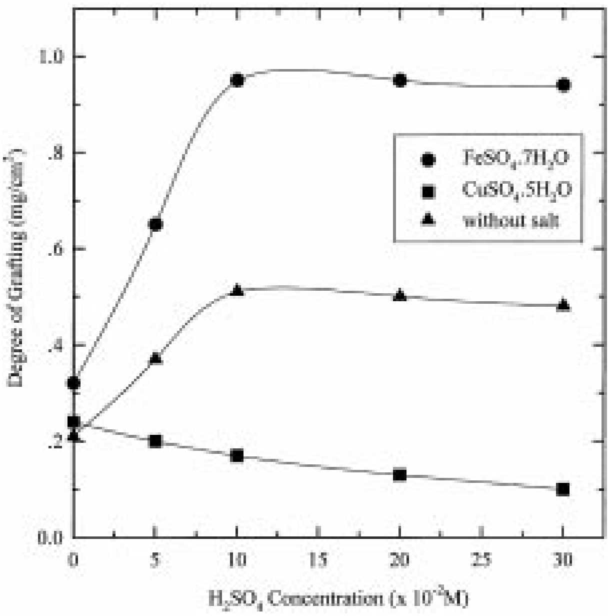


Figure 7 Effect of H_2SO_4 concentration on the grafting of MMA onto 10 kGy preirradiated UHMWPE in 60v% MMA methanol solution 1.5×10^{-4} M salts at 70 °C for 3 h.

increased sulfuric acid. This means that the addition of sulfuric acid and the appropriate concentration of Fe^{2+} can greatly enhance the grafting reaction. Sulfuric acid accelerates the decomposition of hydroperoxides in the presence of Fe^{2+} to form radicals which can initiate the grafting reaction. The OH^- accumulated in reaction medium can be consumed by H^+, which originates from the dissociation of sulfuric acid. Therefore, Equation 8 can progress easily forward in the presence of acid, particularly in the presence of sulfuric acid. In this grafting reaction, it is assumed that strong acid only plays a role in enhancing the redox reaction and partitioning effect which consequently increased grafting yield, suppressing homopolymer.

The changes in chemical structure of the MMA-grafted UHMWPE sheets with the grafting yield were examined by FTIR-ATR and survey scan spectra with an ESCA. Fig. 8 shows the FTIR-ATR spectra of control and MMA-grafted UHMWPE sheet surfaces with the grafting yield. With an increasing grafting yield, the stretching peaks of the carbonyl group (-C = O) at 1730 cm^{-1} and the ether carbon band (-C-O, 1130 ∼ 1160 cm^{-1}) increased, whereas the C-H bending peaks at 1465 cm^{-1} decreased with the grafting yield. MMA-grafted UHMWPE was studied by measuring survey scan spectra with an ESCA. Fig. 9 shows the ESCA survey scan spectra of UHMWPE sheet surfaces for control and MMA-grafted UHMWPE. As shown in Fig. 10, the grafted UHMWPE had oxygen (O-1s : 537.0 eV) peaks as well as carbon (C-1s : 284.6 eV) peaks, there being no oxygen peak for the ungrafted UHMWPE. The oxygen peak of UHMWPE with increased grafting yield increased more and more due to the enhanced amount of carbonyl groups on UHMWPE surfaces. The atomic percentage calculated from the ESCA survey scan spectra in Fig. 10 and its ratio is shown in Table I. From these results, it could be concluded that the UHMWPE was grafted with MMA.

The surface topography of MMA-grafted UHMWPE with the various grafting yields and of control are shown in Fig. 11. As shown in Fig. 11, the grafting layer on the UHMWPE samples increased with increasing grafting yield. With the increasing grafting yield, a bump-like appearence occurred. The surface area of the grafting layer was enhanced remarkably with an increased grafting yield, which is closely related to bonding strength.

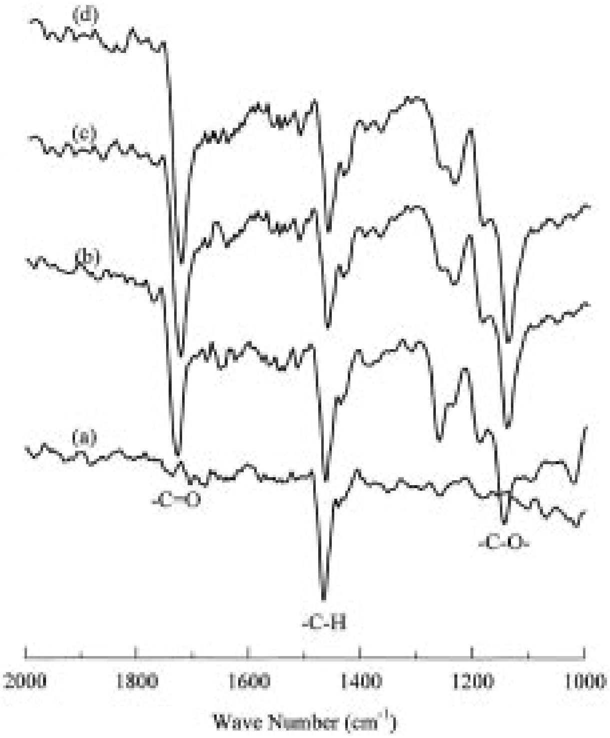


Figure 8 FTIR-ATR spectra of (a) control, (b) 0.12 mg/cm^2, (c) 0.25 mg/cm^2 and (d) 1.04 mg/cm^2 of MMA-grafted UHMWPE surfaces.

Adhesion is the phenomenon in which surfaces are held together by interfacial forces. For the adhesive properties of MMA-grafted UHMWPE, the relation of

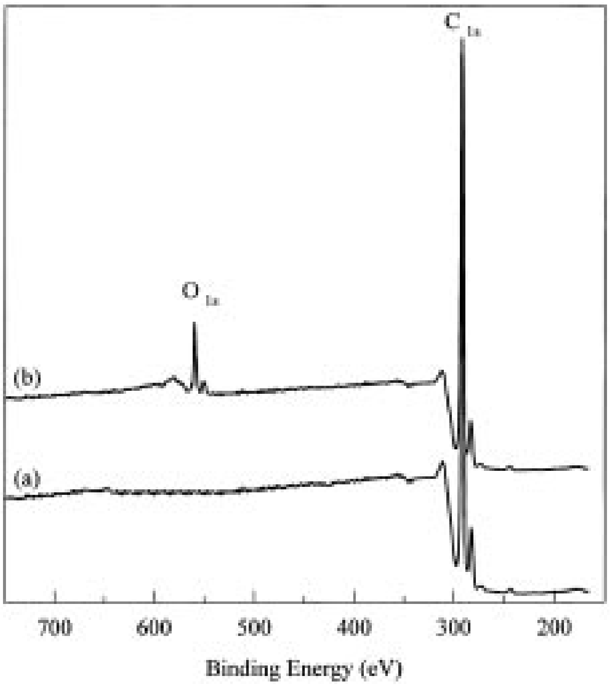


Figure 9 ESCA survey scan spectra of (a) control and (b) MMA-grafted UHMWPE surfaces of 1.04 mg/cm^2 grafting.

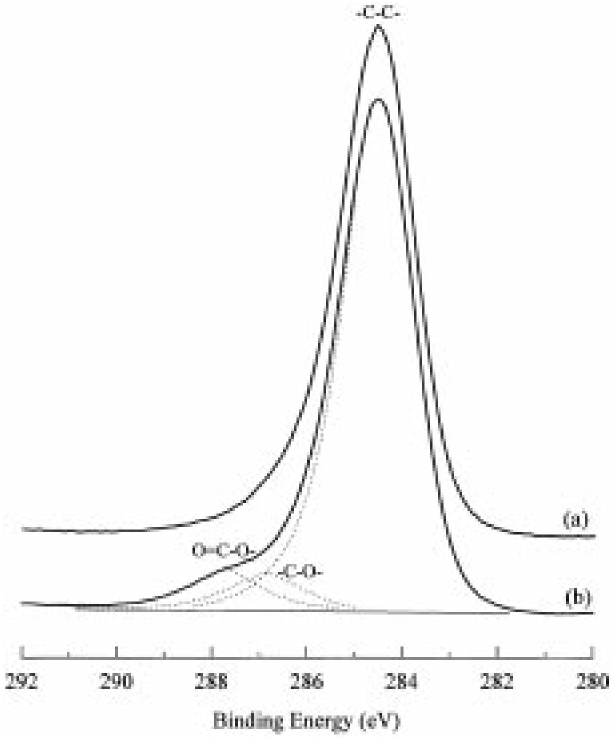


Figure 10 ESCA carbon-1s core level spectra of (a) control and MMA-grafted UHMWPE surfaces of (b) 1.04 mg/cm^2 grafting.

the tensile bonding strength with the water contact angle of MMA-grafted UHMWPE samples was examined, the results are shown in Table II. As shown in Table II, the water contact angle decreased slightly with an increased grafting yield, and the tensile bonding strength increased rapidly with an increased grafting yield on UHMWPE surfaces. Young's concept of the contact angle θ between a drop of liquid and a plane solid surface is directly related to wettability. Adhesion depends on wetting of the surfaces. When $\theta = 0$, the liquid wets the surface completely and spreads freely. Every liquid wets every surface to some extent. Contact angle, θ, is a good inverse measure of wetting and spreadability, and hence of adhesion. As the grafting of MMA onto UHMWPE increased, the contact angle of the grafted-UHMWPE surface became analogous to that of PMMA. Therefore, it is possible to increase the adherent strength of UHMWPE by the surface modification using radiation grafting because the surface of UHMWPE is easily modified to the same composition with bone cement chemically.

Acrylic bone cement used in total hip arthroplasty was developed by Charnley and gave excellent clinical results with good preservation of long-term joint function. Subsequently, replacement arthroplasty with the artificial joint has become the standard and most reliable operative treatment for osteoarthritis of the hip. The aseptic loosening with destruction of the hip joint, however, occurred in some cases even after a long period of good function. It was previously believed that the bone cement itself was generally responsible for aseptic loosening in cemented total hip arthroplasty [28]. In the cemented artificial hip joint, mechanical weaknesses

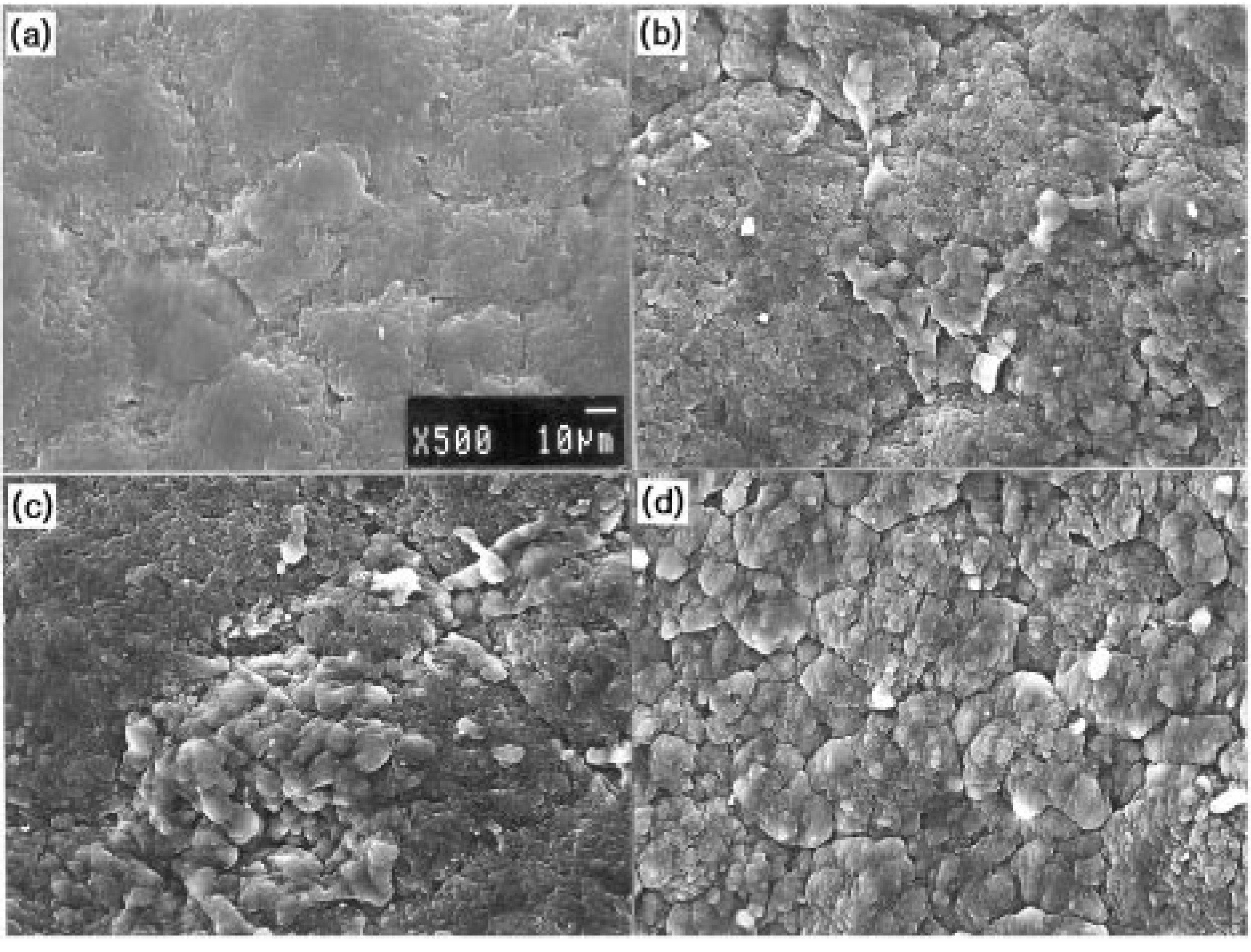


Figure 11 SEM photographs of (a) control and of MMA-grafted UHMWPE surfaces of (b) 0.12 mg/cm^2. (c) 0.25 mg/cm^2 and (d) 1.04 mg/cm^2 grafting.

TABLE I ESCA analysis of control and MMA-grafted UHMWPE sheet surfaces

	UHMWPE	Atomic%[a)]		Ratio[b)]
		Carbon	Oxygen	-C-O-/-C-C-
Grafting	Control	99.997	0.003	0.025
(mg/cm^2)	1.04	68.426	31.574	0.579

a) Analyzed from survey scan spectra.

b) Analyzed from carbon-1s core level spectra.

TABLE II The changes of tensile bonding strength and of water contact angle for control and MMA-grafted UHMWPE with different grafting yields

Sample	Degree of grafting (mg/cm^2)	Water contact angle (°)	Tensile bonding strength (kg/cm^2)
1	0	82	1.11
2	0.04	79	1.89
3	0.12	77	17.05
4	0.17	76	28.51
5	0.25	72	62.51
6	0.45	71	72 (breaking strength)
7	1.04	70	74 (breaking strength)

occur at the interfaces between the UHMWPE and bone cement, or between bone cement and bone. The bonding of PMMA bone cement to UHMWPE nearly depends on the mechanical interlocking. The grafting of MMA onto UHMWPE can be used to improve the adhesive properties of UHMWPE with PMMA bone cement.

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Received 21 July 1998
and accepted 22 July 1999