# Graft Polymerization of Methyl Methacrylate onto Radiation-Peroxidized Ultrahigh Molecular Weight Polyethylene in the Presence of Metallic Salt and Acid

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ABSTRACT: Using a radiation peroxide grafting technique, a ultrahigh molecular weight polyethylene (UHMWPE) stored at room temperature for 10 days after irradiation in air was graft copolymerized with methyl methacrylate (MMA) in the presence of metallic salt and acid. The MMA-grafted UHMWPE samples were analyzed by measuring Fourier transform infrared spectroscopy in attenuated total reflectance (FTIR–ATR) and by electron spectroscopy for chemical analysis (ESCA). The 1,1-diphenyl-2-picrylhydrzyl (DPPH) technique was utilized to evaluate the concentration of peroxide formed in the peroxidized UHMWPE samples by counting the quantity of DPPH consumed from the reaction of peroxide radicals with DPPH. It was shown that the inclusion of an FeSO<sub>4</sub>  $\cdot$ 7H<sub>2</sub>O and sulfuric acid in MMA grafting solutions was extremely beneficial and led to a most unusual synergistic effect in the radiation-peroxidized grafting. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 659–666, 1999

**Key words:** radiation-induced grafting; surface modification; methyl methacrylate; ultrahigh molecular weight polyethylene; metallic salt

### INTRODUCTION

It is well known that Teflon<sup>TM</sup> has attracted much attention as a material for the socket, with a metal head, for the femur of a total hip prosthesis because of its good chemical stability and mechanical properties.<sup>1</sup> Because Teflon was found to wear much too quickly, however, a change was made to high-density polyethylene with an ultrahigh molecular weight.<sup>2</sup> Ultrahigh molecular weight polyethylene (UHMWPE) has a number of mechanical and chemical properties which make it highly suitable for orthopedic implants.<sup>3</sup> It is difficult to adhere UHM-WPE to human bone and organic and inorganic

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materials, however, because it is inert chemically. The grafting technique can be used to modify UH-MWPE. The grafting method needs free radicals or peroxides to modify polymers.<sup>4</sup> The grafting polymerization can be carried out by an ionization radiation,<sup>5,6</sup> UV,<sup>7,8</sup> plasma,<sup>9</sup> or chemical initiator. Among these techniques, the radiation method is one of the most useful methods because of the uniform and extensive creation of active radical sites on the existing polymer substrate.

The methods of achieving a grafting reaction using radiation include simultaneous irradiation of the backbone polymer in the presence of a monomer,<sup>5</sup> preirradiation of the backbone polymer in a vacuum or nitrogen gas and subsequent monomer grafting by trapped radicals,<sup>10</sup> and preirradiation of the backbone polymer in the presence of air or oxygen and subsequent monomer grafting by polymeric

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peroxides such as diperoxides and hydroperoxides.  $^{11}$ 

When polymeric materials are subjected to ionizing radiation in air, trapped radicals or peroxides such as diperoxides and hydroperoxides by dissociation of the polymer backbone or hydrogen are generally formed. When irradiated polymers are exposed to air at room temperature, the trapped radicals in the polymeric material are transformed into peroxide radicals by the addition of molecular oxygen to the free radicals.

In this work, methyl methacrylate(MMA) was grafted to peroxidized UHMWPE, which was stored at room temperature for at least 10 days after  $\gamma$ -ray irradiation in air to endow its bonding strength onto human bone or other materials such as metal and ceramics. The effect of the addition of various cationic salts and acids on the radiation grafting reaction was investigated when MMA was grafted to peroxidized UHMWPE. Using the 1,1-diphenyl-2-picrylhydrzyl (DPPH) method, the concentration of peroxides formed on and near the polymer substrate was examined.

## **EXPERIMENTAL**

#### **Materials**

Commercial UHMWPE with a thickness of 1.0 mm (MW 5.5  $\times$  10<sup>6</sup>, 0.94 g/cm<sup>3</sup>, Saxin Co., Ltd., Osaka, Japan) was used as a substrate for graft polymerization. The UHMWPE was cut into 1.5  $\times$  5.0-cm pieces and ultrasonically cleaned twice in methanol for 1 h each time and dried in a vacuum oven. MMA (Junsel Chemical Co., Ltd., Tokyo, Japan), FeSO<sub>4</sub> ·7H<sub>2</sub>O (Merck, Darmstadt, Germany), and CuSO<sub>4</sub> ·5H<sub>2</sub>O (Waco Pure Chemical Industries, Ltd., Tokyo, Japan) were used without further treatment. DPPH from Sigma Chemical Co. (St. Louis, MO) was used to determine the amount of peroxide formed on the substrate. Other chemicals were reagent grade.

#### Irradiation

The  $\gamma$ -ray irradiation from Co-60 (Korea Atomic Energy Research Institute, AECL type C-188) was carried out at an exposure rate of 4.87 kGy/h in the presence of air to a total dose of 40 kGy.

#### **Peroxide Determination**

For peroxidized UHMWPE, the amount of peroxide formed on and near the substrate was quantified with DPPH.<sup>9,12</sup> The peroxidized UHMWPE stored at room temperature for 10 days after irradiation was put in a  $1.0 \times 10^{-4}$  *M* deaerated toluene solution of DPPH in a glass ampule and kept at 70°C for 5 h to decompose the peroxides formed on and near the polymer substrate. The DPPH molecules consumed were measured from the difference in transmittance at 520 nm between the control and peroxidized sample using an ultraviolet spectrophotometer (Cesil Instruments, CE 292). A Nicolet Model 205 FTIR spectrometer (USA) with a nominal 45° attenuated total reflectance (ATR) was used to examine the peroxidized UHMWPE induced by irradiation.

#### **Grafting Procedure**

The grafting experiment was performed in a glass ampule having a cock, with the methanol and additives being added first, followed by a monomer to a total volume of 50 mL. The peroxidized UHMWPE was immersed in the monomer solution, purged by bubbling nitrogen gas for degassing, and then sealed in a glass ampule. The grafting reaction was carried out by placing the ampule in a water bath set at the relevant temperature. This graft copolymerization was initiated by radicals formed by the decomposition of peroxide on the UHMWPE surface. After the grafting copolymerization reaction, the grafted UHMWPE was taken out of the monomer solution in the glass ampule and extracted by hot acetone in a Soxhlet extractor for over 24 h to remove the unreacted remaining monomers or MMA homopolymers. The degree of grafting was determined by the following:

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

where  $W_g$  and  $W_0$  are weights of the grafted and ungrafted UHMWPE, respectively.

For confirmation of the MMA grafting, MMAgrafted UHMWPE was verified by Fourier transform infrared spectroscopy in attenuated total reflectance (FTIR–ATR) and by electron spectroscopy for chemical analysis (ESCA). X-ray photoelectron spectroscopy (XPS) analysis was carried out with a V. G. SCIENTFIC ESCALAB MK II spectrometer using MgK $\alpha$  X-ray radiation at 1253.6 eV operating at 10<sup>-9</sup> mbar and a photoelectron takeoff angle of 60°. The UHMWPE was cut to form 6-mm disks and then introduced into the UHV spectrometer chamber. MgK $\alpha$  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 (0–1200 eV) were recorded for each sample to obtain a qualitative elemental analysis. Detailed scans over narrow energy ranges were recorded around each peak of C(1s) and O(1s).

# **RESULTS AND DISCUSSION**

When UHMWPE is subjected to ionizing radiation in air, the trapped radicals or peroxides such as diperoxides (POOP) and hydroperoxides (POOH) by the dissociation of the polymer backbone or hydrogen are generally formed. When the hydroperoxides formed on and near the polymer substrate are heated at high temperatures, the dissociation of the peroxide leads to an equal number of PO· and ·OH radicals. This means that the reactive sites in the backbone polymer are generated by the decomposition of diperoxides [eq. (8)] or hydroperoxides [eq. (9)] at high temperatures. When such polymeric peroxides are used to initiate a graft copolymerization reaction, diperoxides generate a graft copolymerization while hydroperoxides lead to an equivalent amount of the graft polymer and homopolymer. These radicals initiate the grafting reaction. The schematic mechanism of UHMWPE during irradiation is as follows:

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

$$\mathbf{P} \cdot + \mathbf{O}_2 \to \mathbf{POO} \cdot \tag{3}$$

$$POO \cdot + PH \rightarrow POOH + P \cdot$$
 (4)

$$POO \cdot + P \cdot \to POOP \tag{5}$$

$$POO \cdot + \cdot OOP \rightarrow POOP + O_2$$
 (6)

$$\mathbf{P} \cdot + \mathbf{P} \cdot \to \mathbf{P} - \mathbf{P} \tag{7}$$

$$POOP \rightarrow PO \cdot + \cdot OP$$
 (8)

$$POOH \rightarrow PO \cdot + \cdot OH \tag{9}$$



**Figure 1** Decomposition of peroxides at 70°C in toulene for peroxidized UHMWPE.

In these equations, P and P represent the UHMWPE chain and the UHMWPE radicals produced by irradiation, respectively.

The DPPH technique was utilized to evaluate the concentration of peroxide formed in the irradiated UHMWPE sheet by counting the quantity of DPPH consumed from the reaction of peroxide radicals with DPPH. Figure 1 shows the decomposed peroxide concentration calculated from the DPPH consumption as a function of the reaction time at 70°C for the UHMWPE sheet irradiated by  $\gamma$ -rays at a dose of 40 kGy. The decomposition of peroxides continued for up to 5 h and then leveled off. Therefore, the concentration of peroxide formed in the irradiated UHMWPE was determined after decomposing the peroxides in the DPPH solution at 70°C for 5 h.

Figure 2 shows the effect of the storage temperature and time on the formation of peroxides on UHMWPE samples which were irradiated to a total dose of 40 kGy. The DPPH technique was utilized to evaluate the concentration of peroxide formed in the irradiated UHMWPE by counting the quantity of DPPH consumed from the reaction of peroxide radicals with DPPH. The decomposed peroxide concentration was calculated from the DPPH consumption as a function of the reaction time at 70°C for the UHMWPE samples irradiated by  $\gamma$ -rays. It was shown that the peroxides of UHMWPE at room temperature increased rap-



**Figure 2** Effect of storage temperature and time on the decomposition of peroxides.

idly with storage time up to 10 days and then leveled off. On the other hand, the peroxide extent of UHMWPE stored at -130°C did not change until 20 days after irradiation. When organic polymers are subjected to ionizing radiation, trapped radicals, capable of initiating graft copolymerization reactions, are generally formed. The trapped radicals at room temperature in the presence of air are easily oxidized to form peroxide because the temperature-dependent diffusion of oxygen is a primary factor. Termination of various active sites increases with increasing storage temperature of the irradiated polymers. On the other hand, the UHMWPE radicals at extremely low temperatures almost do not change owing to the restriction of oxygen diffusion.

The peroxidized UHMWPE sheets after preirradiation were examined by FTIR–ATR. Figure 3 shows the FTIR–ATR spectra of the control and peroxidized UHMWPE surfaces stored at room temperature for 10 days after a total dose of 40 kGy. For the peroxidized sample, the stretching peaks of the carbonyl group (—C=O) at 1730 cm<sup>-1</sup> and ether carbon bands (—C—O, 1130– 1160cm<sup>-1</sup>) increased. From the above result, the structure of the peroxidized UHMWPE sample was confirmed by FTIR–ATR spectra, showing an absorption peak at 1730cm<sup>-1</sup> due to the presence of carboxyl groups in the peroxidized samples and ether carbon bands (—C—O, 1130–1160cm<sup>-1</sup>), as shown in Figure 3.



**Figure 3** FTIR–ATR spectra of (a) control and (b) peroxidized UHMWPE.

The effect of the reaction time on the grafting of MMA onto UHMWPE with the addition of various additives is shown in Figure 4. The effect of the addition of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was much higher than that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , while the grafting reaction was low without the additive. In the case



**Figure 4** Effect of reaction time on the grafting of MMA onto peroxidized UHMWPE in 60 vol % MMA methanol solution containing  $2.5 \times 10^{-3} M$  salts and  $0.1M H_2SO_4$  at 70°C.

of both sulfuric acid and FeSO<sub>4</sub> ·7H<sub>2</sub>O addition, the grafting yield rapidly increased with increased reaction time. On the other hand, in the case of CuSO<sub>4</sub> ·5H<sub>2</sub>O with sulfuric acid addition, the grafting yield was much lower than that of  $CuSO_4 \cdot 5H_2O$ .  $CuSO_4 \cdot 5H_2O$  did not have a good effect on the grafting reaction compared to addition of  $FeSO_4$  ·7H<sub>2</sub>O. It is known that certain transition-metal compounds are effective at inhibiting homopolymerization.<sup>11</sup> In our previous experiment, the  $Fe^{2+}$ ,  $Fe^{3+}$ , and  $Cu^{2+}$  metallic compounds were effective inhibitors of the homopolymerization of acrylic acid or methacrylic acid onto polyethylene.<sup>11</sup> The effect of Cu<sup>2+</sup> and Fe<sup>3+</sup> on graft polymerization was investigated by Collison et al.,<sup>13</sup> who suggested that radical termination occurs by an electron-transfer process from a propagating polymer to a *d*-orbital of the cation. For this purpose, a ferrous ion has been commonly used. The reaction of  $Fe^{2+}$  with hydroperoxide which occurs during irradiation is as follows:

$$POOH + Fe^{2+} \rightarrow PO + Fe^{3+} + OH^{-} \quad (10)$$

Metallic salt plays an important role in decomposing the hydroperoxides by a redox reaction, as shown in eq. (10). In addition, the deactivation process of the grafting chain radical growth is as follows:

$$PO \cdot + Fe^{2+} \rightarrow PO^- + Fe^{3+} + H_2O \qquad (11)$$

This reaction may reduce the grafting reaction.

The grafting yield was much higher in the case of ferrous sulfate than of cupric sulfate, because  $Fe^{2+}$  can be transferred to  $Fe^{3+}$  by oxidation to dissociate hydroxides. However, it should be noted that it is impossible to oxidize  $Cu^{2+}$ . Therefore, it was examined in this experiment whether  $FeSO_4 \cdot 7H_2O$  has a synergistic effect on grafting, as shown in eq. (10), 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 eq. (10). By the addition of sulfuric acid to the grafting solution, the  $OH^-$  accumulated in eq. (10) can be consumed by a reaction with  $H^+$ , which dissociates from sulfuric acid. Therefore, eq. (10) can progress in the presence of acid by the principle of Le Chartelier. However, sulfuric acid had a detrimental



**Figure 5** Effect of  $H_2SO_4$  concentration on the grafting of MMA onto peroxidized UHMWPE in 60 vol % MMA methanol solution containing  $2.5 \times 10^{-3} M$  salt at 70°C for 3 h.

effect on the grafting reaction in the presence of  $CuSO_4$  ·5H<sub>2</sub>O because  $Cu^{2+}$  itself is impossible to oxidize.

The effect of sulfuric acid concentration on the grafting yield is shown in Figure 5. As shown in Figure 5, with the addition of  $FeSO_4 \cdot 7H_2O$ , the grafting yield increased rapidly with the addition of sulfuric acid up to 0.1M and then slightly decreased. Without salt, the grafting yield increased slightly with the addition of sulfuric acid and then slightly decreased, the maximum peak occurring at 0.1M sulfuric acid. In the case of  $CuSO_4 \cdot 5H_2O$ , however, the grafting yield decreased with increased sulfuric acid.

The effect of the type of acid on the grafting yield is shown in Figure 6. The grafting yield followed in the order of  $H_2SO_4 > HCl > HNO_3 > CH_3COOH$ .

When peroxidized UHMWPE in the MMA methanol solution is heated, the grafting of MMA to UHMWPE is initiated by peroxy radicals. However, undesirable homopolymerization initiated by the OH radical formed in the thermodecomposition reaction takes place simultaneously, which leads not only to a lower grafting yield but also to an enhancement of homopolymerization, and the homopolymer anchored on the UHMWPE is difficult to remove. To prevent homopolymerization,



**Figure 6** Effect of acid concentration on the grafting of MMA onto peroxidized UHMWPE in 60 vol % MMA methanol solution containing  $2.5 \times 10^{-3} M$  FeSO<sub>4</sub> ·7H<sub>2</sub>O at 70°C for 3 h.

Nho et al. reported in a previous article a method of using a reducing agent to decompose the peroxy species by converting OH to inactive ions.<sup>11</sup> In the article,<sup>11</sup> the grafting reaction was severly limited without metallic salt because of the homopolymer formation during the grafting reaction. Therefore, in this study, the effect of metallic salt concentration on the grafting yield was examined. Figure 7 shows the effect of the  $FeSO_4 \cdot 7H_2O$  and  $CuSO_4$  $\cdot 5H_2O$  concentration on the grafting yield in the presence and absence of sulfuric acid. For  $FeSO_4$  $\cdot$ 7H<sub>2</sub>O, the grafting yield rapidly increased with increased  $FeSO_4 \cdot 7H_2O$  concentration until 2.5 imes 10<sup>-3</sup> M salt and then decreased with further increased concentration of FeSO<sub>4</sub> ·7H<sub>2</sub>O without regard to any additional sulfuric acid. In the presence of sulfuric acid, however, the grafting yield was much higher than in the absence of sulfuric acid. The optimum concentration of metallic salt exists in the grafting solution. The reason why the further addition of salt reduces the grafting yield is due to scavenged PO, as shown eq. (11). In the case of  $CuSO_4 \cdot 5H_2O$  without sulfuric acid, the grafting yield increased slightly with increased  $CuSO_4$  ·5H<sub>2</sub>O concentration up to 2.5  $\times 10^{\circ}$  M and then decreased with the salt concentration. The addition of  $CuSO_4 \cdot 5H_2O$  in the presence of sulfuric acid decreased the grafting yield.



**Figure 7** Effect of salt concentration on the grafting of MMA onto peroxidized UHMWPE in 60 vol % MMA methanol solution containing  $0.1M \text{ H}_2\text{SO}_4$  at 70°C for 3 h.

This is closely related to the fact that it is impossible for  $Cu^{2+}$  to be oxidized to  $Cu^{3+}$  by redox systems.



**Figure 8** Effect of reaction on the grafting of MMA onto peroxidized UHMWPE in 60 vol % MMA methanol solution containing  $2.5 \times 10^{-3} M \text{ FeSO}_4 \cdot 7 \text{H}_2\text{O}$  and  $0.1M \text{ H}_2\text{SO}_4$ .



**Figure 9** Logarithmic plots of grafting rate versus reciprocal of grafting temperature. Grafting conditions are the same as in Figure 8.

The reaction time is one of the important factors controlling the grafting. Figure 8 shows the effect of reaction time and temperature on the grafting of MMA onto peroxidized UHMWPE after irradiation. As shown in Figure 8, the grafting yield at 70°C was much higher than that at 50°C, while the grafting reaction was remarkably low at 30°C. The reason why the grafting yield is low at low temperatures can be attributable to the extremely low decomposition rate of peroxide at low temperatures. However, it is possible that the reactive sites on the backbone polymer can easily be generated by the decomposition of hydroperoxide species at high temperatures with cationic salt and/or acid, leading to the greater grafting reaction.

Based on the data in Figure 8, logarithmic plots of the grafting rate against the reciprocal grafting temperature are shown in Figure 9. The increase in grafting rate with grafting temperature follows the Arrhenius relationship as shown in eq. (12):

$$\log K = \log A - \frac{E_a}{2.3RT} \tag{12}$$

where K is the grafting reaction rate; A, a temperature-independent constant;  $E_a$ , the activation energy; R, the Boltzmann's constant; and T, the absolute temperature. Based on the slopes of the



**Figure 10** FTIR-ATR spectra of (a) control and (b) 4.55 mg/cm<sup>2</sup> and (c) 12.05 mg/cm<sup>2</sup> of MMA-grafted UHMWPE surfaces.



Figure 11 ESCA survey scan spectra of (a) control and MMA-grafted UHMWPE surfaces of (b)  $4.55 \text{ mg/} \text{ cm}^2$  and (c)  $12.05 \text{ mg/cm}^2$  grafting.



Figure 12 ESCA carbon 1s core-level spectra of MMA-grafted UHMWPE surfaces of  $12.05 \text{ mg/cm}^2$  grafting.

Arrhenius plots, the activation energy of grafting was 20 kcal/mol. This value is apparently too high for a reaction of a vinyl monomer by free radicals. Therefore, the high apparent activation energy may be due mainly to a monomer diffusion process.

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 X-ray photoelectron spectrometer. Figure 10 shows the FTIR–ATR spectra of the control and MMA-grafted UHMWPE sheet surfaces with the grafting yield. With increasing grafting yield, the stretching peaks of the carbonyl group (—C=O) at 1730 cm<sup>-1</sup> and the ether carbon band (—C—O, 1130–1160 cm<sup>-1</sup>) increased, whereas the C—H bending peaks at 1465

 $cm^{-1}$  decreased with the grafting yield. For the grafting of UHMWPE, the control and MMAgrafted UHMWPE sheet surfaces were examined by measuring the survey scan spectra with an X-ray photoelectron spectrometer. Figure 11 shows the ESCA survey scan spectra of UHMWPE sheet surfaces for control and MMAgrafted UHMWPE. As shown in Figure 11, 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 increasing amount of carboxyl groups and ether carbon on the UHMWPE surfaces, as shown in Figure 12. However, there was a trace peak of UHMWPE even after 12.05 mg/cm<sup>2</sup> of MMA-grafted UHMWPE. From these results, it could be concluded that a grafting layer was produced both on the UHMWPE sheet surface and in the bulk of UHMWPE.

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