

Radiation-Induced Graft Copolymerization of MMA Monomer onto UHMWPE: Adhesion Improvement

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ABSTRACT: Graft copolymerization of methyl methacrylate monomer onto ultra high molecular weight polyethylene (UHMWPE) and acid-etched UHMWPE was conducted using preirradiation method in air in the presence of a Mohr salt and sulfuric acid to improve adhesion to the bone cement. The grafted samples were characterized by Fourier transform infrared (FTIR) spectroscopy, gravimetric method, goniometry, and interfacial bonding strength measurements. The FTIR results showed the presence of ether, carbonyl, and hydroxyl groups for grafted films. The gravimetric results showed that the chromic acid etching and graft copolymerization had a synergetic effect so, the irradiated, then chromic acid etched at room temperature and grafted sample (Rad etch25) had the

highest grafting degree. The interfacial bonding strength between UHMWPE and poly methyl methacrylate bone cement was considerably improved by graft copolymerization and chromic acid etching. The surface morphology was studied by scanning electron microscopy. The substitution of polar groups into the backbone of UHMWPE by chromic acid etching and graft copolymerization changed its contact angles with water and methylene iodide and increased its surface energy, as evidenced by contact angle measurements. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1086–1092, 2008

Key words: UHMWPE; γ -irradiation; grafting; adhesion; MMA

INTRODUCTION

Ultra high molecular weight polyethylene (UHMWPE) has been used in a variety of applications, such as implantable prosthetic devices, particularly total joint replacements.^{1–4} However, it is a nonpolar and chemically inert material and because of its low surface energy, the bonding strength of poly methyl methacrylate (PMMA) bone cement to UHMWPE is extremely low and depends on the mechanical interlocking.^{5–7}

Chemical surface modification of UHMWPE offers a new possibility to improve the chemical and physical properties such as adhesion.^{6,8} Various methods have been employed to improve the surface properties of UHMWPE.⁹ Surface oxidation through chemical etching is the primary mechanism of these surface modification techniques and show better wettability and improved adhesion properties than unmodified UHMWPE.³ Surface roughening and oxidation of the UHMWPE contribute to the enhanced adhesion by chemical etching.^{7,10}

Another method to improve the adhesive properties of UHMWPE with PMMA bone cement is the graft copolymerization of methyl methacrylate

(MMA) monomer onto UHMWPE. The grafting method needs free radicals or peroxides to modify the surface of polymers. Graft copolymerization can be achieved by ionizing radiation, ultraviolet light, or chemical initiators. Of course, radiation grafting is one of the most promising methods because of its large penetration in polymer matrix, rapid and uniform formation of active sites for initiating grafting throughout the matrix. The methods of achieving grafting reaction using radiation include (1) synchronized irradiation of the backbone polymer in the presence of the monomer, (2) preirradiation of the backbone polymer in vacuum or nitrogen gas and subsequent monomer grafting by trapped radicals, and (3) preirradiation of the backbone polymer in the presence of air or oxygen.^{1,11–17} The trapped radicals, formed by irradiation in air, are transformed gradually into peroxides and hydroperoxide species, which in second step in contact with monomer at higher temperature may result in undesirable homopolymerization initiated by the mobile hydroxyl radicals formed in the thermal decomposition reaction. It is possible to solve this problem with a reducing agent, such as metallic salt (Mohr salt), to decompose the peroxide species.¹ Fe²⁺ ion as a reducing agent, decompose the hydroperoxides, thereby converting hydroxyl radicals into inactive hydroxide ions, which can prevent undesirable homopolymerization.^{11–13}

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Various methods have been developed to promote the irradiation method, including the change of the type of rays, variable range of exposure dose, the investigation of a free radical concentration, variable environment, the use of additives, and the control of MMA monomer concentration in grafting solution. Most studies are carried out with the high dosage, 25 kGy or more. However, a high exposure caused changes in crystallinity as well as deterioration of UHMWPE. Therefore, the surface modification of UHMWPE was required with a low exposure level for preventing deterioration from UHMWPE.^{18,19}

In our previous works,^{2,20,21} we studied the surface characteristics of UHMWPE oxidized with chromic acid. In this study, an attempt was made to graft copolymerize MMA monomer onto UHMWPE and acid etched UHMWPE using preirradiation method in air in the presence of a metallic salt and sulfuric acid to improve the bonding strength between UHMWPE and bone cement.

EXPERIMENTAL

Materials

UHMWPE powder (Product No. 429015) with a bulk density of 0.94 g/cm³, particle size of 150–180 μm, intrinsic viscosity of 25.5 dL/g, and a viscosity-average molecular weight of 4,538,730 was provided by Sigma-Aldrich (Oakville, ON, Canada) and used as a substrate for graft copolymerization. The samples were prepared by compression molding of the powder, cleaned twice in methanol for 1 h each time, and dried in a vacuum oven. MMA monomer (Merck AG, Darmstadt, Germany) and FeSO₄·H₂O salt (Merck AG) were used as received without further treatment. Methanol, sulfuric acid, and potassium dichromate were reagent grade (Merck AG).

Chemical etching of UHMWPE

To investigate the effect of chemical etching on the wetting properties of UHMWPE, some samples were etched by chromic acid (CA) at two temperatures (room temperature and 80°C) before irradiation and some of the samples were etched at the same temperatures after irradiation. A chromic acid solution was prepared by mixing of potassium dichromate (K₂Cr₂O₇), sulfuric acid (H₂SO₄), and distilled water in a 7 : 150 : 12 mass ratio. The UHMWPE samples were submerged in the etching solution for 30 min at room temperature and for 5 min at 80°C. After etching, the samples were washed in distilled water and acetone, dried in a vacuum oven at room temperature for 12 h and stored.

Irradiation

The irradiations were carried out on UHMWPE samples (etched or original) using γ-rays from Co-60 source, at a dose rate of 1.51 kGy/h, in air at room temperature with a total dose of 30 kGy.

Graft copolymerization

The irradiated UHMWPE samples were stored at −10°C. At first, 80 mL methanol as a reaction media, 8.34 mg Mohr salt (Fe₂SO₄·7H₂O) as a homopolymerization inhibitor, and 1.96 g sulfuric acid as a reaction accelerator were placed in the glass ampule, then followed by adding 120 mL MMA monomer to achieve 60 vol % monomer concentration. The preirradiated and acid etched UHMWPE samples were immersed in the monomer solution, purged with bubbling nitrogen gas for degassing, and sealed. The grafting reaction was carried out by placing the ampules in a water bath at 70°C for 5 h. After completion of reaction time, the grafted samples were taken out of the glass ampule and extracted by hot acetone in a Soxhlet extractor over 24 h to remove the unreacted monomers or remaining PMMA homopolymers. The degree of grafting (DG) was determined as:

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

where, W_g and W_0 are the weights of the grafted and initial UHMWPEs, respectively.¹

FTIR spectroscopy

The graft copolymerization on the UHMWPE and acid etched UHMWPE films with an average thickness of 200 μm, were studied by a UNICAM Matson 1000 Fourier transform infrared (FTIR) spectrometer.

Interfacial bonding strength

The bonding strength between PMMA sheets and UHMWPE-g-PMMA samples with various grafting degrees were measured in tension mode using a Zwick/Roell tensile machine (model TI-FR010TH-A50) at room temperature. All specimens for interfacial bonding strength were in dimensions 15 × 5 × 7 mm³. The UHMWPE-g-PMMA and Plexiglas sheets were overlapped on both ends to an area of 1.5 cm², and the overlapped area was coated with EUROFIX RO bone cement (Synergie Ingenierie Medicale, S. A. R. L. France). This cement is a self-polymerizing acrylic compounds with spontaneous solidification, consisting a powder fraction composed

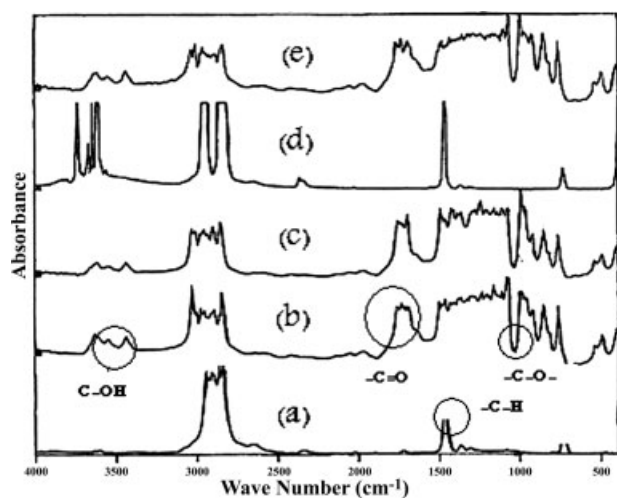


Figure 1 FTIR spectra of (a) UHMWPE (b) No etch rad, (c) Etch25 rad, (d) only irradiated, and (e) Rad etch25 grafted films with thickness of 200 μm in 60 vol % MMA monomer and methanol solution containing $1.5 \times 10^{-4}\text{M}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.05M H_2SO_4 at 70°C for 5 h.

of a PMMA with a polymerization initiator (benzoyl peroxide) and barium sulfate for radio opacity, and a liquid fraction composed of a MMA monomer stabilized with hydroquinone and activated with *N,N*-dimethyl-*p*-toluidine. When the monomer and the polymer come into contact, and are properly mixed, *N,N*-dimethyl-*p*-toluidine activates benzoyl peroxide which initiates the polymerization of the monomer that has attached and dissolved the polymer particles. The polymerization process is gradual and the matrix, that is fluid at first, becomes doughy and finally reaches a solid state. The reaction is exothermic, with variable maximum temperature depending on reaction volume and heat dissipation capacity. It can reach 80°C, according to thickness. After 1 min, the bone cement adhesives were coated on spaces overlapped between UHMWPE-*g*-PMMA and Plexiglas sheets. The coating was adjusted to the finite thickness of 0.7 mm by using a spacer. The bonding strength, modulus, and strain at break of UHMWPE-*g*-PMMA samples to Plexiglas sheets were measured after aging for 12 h at room temperature. The measurements were carried out at a crosshead speed of 5 mm/min and a gauge length of 50 mm. The bonding strength of the samples was measured three times for each sample and the average of the results was reported.

Contact angle measurements

The contact angles of all prepared samples (UHMWPE-*g*-PMMA) were measured with a Krüss optical contact angle goniometer (model G10). Contact angles were evaluated using the sessile drop method, with deionized water as the polar and methylene iodide as the nonpolar liquids, respec-

tively. Each measurement was taken five times in different areas of the surface at room temperature to obtain an average value for the entire surface.

The harmonic mean method, which is suitable for surfaces with low energy, was used to calculate surface tension of the samples. Substitution of the harmonic-mean equation in Young's equation gives,¹⁰

$$(1 + \cos \theta_i) \gamma_i = 4 \left(\frac{\gamma_i^d \gamma_s^d}{\gamma_i^d + \gamma_s^d} + \frac{\gamma_i^p \gamma_s^p}{\gamma_i^p + \gamma_s^p} \right) \quad (2)$$

where, θ_i is the contact angle; γ_i^d and γ_i^p are the dispersion and polar components of the surface tension of the testing liquids, which for deionized water are 21.8 and 51 dyn/cm, respectively, and for methylene iodide 50.8 dyn/cm and 0, respectively; γ_s^d and γ_s^p are the dispersion and polar components of the solid surface tension, which can be obtained by measuring the contact angles of the liquids with the solid surface and solving the eq. (2) simultaneously for the two liquids.¹⁰

Scanning electron microscopy

The surface topology and cryogenic fractured cross sectional morphologies of the grafted UHMWPEs, were observed by a Cam Scan scanning electron microscope (model MV2300) working at 15–30 kV. All samples were coated with a thin layer of gold prior to scanning electron microscopy (SEM) observations.

RESULTS AND DISCUSSION

FTIR results

The changes in the chemical structure of the UHMWPE-*g*-PMMA films examined by FTIR spectroscopy. Figure 1 shows the representative FTIR spectra for control sample and films with different processes (with specification mentioned in Table I).

TABLE I
The Specifications of Samples Processed in Different Grafting Reaction was Conducted for all the Samples in 60 vol % MMA Monomer and Methanol Solution Containing $1.5 \times 10^{-4}\text{M}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.05M H_2SO_4 at 70°C for 5 h

Samples	Specification
UHMWPE	Pure samples without any treatment
No etch rad	Irradiated and grafted samples
Etch 25 rad	Etched at room temperature, irradiated, and grafted samples
Rad etch 25	Irradiated, etched at room temperature, and grafted samples
Etch 80 rad	Etched at 80°C, irradiated, and grafted samples
Rad etch 80	Irradiated, etched at 80°C, and grafted samples

The absorbance bands of carboxyl (2640 cm^{-1}), carbonyl (1730 cm^{-1}), ether ($1130\text{--}1160\text{ cm}^{-1}$), and hydroxyl groups (3373 cm^{-1}) were not detected in the control sample. For the irradiated UHMWPE, hydroxyl and hydroperoxide groups were appeared. It is observed that in the grafted UHMWPEs, the heights of the hydroxyl and hydroperoxide groups were decreased and the carbonyl and ether groups were detected due to the presence of PMMA on UHMWPE substrate.

Degree of grafting

The DG of films was calculated by eq. (1). Figure 2 shows DG for the grafted samples. These results indicate that the irradiated, etched at room temperature and grafted sample (Rad etch 25) has a maximum DG among the samples.

Irradiation of polymers with ionization radiation produces several chemical effects such as degradation, crosslinking as well as copolymerization and grafting in the presence of monomer.¹² Also chemical etching of UHMWPE with chromic acid alters both the surface chemistry and surface properties such as roughness. Depending on surface crystalline morphology, highly complex root-like cavities may form on the etched surface, which results in dramatic improvements in the wettability and bondability. In addition to the introduction of polar functional groups to the surface of the polymer, chromic acid preferentially etches the amorphous regions of the samples. On the other hand, gamma radiation creates predominately free radicals in amorphous region, thus, etching sequence and temperature are very important and determinant in graft copolymerization. Under appropriate experimental conditions for homogenous diffusion in the polymer, modification of polymer properties can be accomplished not only at the surface, but also throughout the internal phase of polymer.^{11,12}

Obviously, chromic acid etching at room temperature before irradiation (in Etch25 rad sample) reduces free radical density in amorphous region, because chromic acid preferentially etches the amorphous regions of the samples, which results in the DG to be reduced compared to unetched irradiated (No etch rad) sample. There is the same trend in the sample which has been etched at 80°C before irradiation and grafting. This effect is not observed in the sample which have been etched and grafted after irradiation (Rad etch 25 sample), because in this case irradiation is conducted on the neat UHMWPE and chemical etching improve wettability and diffusion of MMA monomer onto the sample and causes DG to be increased.

The etching at high temperature (80°C) causes the irradiated sample to be crosslinked and the grafting

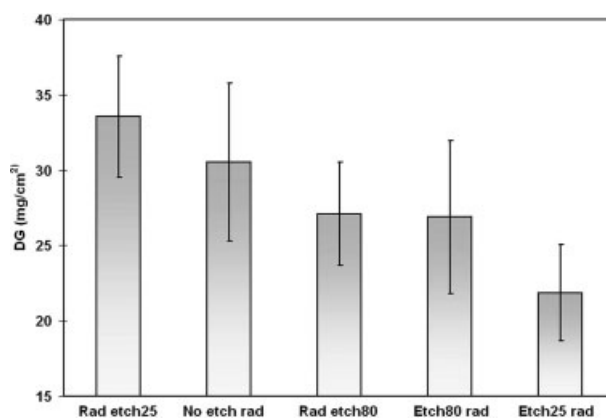


Figure 2 Comparison degree of grafting of films with thickness of $200\text{ }\mu\text{m}$ grafted in 60 vol % MMA monomer and methanol solution containing $1.5 \times 10^{-4}\text{M}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.05M H_2SO_4 at 70°C for 5 h.

degree to be reduced, because the produced free radicals from gamma irradiation are used in crosslinking instead of grafting reaction.

Interfacial bonding strength

UHMWPE is inherently a chemically inert polymer, thus its adhesion strength to PMMA bone cement is extremely low. Because of this problem, mechanical interlocking controls the bonding of UHMWPE prosthesis to PMMA bone cement in artificial joints. It is possible to increase the adhesion strength of UHMWPE by surface modification using chromic acid etching and radiation grafting of MMA monomer, because the chemical etching increases the wettability of the UHMWPE surface with MMA monomer and MMA grafting modifies the surface of UHMWPE to the same chemical composition of the bone cement. In chromic acid etching, the dissolution of polymers by hexavalent chromium in acid media proceeds through the formation of a tetravalent chromium intermediate, which hydrolyzes to alcohol. Further oxidation causes chain scission, which yields olefins, aldehydes, ketones, or carboxylic acids. Therefore, the modification mechanism involves the abstraction of hydrogen atoms from the polymer backbone and their replacement with polar groups (hydroxyl, carbonyl, and carboxylic acid groups) originating from the oxidizing agents.¹⁰ It is conceivable that hydrogen bonds are formed between the polar groups and the bone cement, which results in improved adhesion. The presence of polar functional groups on the surface of modified UHMWPE increases the surface tension and wettability of the polymer, and may act as sites for chemical or physical interactions with the bone cement.

TABLE II
The Variations of Bonding Strength, Modulus, and Strain at Break of the Sheets with Degree of Grafting in Adhesion Tests with Dimensions: $15 \times 50 \times 7 \text{ mm}^3$; grafted in 60 vol % MMA Monomer and Methanol Solution Containing $1.5 \times 10^{-4} \text{ M FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $0.05 \text{ M H}_2\text{SO}_4$ at 70°C for 5 h

Sample	DG (mg/cm ²)	Bonding strength (MPa)	Modulus (MPa)	Strain at break (%)
Etch 25 rad	22	12.47 (breaking)	234.48	9.04
No etch rad	30.5	12.17 (breaking)	255.85	9.71
Rad etch 25	33.5	11.26 (breaking)	259.4	9.05
Etch 80 rad	26.9	10.11 (breaking)	183.99	10.93
Rad etch 80	27.1	8.83 (breaking)	241.38	6.61
UHMWPE	0	0	0	0

To investigate the interfacial bonding strength of UHMWPE-g-PMMA and PMMA bone cement, the tensile bonding tests were carried out and the variations of bonding strength, modulus, and strain at break with DG in adhesion tests for different samples are presented in Table II. The results show that most of the grafted samples have higher bonding strength with bone cement than Plexiglas and pure UHMWPE sheets. During the grafting reaction, some of the MMA monomers diffuse into the irradiated UHMWPE. In the reaction temperature (70°C), there are three simultaneous reactions: UHMWPE cross-linking, MMA grafting, and MMA homopolymerization. The homopolymerized methyl methacrylates are entrapped inside the crosslinked UHMWPE and Soxhlet extraction cannot extract them. Thus, there are two important adhesion mechanisms in the grafted samples: chemical bonding between homopolymerized or grafted PMMA onto UHMWPE and bone cement, and mechanical interlocking between PMMA chains in bone cement and entrapped PMMA inside the crosslinked UHMWPE. The diffusion of MMA into the UHMWPE and its homopolymerization are illustrated in detail by SEM.

To study the fracture mechanisms at the interface of the grafted UHMWPE and bone cement, the SEM micrographs were prepared from adhesion tests fracture interface as shown in Figures 3(a,b). These micrographs show that in most of the grafted UHMWPE samples the rupture was carried out from the bulk (not interface) of the bone cement or Plexiglas as evidence of desirable adhesion between grafted UHMPE and bone cement.

Contact angle measurements

The variations of contact angles and surface tensions of the samples, including the dispersion component (γ^d) and the polar component (γ^p), with DG are presented in Table III. The results showed that graft copolymerization of MMA onto UHMWPE increased its surface energy because of substitution of polar groups into the backbone of the polymer. Increasing

the polarity of the UHMWPE surface, improved its wettability and adhesion with PMMA bone cement, as represented in the previous section, and thus

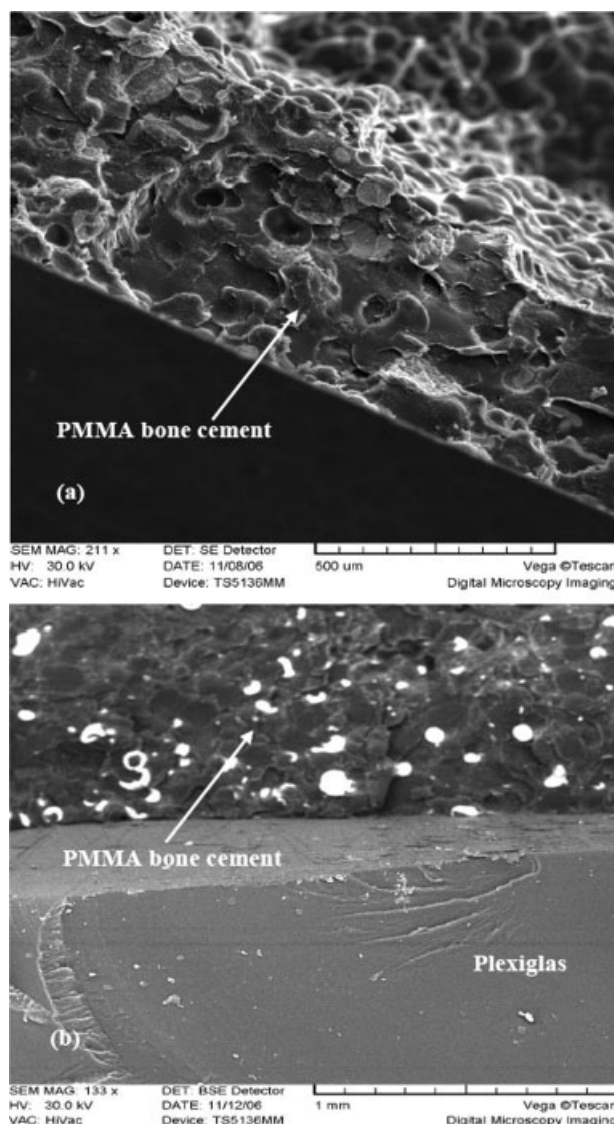


Figure 3 Tensile fracture interface in (a) bone cement and (b) Plexiglas and bone cement interface. Sheets dimensions were $15 \times 50 \times 7 \text{ mm}^3$.

TABLE III
The Variations of Contact Angles and Calculated Surface Tension with Degree of Grafting in the Grafted Films with Thickness of 200 μm in 60 vol % MMA Monomer and Methanol Solution Containing $1.5 \times 10^{-4}\text{M}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.05M H_2SO_4 at 70°C for 5 h

Sample	DG (mg/cm^2)	Surface tension at room temperature (mN/m)			Contact angle ($^\circ$)	
		γ	γ^d	γ^p	Water	Methylene iodide
Etch 25 rad	22	48.34	37.59	10.75	75.8	45.5
No etch rad	30.5	43.97	34.94	9.03	80.9	50.9
Rad etch 25	33.5	47.34	37.16	10.18	77.2	46.4
Etch 80 rad	26.9	33.92	31.79	2.13	100.2	57.3
Rad etch 80	27.1	50.68	39.63	11.05	74.2	41.1
UHMWPE	0	36	34.25	1.75	100.8	30.7

improved their interfacial bonding strength. As shown in Figure 4, the grafting layer on the UHMWPE samples increased with increasing grafting degree and a bump-like appearance occurred. The surface area of the grafting layer was enhanced with increasing DG, which may be related to interfacial bonding strength. As it is observed in Figure 4(b), Rad etch25 sample with highest DG has much more grafting layer than the Etch 25 rad sample [Fig. 4(a)]. These topologies confirm the previous gravimetric results. Thus, two determinant parameters in surface tension measurement are surface polarity and surface topology.

Morphological studies

SEM micrographs from fractured surface of Rad etch25 and Etch25 rad samples in liquid nitrogen are shown in Figure 5(a,b), respectively. These figures show that etching at room temperature and then irradiation (Etch25 rad) produces a PMMA rich phase near the surface that confirm the high tensile bonding strength of this sample. In this sample, the dominant adhesion mechanism is mechanical interlocking between entrapped PMMA and crosslinked UHMWPE, in addition to chemical bonding between grafted MMA units and PMMA in the bone cement. In the Rad etch25 sample, the grafted and homopolymerized PMMA have been dispersed in the bulk of UHMWPE substrate thus, it has lower bonding strength compared to Etch25 rad sample, because the chemical bonding is the only dominant adhesion mechanism.

CONCLUSIONS

In this article, an attempt was made to graft copolymerize MMA monomer onto UHMWPE and acid etched UHMWPE using preirradiation method in air in the presence of a metallic salt and sulfuric acid to improve the bonding strength between UHMWPE

and bone cement. The effect of the grafted MMA units onto the UHMWPE was investigated by various tests. The FTIR results showed the presence of ether, carbonyl, and hydroxyl groups on the grafted

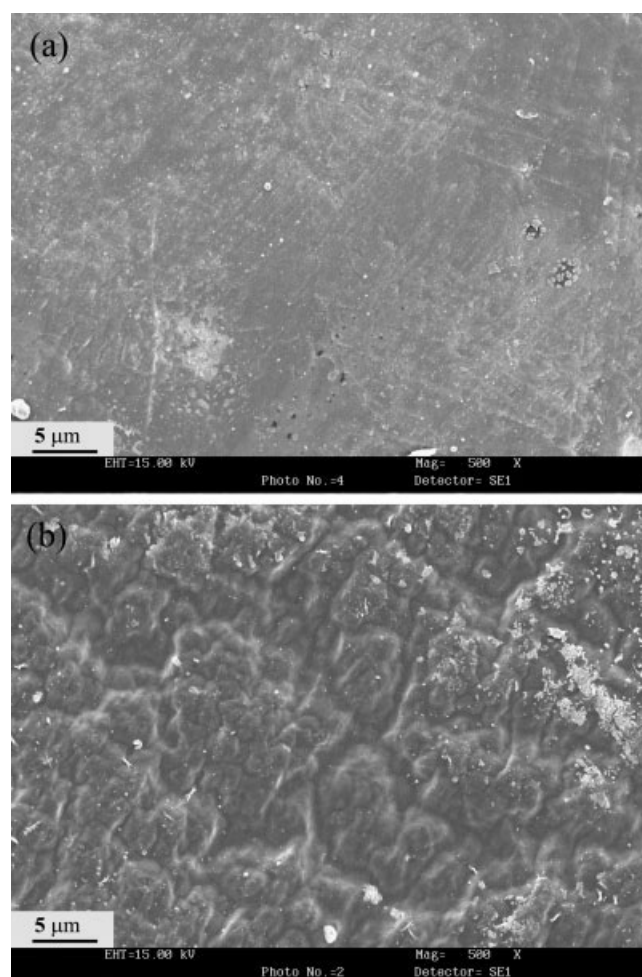


Figure 4 Surface topologies of grafted (a) Etch25 rad (DG: 22 mg/cm^2) and (b) Rad etch25 (DG: 33.5 mg/cm^2) films with thickness of 200 μm in 60 vol % MMA monomer and methanol solution containing $1.5 \times 10^{-4}\text{M}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.05M H_2SO_4 at 70°C for 5 h.

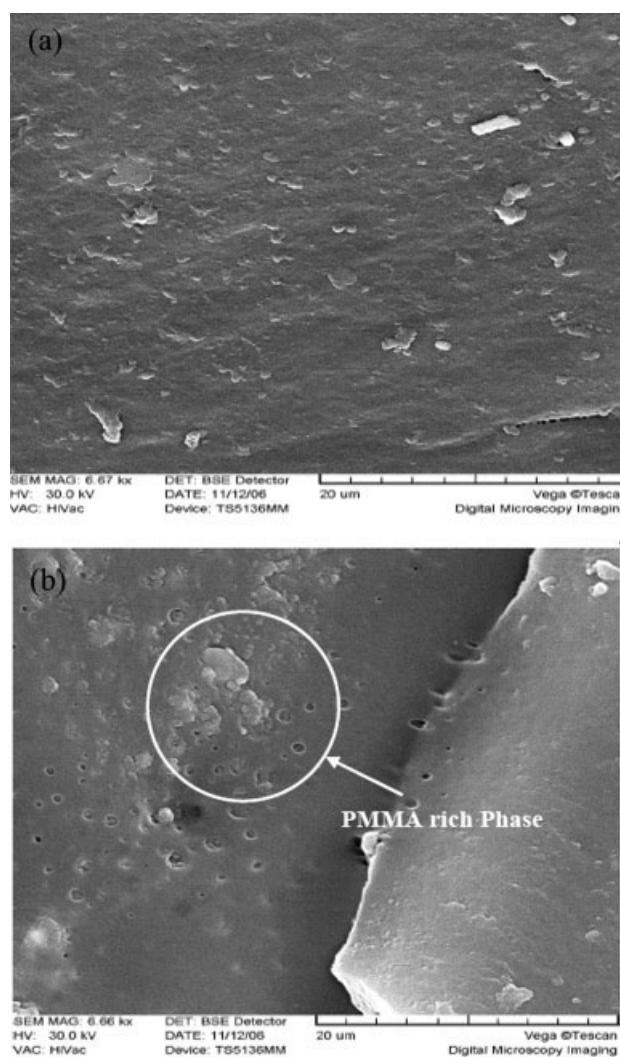


Figure 5 SEM micrographs from fractured surface of (a) Rad etch25 and (b) Etch25 rad films in liquid nitrogen with thickness of 200 μm grafted in 60 vol % MMA monomer and methanol solution containing $1.5 \times 10^{-4}\text{M}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.05M H_2SO_4 at 70°C for 5 h.

films. To identify the amount of grafted MMA units, the grafting degree was measured by a gravimetric method. These results showed that the irradiated, then chromic acid etched at room temperature and grafted samples (Rad etch25) had the highest grafting degree. The interfacial bonding strength between UHMWPE and PMMA bone cement was considerably improved by graft copolymerization and in most of the samples, the fracture was happened in

the bulks of bone cement or Plexiglas sheets. The results of morphological studies showed that the Etch25 rad sample had higher grafted MMA units near the surface than the other samples. The contact angle measurements indicated that the graft copolymerization of MMA onto UHMWPE increased the surface tension of substrate because of the replacement of the hydrogen in the UHMWPE with MMA polar units and furthermore surface roughening in the grafted samples. Finally the results of this study revealed that, the chromic acid etching and MMA graft copolymerization had a synergetic effect in grafting efficiency and improvement in adhesion of UHMWPE with commercial bone cement.

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