

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

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ABSTRACT: An attempt was made to graft methyl methacrylate (MMA) onto ultrahigh molecular weight polyethylene preirradiated in air in the presence of a metallic salt and acid. The grafting yield increased with increasing monomer concentration. The maximum grafting yield was around a 60 vol % monomer concentration. The results showed that the inclusion of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and sulfuric acid in MMA grafting solutions was extremely beneficial and led to a most unusual synergistic effect in the radiation grafting, much

more than with only a metallic salt. However, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ led to a detrimental effect. It is believed that sulfuric acid accelerates the decomposition of hydroperoxides in the presence of metallic salts such as Fe^{2+} , inhibiting homopolymerization. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2348–2356, 2002

Key words: radiation; polyethylene (PE)

INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) has been used in a variety of applications, such as implantable prosthetic devices, particularly total joint replacements,^{1–4} because of its excellent mechanical properties and its resistance to chemicals and abrasion. In 1960, Charnley⁵ chose Teflon with the lowest coefficient of friction for the socket and metal head of a femur in a total hip prosthesis. However, Teflon was found to wear much too quickly.⁶ A change was made to high-density polyethylene with an ultrahigh molecular weight, and this has been used until the present time. UHMWPE has a number of mechanical and chemical properties that make it highly suitable for orthopedic implants.⁷ However, it is difficult to adhere UHMWPE to human bone and organic and inorganic materials because UHMWPE is inactive chemically. Grafting techniques can be used to modify the surfaces of polymers.⁸ The grafting method needs free radicals or peroxides to modify the surfaces of polymers and can be carried out by ionization radiation,^{9,10} UV,^{11,12} plasma,¹³ or chemical initiators. Among these techniques, radiation methods are among the more useful methods because of the uniform and rapid creation of active radical sites. The methods for

achieving a grafting reaction with radiation include (1) simultaneous irradiation of a backbone polymer in the presence of a monomer;⁹ (2) preirradiation of a backbone polymer in a vacuum or nitrogen gas and subsequent monomer grafting by trapped radicals;¹⁴ 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.¹⁵

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 transformed gradually into peroxides and hydroperoxide species, which may result in undesirable homopolymerization initiated by the mobile $\cdot\text{OH}$ radical formed in the thermal decomposition reaction. It is possible to solve this problem with a reducing agent, such as metallic salt, to decompose the peroxy species. O'Neill¹⁶ used only an Fe^{2+} ion as a reducing agent to decompose the hydroperoxides, thereby converting hydroxyl radicals into inactive hydroxide ions, which can prevent undesirable homopolymerization. Nho and Jin¹⁵ reported the effect of a metallic salt and sulfuric acid on the radiation grafting of acrylic acid and methacrylic acid onto radiation-peroxidized polyethylene film. So far, although the radiation-initiated grafting of methyl methacrylate (MMA) onto various polymer substrates has been studied, the addition effect of a cationic salt and acid on the radiation grafting of MMA onto UHMWPE has still not been reported. The grafting of MMA onto

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UHMWPE is considered interesting because bone cement consists of poly(methyl methacrylate).

The grafting reaction reported in this article was carried out with a preirradiation method in which the substrate polymer of UHMWPE was preirradiated with γ rays in air. The effect of the storage temperature of preirradiated UHMWPE, the monomer concentration, the reaction temperature, the reaction time, and the addition of various cationic salts and acids on the radiation grafting reaction were investigated.

EXPERIMENTAL

Materials

Commercial UHMWPE 1.0 mm thick (molecular weight = 5.5×10^6 , 0.94 g/cm³; Saxin Co., Ltd.) was used as a substrate for graft polymerization. The UHMWPE was cut into 1.5 cm \times 5.0 cm pieces, ultrasonically cleaned twice in methanol for 1 h each time, and dried in a vacuum oven. MMA (Junsei Chemical Co., Ltd.), FeSO₄ · 7H₂O (Merck AG), and CuSO₄ · 5H₂O (Waco Pure Chemical Co., Ltd.) were used as supplied without further treatment. Other chemicals were reagent-grade.

Grafting procedure

The γ -ray irradiation from a Co-60 source was carried out at an exposure rate of 4.87 kGy/h in the presence of air to a total dose of 30 or 40 kGy. The irradiated UHMWPE sheets were stored in a refrigerator, which was kept at -130°C , until the grafting reaction. The grafting experiments were performed in a glass ampule with a stopcock. The methanol and additives were added first and were followed by a monomer for a total volume of 50 mL. The preirradiated UHMWPE was immersed in the monomer solution, purged with bubbling nitrogen gas for degassing, and then sealed in a glass ampule. The grafting reaction was carried out by the ampules being placed in a water bath set at a 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 the glass ampule and extracted by hot acetone in a Soxhlet extractor over 24 h for the removal of unreacted monomers or MMA homopolymers remaining. The degree of grafting was determined as follows:

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

where W_g and W_o are the weights of the grafted and ungrafted UHMWPEs, respectively.

The grafting efficiency was evaluated in the following manner. After the grafting reaction, the grafting

solution was poured into water for precipitation of the homopolymer. The homopolymer that adhered to the polymer film and to the ampule was also collected to measure the quantity of the homopolymer. The grafting efficiency was calculated as the weight of the graft divided by the weight of the homopolymer plus the weight of the graft.

The grafted UHMWPE was verified by Fourier transform infrared spectroscopy in the attenuated total reflectance mode (FTIR-ATR) and by electron spectroscopy for chemical analysis (ESCA). A Nicolet 5SXC spectrophotometer with a nominal 45° attenuated total reflectance was used to examine grafting onto UHMWPE by irradiation. ESCA, for an examination of the grafting onto the UHMWPE sheet by irradiation, was carried out with a V. G. Scientific Escalab MK II spectrometer, with Mg K α X-ray radiation at 1253.6 eV, operating at 10^{-9} mbar and photoelectron takeoff angles of 60° . The control and UHMWPE samples were cut into 6-mm disks and then introduced into the UHV spectrometer chamber. Mg K α radiation was used with the analyzer operating at a constant bandpass energy of 20 eV. The spectrometer was calibrated under the assumption that the binding energy of the Au 4f_{7/2} line was 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.

Peroxide determination

For peroxidized UHMWPE, the amount of peroxide formed on and near the substrate was quantified with DPPH.¹⁷ The peroxidized UHMWPE stored at room temperature for 10 days after irradiation was put in a 1.0×10^{-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 irradiated sample with an ultraviolet spectrophotometer (Cesil Instruments, CE 292).

RESULTS AND DISCUSSION

When UHMWPE is 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. The schematic mechanism of UHMWPE during irradiation is as follows:





In these schemes, P and P· 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 ·OH radical formed in the thermal decomposition reaction. It is possible to obviate this problem with a reducing agent, such as metallic salt, to decompose the peroxy species. O'Neill¹⁶ used only Fe²⁺ ions as the reducing agent to decompose the hydroperoxides, thereby converting hydroxyl radicals into inactive hydroxide ions, which can prevent undesirable homopolymerization. Nho and Jin¹⁵ reported on the effect of a metallic salt and sulfuric acid on the radiation grafting of acrylic acid and methacrylic acid onto radiation-peroxidized polyethylene film. It is known that free radicals, created by irradiation in solid polymers, are immobilized and may remain trapped for a considerable length of time. The major factor governing the trapping of radicals is the physical state of the irradiated polymer. In the preirradiation process, the polymeric material is irradiated, and the monomer is subsequently in contact with the irradiated polymer. Grafting is induced by macroradicals trapped in the irradiated polymer. Virtually no homopolymer is produced by this method, and there is no limitation to any particular polymer/monomer combination because the monomer itself is not irradiated. Although the method has been successfully used for grafting various vinyl monomers onto polyethylene, the grafting yield obtained by this method will depend on the efficiency of the trapped radicals. The main factor governing the trapping of radicals is the physical state of the irradiated polymer. For rubbery and noncrystalline polymers, the mobility of radicals is fairly significant, and their survival time after irradiation is not long in comparison with that of polymers having high crystallinity. The usefulness of the grafting method depends largely on the crystallinity of the polymer and also on the relative reaction rates of the monomer with trapped radicals and the thermal decay of radicals at the temperature required for grafting. The lifetime of the trapped free radicals depends on the temperature of storage because it can affect the mobility of polymer radicals. The relation between the grafting reaction and the storage time and storage temperature is important for practical applications. The UHMWPE was stored under various storage conditions for a

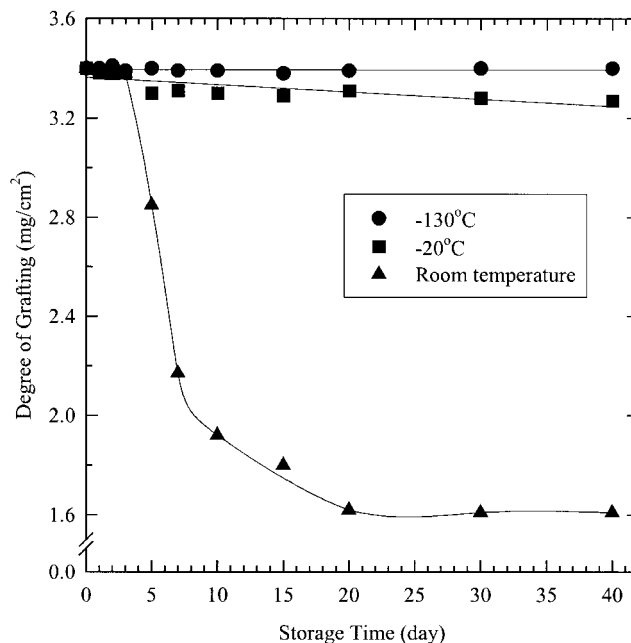


Figure 1 Effect of the storage temperature and time on the grafting of MMA onto 40 kGy-preirradiated UHMWPE in a 60 vol % MMA methanol solution at 50°C for 3 h.

certain period of time immediately after irradiation. Figure 1 shows the effect of the storage temperature and time on the grafting of MMA onto UHMWPE preirradiated to a total dose of 40 kGy. The grafting yield of the irradiated UHMWPE stored at room temperature remained constant for 3 days, decreased rapidly with storage between 3 and 20 days, and then leveled off. When the storage temperature was -20°C , the grafting yield decreased slightly with an increase in storage time. However, the grafting yield at a storage temperature of -130°C remained nearly constant until 40 days at least. A constant grafting yield, even after 40 days of storage at -130°C , can be attributed to the stoppage in the termination of free radicals [eqs. (5)–(7)], which comes from the high crystallinity of UHMWPE and the restriction of chain segmental motion at such a low temperature. The termination rate of various active sites increases with the storage temperature of the irradiated polymers increasing. Therefore, the storage temperature is one of the most important factors in controlling the trapped radicals of an irradiated sample.

The DPPH technique was used to evaluate the concentration of peroxide formed in the irradiated UHMWPE sheet by the measurement of the quantity of DPPH consumed from the reaction of peroxide radicals with DPPH. Figure 2 shows the effect of the storage temperature and time on the formation of peroxides on UHMWPE samples that were irradiated to a total dose of 40 kGy. The DPPH technique was used to evaluate the concentration of peroxide formed in the irradiated UHMWPE by the measurement of the

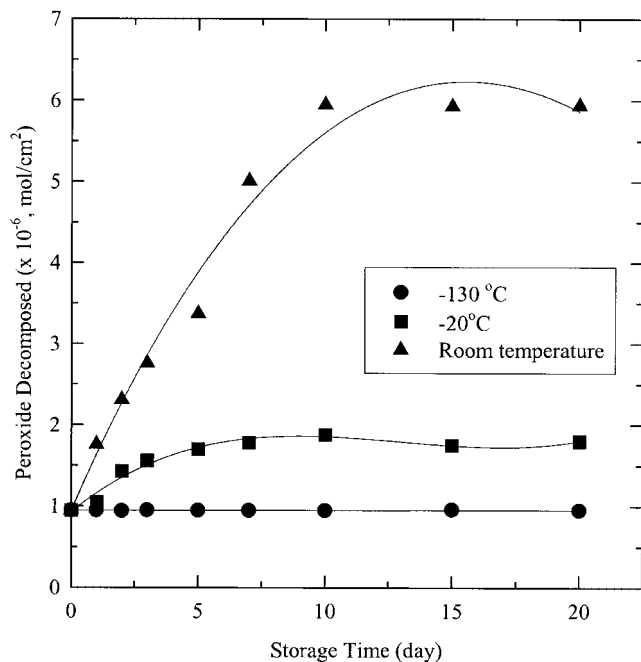


Figure 2 Effect of the storage temperature and time on the decomposition of peroxides formed by 40 kGy irradiation.

quantity of DPPH consumed from the reaction of peroxide radicals with DPPH. The decomposed peroxide concentration was calculated from the DPPH consumption for the UHMWPE samples irradiated by γ rays. The peroxides of UHMWPE at room temperature increased rapidly with storage time up to 10 days and then leveled off. However, 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 peroxides because the chain segmental motion of UHMWPE is possible. The termination of various active sites increases with the storage temperature of irradiated polymers increasing. However, the UHMWPE radicals at extremely low temperatures almost do not change because of the restriction of chain segmental motion.

The effect of the monomer concentration in methanol on the grafting yield is shown in Figure 3. With the addition of sulfuric acid and a salt, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, the grafting yield was much higher than with the addition of a salt, whereas the grafting yield was remarkably low without additives. In most of the grafting reactions, the reactive sites on the backbone polymer can be generated by the decomposition of hydroperoxide species at high temperatures. In particular, the addition of an acid and salt can induce the decomposition of the hydroperoxide species. The maximum grafting yield occurred around a 60 vol % monomer concen-

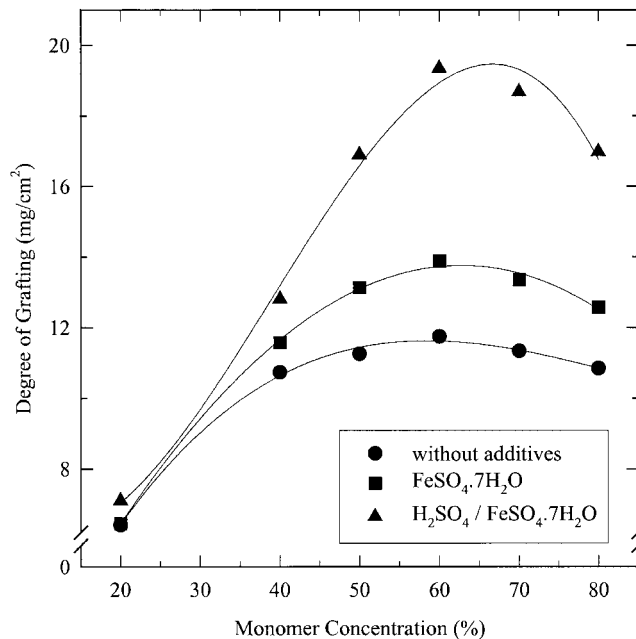


Figure 3 Effect of the monomer concentration on the grafting of MMA onto 30 kGy-irradiated UHMWPE in a methanol solution containing 0.05M H_2SO_4 and 1.5×10^{-4} M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at 70°C for 3 h.

tration. In the grafting reaction, the reaction temperature is one of the important factors in controlling grafting. The effect of the reaction temperature on the grafting yield of MMA onto UHMWPE was examined. As shown in Figure 4, the grafting yield increased with the reaction temperature. Also, with the addition

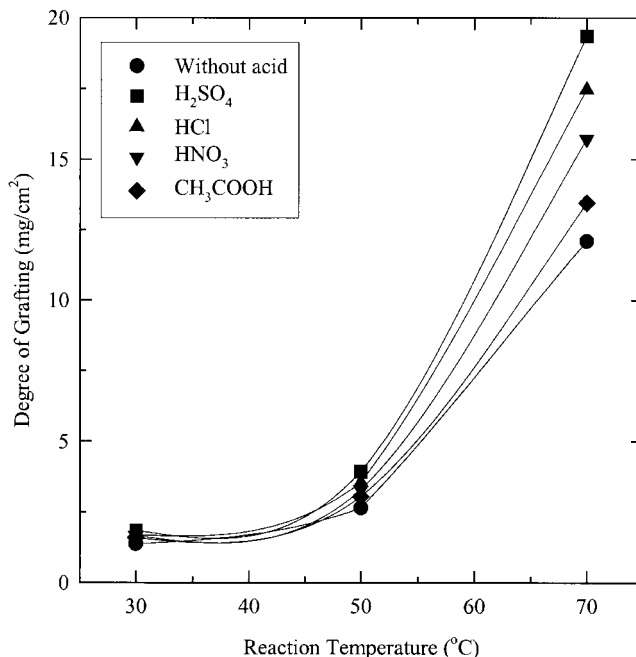


Figure 4 Effect of the reaction temperature on the grafting of MMA onto 30 kGy-preirradiated UHMWPE in a 60 vol % MMA methanol solution containing 0.05M acids for 3 h.

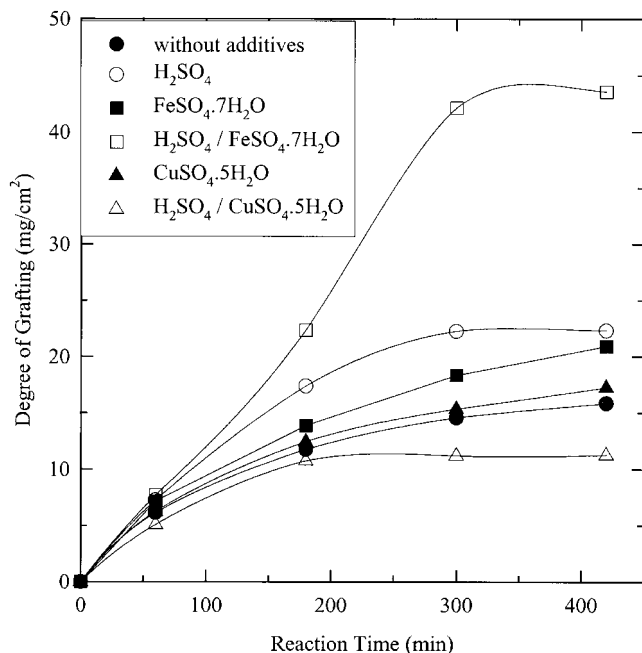
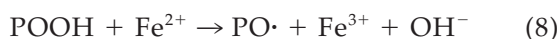


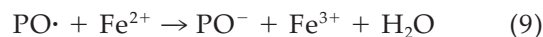
Figure 5 Effect of the reaction time on the grafting of MMA onto 30 kGy-preirradiated UHMWPE in a 60 vol % MMA methanol solution containing 0.1M H_2SO_4 and 1.5×10^{-4} M salts at 70°C.

of sulfuric acid, a synergistic effect occurred. The effect of acids on the grafting yield was in the following order: $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3 > \text{CH}_3\text{COOH}$.

The effect of the reaction time on the grafting of MMA onto UHMWPE with the addition of various additives is shown in Figure 5. With the addition of sulfuric acid, the grafting yield increased with an increase in the reaction time. The addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was much higher than that of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, whereas the grafting yield was low in the absence of additives. With the addition of both sulfuric acid and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, the grafting yield rapidly increased with an increase in the reaction time. However, with the addition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with sulfuric acid, the grafting yield was much lower than with only $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. It has been shown that certain transition-metal compounds are effective in inhibiting homopolymerization.¹⁵ In our previous experiments, the Fe^{2+} , Fe^{3+} , and Cu^{2+} metallic compounds were effective inhibitors of the homopolymerization of acrylic acid or methacrylic acid onto polyethylene.¹⁵ The effect of Cu^{2+} and Fe^{3+} on graft polymerization was investigated by Collinson et al.,¹⁸ 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+} on the hydroperoxide formed during irradiation is as follows:



A metallic salt plays an important role in decomposing the hydroperoxides by a redox reaction, as shown in eq. (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. The grafting yield was much higher for ferrous sulfate than cupric sulfate because Fe^{2+} can be transferred to Fe^{3+} by oxidation to dissociate hydroxides. However, it is impossible to oxidize Cu^{2+} . Therefore, in this experiment, we examined whether $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ would lead to a synergistic effect on grafting, as shown in eq. (8), in the presence of sulfuric acid. From the results, 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 could initiate the grafting reaction, as shown in eq. (8). By the addition of sulfuric acid to the grafting solution, the OH^- accumulated in eq. (8) can be consumed by the reaction with H^+ , which is dissociated from sulfuric acid. Therefore, eq. (8) can progress in the presence of an acid by the principle of Le Chatelier. Garnett et al.¹⁹ stated that for a typical system, such as the grafting of styrene in a monomer solution to polyethylene initiated by either cobalt-60 or UV, the inclusion of a mineral acid in the monomer solution leads to an increase in the concentrations of the monomer in the grafting monomer solution absorbed within the backbone polymer in comparison with the original

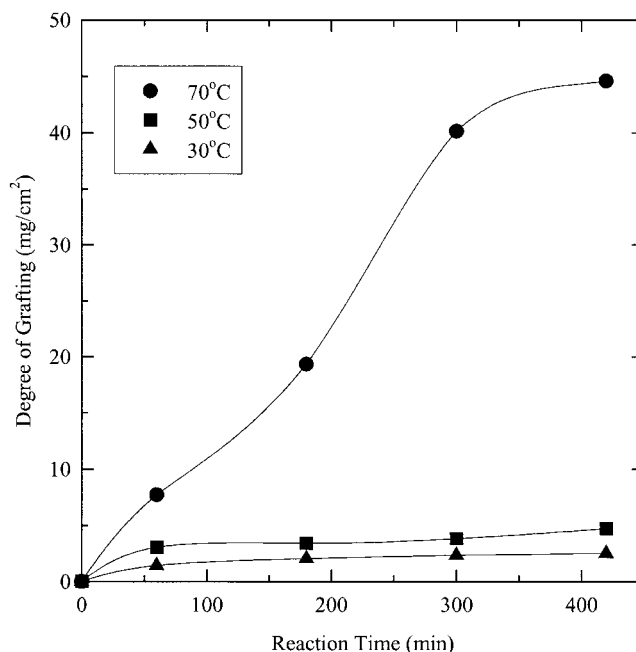


Figure 6 Effect of the reaction time on the grafting of MMA onto 30 kGy-preirradiated UHMWPE in a 60 vol % MMA methanol solution containing 0.05M H_2SO_4 and 1.5×10^{-4} M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

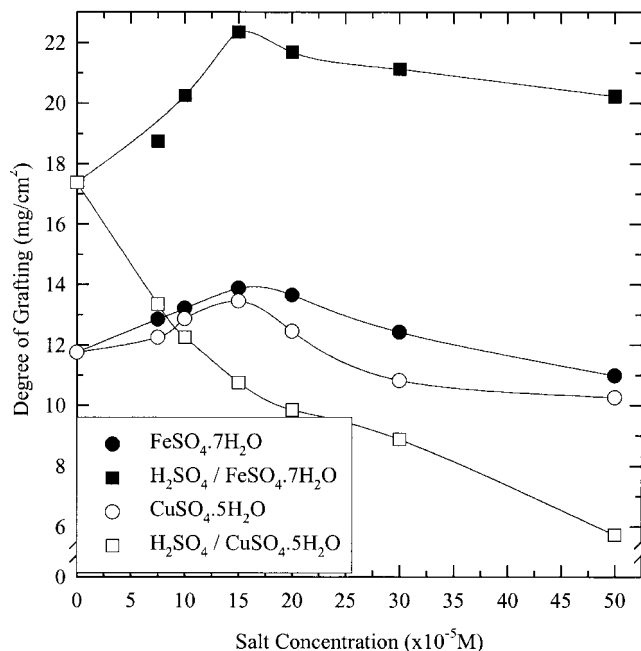


Figure 7 Effect of the salt concentration on the grafting of MMA onto 30 kGy-preirradiated UHMWPE in a 60 vol % MMA methanol solution containing 0.1M H₂SO₄ at 70°C for 3 h.

bulk grafting monomer solution. In published work associated with the grafting of styrene onto polyethylene in methanol solutions, it has been reported that the partitioning of a monomer into a backbone polymer was significantly improved by the inclusion of sulfuric acid in the grafting solution. In any grafting system at any one time, there is an equilibrium concentration of the monomer absorbed within the grafting region of the backbone polymer. This grafting region may be continually changing as grafting proceeds. The degree to which the monomer will be absorbed by this grafting region will depend on the chemical structure of the region. The extent of this improved monomer partitioning depends on the polarity of the monomer, the substrate, the solvent, and the concentration of sulfuric acid.

It is reasonable to assume that, while partitioning in the grafting solution involving cationic salts and sulfuric acid proceeds, the concentration of cationic salts in the bulk monomer solution will be greater than in the solution absorbed within the substrate because of the difference in the solubilities of cationic salts between the methanol-rich region and the monomer-rich region of the system. The bulk monomer solution will, therefore, contain higher concentrations of cationic salts and acids, and the ionic strength of the solution will be correspondingly higher than that of the equivalent absorbed in the backbone polymer. The partitioning phenomena will, therefore, be continually maintained at maximum efficiency during the grafting process because, as the monomer solution absorbed within the backbone polymer is depleted in MMA on account of grafting, more replacement monomer will rapidly diffuse into the backbone polymer from the bulk solution.

The reaction time and temperature are important factors controlling grafting. Figure 6 shows the effect of the reaction time and temperature on the grafting of MMA onto UHMWPE irradiated at 30 kGy. The grafting yield at 70°C was much higher than that at 50°C, whereas the grafting reaction was remarkably low at 30°C. Most of the grafting reaction at particularly low reaction temperatures can be attributable to the trapped radicals. However, it is possible that the reactive sites for the grafting reaction on the backbone polymer can be generated by the decomposition of hydroperoxide species at high temperatures with cationic salts and/or acids, as well as trapped radicals. Therefore, a high temperature is an advantage for a radiation grafting reaction.

By the heating of irradiated UHMWPE in an MMA methanol solution, the grafting of MMA to UHMWPE initiated by peroxyradicals proceeds. However, undesirable homopolymerization initiated by the ·OH radical formed in the thermodecomposition reaction takes place simultaneously. This leads to not only a lower grafting yield but also an enhancement of homopolymerization, and the homopolymers anchored on the

TABLE I
Grafting Efficiency (%) of MMA onto 30 kGy-Preirradiated UHMWPE in 60 vol MMA Methanol Solution at 70°C for 3 h

| Salt concentration (× 10 ⁻⁵ M) | FeSO ₄ ·7H ₂ O | H ₂ SO ₄ /FeSO ₄ ·7H ₂ O | CuSO ₄ ·5H ₂ O | H ₂ SO ₄ /CuSO ₄ ·5H ₂ O |
|-------------------------------------------|--------------------------------------|----------------------------------------------------------------------|--------------------------------------|----------------------------------------------------------------------|
| 0 | 92.8 | 96.2 | 92.8 | 96.2 |
| 7.5 | 93.1 | 97.2 | 93.0 | 93.0 |
| 10 | 94.0 | 99.0 | 93.8 | 93.0 |
| 15 | 95.4 | 99.5 | 95.0 | 92.5 |
| 20 | 95.3 | 99.2 | 94.2 | 92.2 |
| 30 | 94.5 | 99.1 | 93.6 | 91.3 |
| 50 | 93.5 | 98.7 | 92.5 | 90.6 |

UHMWPE are difficult to remove. To prevent homopolymerization, Nho and Jin¹⁵ reported a method of using a reducing agent to decompose the peroxy species by converting $\cdot\text{OH}$ into inactive ions. The grafting reaction was limited without the metallic salt because of homopolymer formation during the grafting reaction. Therefore, in this study, the effect of the metallic salt concentration on the grafting yield was examined. Figure 7 shows the effect of the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentrations on the grafting yield in the presence and absence of sulfuric acid. For $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, the grafting yield increased with an increasing concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ until $1.5 \times 10^{-4} \text{ M}$ and then decreased with a further increase in the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration, without regard to the addition of sulfuric acid. The addition of sulfuric acid caused a higher grafting yield. For $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ without sulfuric acid, the grafting yield increased with an increasing concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ until $1.5 \times 10^{-4} \text{ M}$ and then decreased with a further increasing salt concentration. However, the grafting yield rapidly decreased with an increasing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentration in the presence of sulfuric acid. In a previous study¹⁵ on the effect of a metallic salt and sulfuric acid on the radiation grafting of acrylic acid and methacrylic acid onto radiation-peroxidized polyethylene film, we could not carry out the grafting reaction because of the excessive formation of homopolymers without the metallic salt. However, in this study, the grafting reaction without metallic salt progressed well, although the grafting yield was a little low. Table I shows the grafting efficiency of

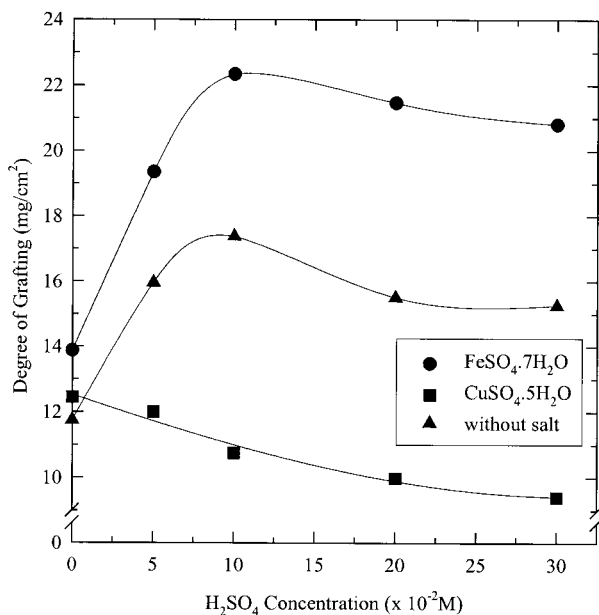


Figure 8 Effect of the H_2SO_4 concentration on the grafting of MMA onto 30 kGy-preirradiated UHMWPE in a 60 vol % MMA methanol solution containing $1.5 \times 10^{-4} \text{ M}$ salts at 70°C for 3 h.

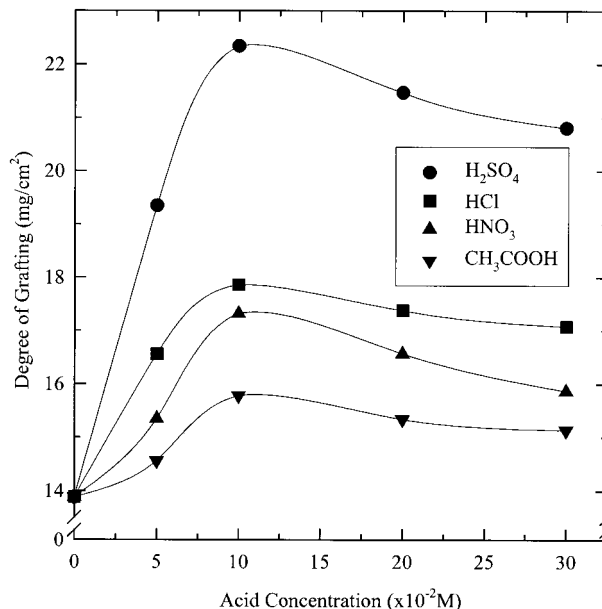


Figure 9 Effect of the acid concentration on the grafting of MMA onto 30 kGy-preirradiated UHMWPE in a 60 vol % MMA methanol solution containing $1.5 \times 10^{-4} \text{ M}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at 70°C for 3 h.

MMA onto 30 kGy-preirradiated UHMWPE in a 60 vol % MMA methanol solution as a function of the additives. The grafting efficiency was calculated as the weight of the graft divided by the weight of the homopolymer plus the weight of the graft. The grafting efficiency was directly proportional to the grafting yield. According to Table I, additives such as $\text{H}_2\text{SO}_4/\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ enhanced the grafting yield while limiting the homopolymer.

The effect of the sulfuric acid concentration on the grafting yield is shown in Figure 8. With the addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, the grafting yield increased rapidly with the addition of up to 0.1M sulfuric acid and then slightly decreased. Without a salt, the grafting yield increased rapidly with the addition of sulfuric acid and then slightly decreased, the maximum peak occurring at 0.1M sulfuric acid. With $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, however, the grafting yield decreased slightly with an increase in 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 that can initiate the grafting reaction. The OH^- accumulated in the reaction medium can be consumed by H^+ , which originates from the dissociation of sulfuric acid. Therefore, eq. (8) can progress easily forward in the presence of an acid, particularly in the presence of sulfuric acid. The addition effect of acids on the grafting yield was in the following order: $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3 > \text{CH}_3\text{COOH}$ (see Fig. 9). From this grafting reaction, it is assumed that a strong acid only plays a role in

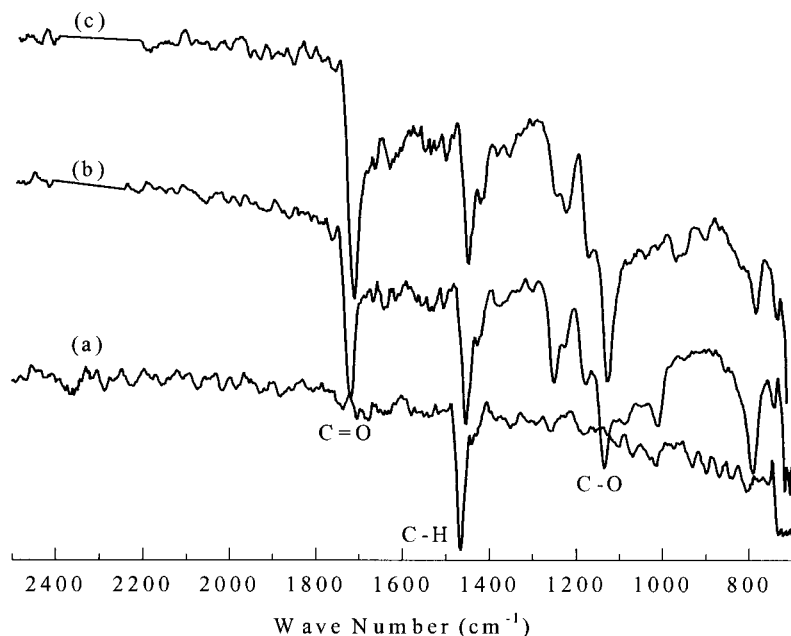


Figure 10 FTIR-ATR spectra of (a) a control and (b) 4.35 mg/cm² and (c) 11.26-mg/cm² MMA-grafted UHMWPE surfaces.

enhancing the redox reaction and the partitioning effect effectively, consequently increasing the grafting yield and suppressing homopolymers.

The changes in the chemical structure of the MMA-grafted UHMWPE sheets with the grafting yield were examined by FTIR-ATR and survey scan spectra with X-ray photoelectron spectrometry (XPS). Figure 10 shows the FTIR-ATR spectra of the control and MMA-grafted UHMWPE sheet surfaces with the grafting

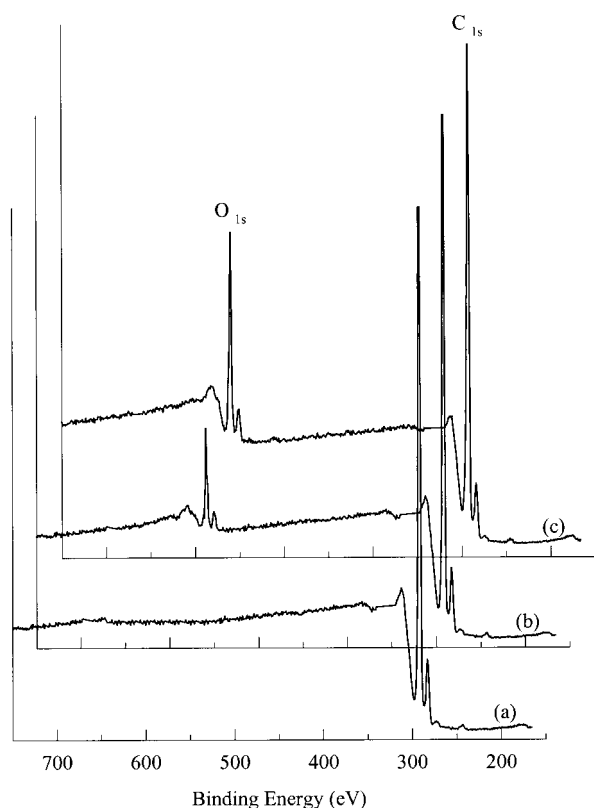


Figure 11 ESCA survey scan spectra of (a) a control and (b) 4.35 mg/cm² and (c) 11.26 mg/cm² MMA-grafted UHMWPE surfaces.

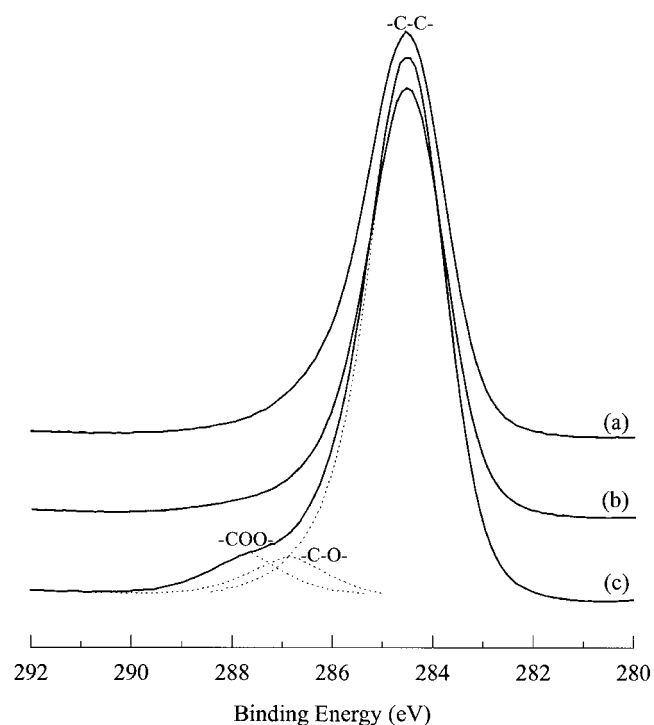


Figure 12 ESCA carbon 1s core-level spectra of (a) a control and (b) 4.35 mg/cm² and (c) 11.26 mg/cm² MMA-grafted UHMWPE surfaces.

TABLE II
ESCA of Control and MMA-Grafted UHMWPE Sheet Surfaces

| UHMWPE | | Atom % ^a | | Ratio ^b |
|--------------------------------|---------|---------------------|--------|--------------------|
| | | Carbon | Oxygen | -C-O-/-C-C- |
| Grafting (mg/cm ²) | Control | 99.997 | 0.003 | 0.025 |
| | 4.35 | 72.431 | 27.568 | 0.764 |
| | 11.26 | 64.867 | 35.133 | 0.946 |

^a Analyzed from survey scan spectra.

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

yield. With increased grafting yield, the stretching peaks of carbonyl groups (—C=O) at 1730 cm^{-1} and ether carbon bands (—C—O) at $1130\text{--}1160\text{ cm}^{-1}$ increased, whereas the C—H bending peaks at 1465 cm^{-1} decreased. MMA-grafted UHMWPE was examined by the measurement of survey scan spectra with XPS. Figure 11 shows ESCA survey scan spectra for the surfaces of the control and MMA-grafted UHMWPE sheets. The grafted UHMWPE had oxygen (O-1s, 537.0 eV) peaks as well as carbon (C-1s, 284.6 eV), whereas there was no oxygen peak for the ungrafted UHMWPE. With the increasing grafting yield, the oxygen peak of UHMWPE increased more and more because of the increasing number of carbonyl groups on UHMWPE surfaces. The atom percentages calculated from the ESCA survey scan spectra in Figure 12 and their ratios are shown in Table II.

CONCLUSIONS

An attempt was made to graft MMA onto UHMWPE preirradiated in air in the presence of a metallic salt and acid. The grafting yield increased with an increasing monomer concentration. The maximum grafting yield occurred around a 60 vol % monomer concentration. The inclusion of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and sulfuric acid in MMA grafting solutions was extremely beneficial and led to a most unusual synergistic effect in the radiation grafting, much more than with only a metallic salt. The addition effect of acids on the grafting

yield was in the following order: $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3 > \text{CH}_3\text{COOH}$.

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