

Irradiation Grafting of Methyl Methacrylate Monomer onto Ultra-High-Molecular-Weight Polyethylene: An Experimental Design Approach for Improving Adhesion to Bone Cement

Somayeh Ravanbakhsh,¹ Mostafa Rezaei,¹ Nasrin Sheikh,² Amin Heidari¹

¹*Institute of Polymeric Materials, Polymer Engineering Department, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran*

²*Radiation Applications Research School, Nuclear Science and Technology Research Institute, P.O. Box 11365-3486, Tehran, Iran*

Received 6 May 2009; accepted 11 October 2009

DOI 10.1002/app.31613

Published online 10 December 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The grafting of methyl methacrylate (MMA) onto ultra-high-molecular-weight polyethylene (UHMWPE) and chromic acid etched UHMWPE was conducted with a preirradiation method in air in the presence of a Mohr salt and sulfuric acid. The grafted samples were characterized by Fourier transform infrared (FTIR) spectroscopy, a gravimetric method, differential scanning calorimetry, scanning electron microscopy (SEM), and interfacial bonding strength measurements. The FTIR results showed the presence of ether and carbonyl groups in the MMA-grafted UHMWPE (MMA-g-UHMWPE) samples. The Taguchi experimental design method was used to find the best degree of grafting (DG) and bonding strength. The efficient levels for different variables were calculated with an analysis of variance of the results. SEM

micrographs of MMA-g-UHMWPE samples showed that with increasing DG and chromic acid etching, the MMA-g-UHMWPE rich phase increased on the surface; this confirmed the high interfacial bonding strength of the grafted samples with bone cement. The grafting of the MMA units onto UHMWPE resulted in a lower crystallinity, and the crystallization process proceeded at a higher rate for the MMA-g-UHMWPE samples compared to the initial UHMWPE; this suggested that the MMA grafted units acted as nucleating agents for the crystallization of UHMWPE. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 886–894, 2010

Key words: adhesion; biomaterials; graft copolymers; irradiation; polyethylene (PE)

INTRODUCTION

Ultra-high-molecular-weight polyethylene (UHMWPE) is a high performance polymer with a very high impact resistance, low wear rate, low friction, biocompatibility, and sterilizability, which make it highly suitable for orthopedic implants. However, the bonding strength of poly(methyl methacrylate) (PMMA) bone cement to UHMWPE is extremely low.^{1,2} The chemical surface modification of UHMWPE offers a new possibility for improving its chemical and physical properties, such as adhesion.^{3,4} Various methods have been used to improve the surface properties of UHMWPE. Surface oxidation through chemical etching is the primary mechanism of these surface modification techniques, and with this modification, samples have shown better wettability and improved adhesion

properties than the unmodified UHMWPE.^{5,6} Furthermore, the graft copolymerization of methyl methacrylate (MMA) monomer onto UHMWPE can be used to improve the adhesive properties of UHMWPE with PMMA bone cement. Irradiation methods are more useful grafting methods because of the uniformity and rapid creation of active radical sites. Irradiation grafting methods include the simultaneous irradiation of a backbone polymer in the presence of a monomer, the preirradiation of a backbone polymer in a vacuum or nitrogen gas and subsequent monomer grafting by a trapped radical, and the preirradiation of a backbone polymer in the presence of air or oxygen and subsequent monomer grafting by polymeric peroxides, such as diperoxides and hydroperoxides.^{1,2} To eliminate undesirable homopolymerization reactions by the decomposition of the peroxide species, a reducing agent, such as a metallic salt (Mohr salt), is used.^{7–9} For medical applications, the preirradiation method is recommended because of the ease of application and uniform MMA-grafted layer onto the UHMWPE surface.¹⁰

Correspondence to: M. Rezaei (rezaei@sut.ac.ir).

In the previous studies,^{11–13} we examined the surface characteristics of UHMWPE oxidized with chromic acid and the graft copolymerization of MMA monomer onto UHMWPE and acid-etched UHMWPE using a preirradiation method in air. The presence of polar functional groups on the surface of a modified UHMWPE increases the surface tension and wettability of the polymer and may provide sites for chemical or physical interactions with bone cement.

Many studies have been conducted on the irradiation grafting of MMA onto UHMWPE,^{1,2,10,13} but a systematic study based on the experimental design of the variables and statistical analysis of the results to find the percentage contribution of each variable with various levels on the designed objective functions has not been considered before. In this study, we tried to construct an experimental design array based on the Taguchi methodology to obtain efficient conditions of the graft copolymerization of MMA onto UHMWPE (MMA-g-UHMWPE) with different factors, such as irradiation dose, grafting temperature, chromic acid etching, grafting time, and monomer concentration, and to determine the percentage contribution of each variable on the designed objective functions. A full factorial design needed too many experiments. The objective functions were degree of grafting (DG) and interfacial bonding strength. The analysis of variance (ANOVA) method was used for statistical consideration. Furthermore, the morphological changes and the effect of MMA irradiation grafting on the thermal properties, degree of crystallinity, and crystallization rate of MMA-g-UHMWPE samples were examined and compared with the neat UHMWPE sample; these have not been considered before.

EXPERIMENTAL

Materials

UHMWPE powder (product number 429015) with a bulk density of 0.94 g/cm³, a particle size of 150–180 μm, an intrinsic viscosity of 25.5 dL/g, and a viscosity-average molecular weight of 4,538,730 was provided by Sigma–Aldrich (Oakville, Canada) and was used as a substrate for the graft copolymerization. The samples were prepared by the compression molding of the powder,^{13,14} cleaned twice in acetone for 1 h each time, and dried in a vacuum oven. The MMA monomer (Merck AG, Darmstadt, Germany) and FeSO₄·H₂O salt (Merck AG) were used as received without further treatment. Methanol, sulfuric acid (H₂SO₄; 98 wt %), and potassium dichromate (K₂Cr₂O₇) were reagent grade (Merck AG). Osmium tetroxide (OsO₄; Merck AG) was used as a staining agent in the scanning electron microscopy (SEM) observations.

Chemical etching of UHMWPE

The chemical etching of UHMWPE with chromic acid alters both the surface chemistry and surface properties, such as roughness. Depending on the 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.^{11,13,15} Chemical etching was performed before irradiation for 30 min at room temperature. A chromic acid solution was prepared by the mixture of K₂Cr₂O₇, H₂SO₄ (98 wt %), and distilled water in a 7:150:12 mass ratio.^{11–15} 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 with γ-rays from a Co-60 source with doses of 5, 10, 20, and 30 kGy at a dose rate of 1.51 kGy/h in air at room temperature. The irradiated UHMWPE samples were stored at –10°C.

Graft copolymerization

First, 80 mL of methanol as a reaction media, 8.34 mg of Mohr salt (FeSO₄·7H₂O) as a homopolymerization inhibitor, and 1.96 g of H₂SO₄ (98 wt %) as a reaction accelerator were placed in the glass ampule; this was followed by the addition of 120 mL of MMA monomer to achieve a 60 vol % monomer concentration. To prepare 30, 40, and 50 vol % monomer concentrations, the amounts of Mohr salt and H₂SO₄ were kept constant (8.34 mg of Mohr salt and 1.96 g of H₂SO₄). The preirradiated and acid-etched UHMWPE samples were immersed in the monomer solution, purged with bubbling nitrogen gas for degassing, and sealed. The grafting reactions were performed as shown in Table I. We carried out

TABLE I
Selected Variables for the Irradiation
Grafting of UHMWPE

Variable	Level			
	1	2	3	4
Dose (kGy)	5	10	20	30
Grafting temperature (°C)	50	55	60	70
Etching	Yes	No	—	—
Grafting time (h)	0.5	1	3	5
Monomer concentration (vol %)	30	40	50	60

the grafting reaction by placing the ampules in a water bath. After the reaction time was complete, the grafted samples were taken out of the glass ampule and extracted by hot acetone in a Soxhlet extractor for 12 h to remove the unreacted monomers or remaining PMMA homopolymers. DG was determined as follows:

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

where W_g and W_0 are the weights of the grafted and ungrafted UHMWPE samples, respectively.^{1,13}

Characterization of MMA-g-UHMWPE

Fourier transform infrared (FTIR) spectroscopy

The graft copolymerization of the UHMWPE and acid-etched UHMWPE films, with an average thickness of 100 μm , were studied with a UNICAM Mattson 1000 FTIR spectrometer (Leeds, U.K.) between 400 and 4000 cm^{-1} .

Interfacial bonding strength

The bonding strength between the PMMA sheets and the MMA-g-UHMWPE samples with various DGs were measured in tension mode with a Zwick/Roell tensile machine (model TI-FR010TH-A50, Ulm, Germany) at room temperature. All specimens for interfacial bonding strength measurement had dimensions of 1.5 \times 0.5 \times 5.5 cm^3 . The MMA-g-UHMWPE and Plexiglas sheets were overlapped on both ends to an area of 1.5 cm^2 , and the overlapped area was coated with EUROFIX RO bone cement (Synergie Ingenierie Medicale, S. A. R. L., Chamberet, France). This cement was a self-polymerizing acrylic compounds with spontaneous solidification, consisting of a powder fraction composed 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 were properly mixed, *N,N*-dimethyl-*p*-toluidine activated benzoyl peroxide, which initiated the polymerization of the monomer that had attached and dissolved the polymer particles. The polymerization process was gradual, and the matrix, which was fluid at first, became doughy and finally reached a solid state. The reaction was exothermic, with a variable maximum temperature dependent on the reaction volume and heat dissipation capacity. It could reach 80°C, according to thickness. After the powder and liquid fractions were mixed, the bone cement adhesives were coated on spaces overlapped between MMA-g-UHMWPE

and Plexiglas sheets. The interfacial bonding strength of the MMA-g-UHMWPE samples to Plexiglas sheets were measured after they were aged for 12 h at room temperature. The measurements were carried out at a crosshead speed of 0.1 mm/min and a gauge length of 50 mm.

SEM

The surface topology and cryogenic fractured cross-sectional morphologies of the grafted UHMWPEs were observed by a Cam Scan scanning electron microscope (model VEGA 11, Cambridgeshire CB5 9PY, UK) working at 15 kV. All samples were stained with OsO_4 and coated with a thin layer of gold before the SEM observations.

Differential scanning calorimetry

The melting and crystallization points and the heats of fusion were determined with a Netzsch differential scanning calorimeter (model F3 200, Selb, Germany) calibrated with an indium standard at a heating rate of 10°C/min under nitrogen purge. Nonisothermal crystallization experiments were carried out with the following procedure: the samples were equilibrated at a temperature of 25°C, heated to 180°C at a rate of 10°C/min, and soaked at this temperature for 10 min to eliminate any previous thermal history. Afterward, they were cooled to room temperature at a cooling rate of 10°C/min. The exotherms were recorded as a function of time. The degree of crystallinity (X_c) of the samples was calculated with the following equation:

$$X_c (\%) = \frac{\Delta h}{\Delta h_{100}} \times 100 \quad (2)$$

where Δh is the heat of crystallization of the sample and Δh_{100} is the heat of crystallization of a 100% crystalline sample (taken to be 288 J/g).¹⁶

RESULTS AND DISCUSSION

Experimental design

Finding efficient conditions of the grafting variables was the main objective of this research. There are many variables affecting the graft copolymerization of MMA onto UHMWPE. Some of these variables were selected in this study. These variables and the related levels are presented in Table I.

A complete factorial design for this study would have required $4^4 + 2^1 = 258$ experiments. However, with Taguchi design, the same study was carried out with 16 experiments with an L_{16} orthogonal array, as indicated in Table II.¹⁷ In this design, variables 1, 2, 4, and 5 had 4 levels, and variable 3 had 2

TABLE II
L₁₆ Taguchi Standard Array

Test	Level				
	Variable 1	Variable 2	Variable 3	Variable 4	Variable 5
1	1	1	1	1	1
2	1	2	1	2	2
3	1	3	2	3	3
4	1	4	2	4	4
5	2	1	1	4	3
6	2	2	1	3	4
7	2	3	2	2	1
8	2	4	2	1	2
9	3	1	2	2	4
10	3	2	2	1	3
11	3	3	1	4	2
12	3	4	1	3	1
13	4	1	2	3	2
14	4	2	2	4	1
15	4	3	1	1	4
16	4	4	1	2	3

Variables 1, 2, 4, and 5 had four levels, and variable 3 had two levels.

levels. The designed experiments according to the variables and the related levels of this study (Table I) and the L₁₆ Taguchi orthogonal array (Table II) are presented in Table III. Different experiments were conducted on the samples and replicated three times. These experiments were carried out randomly to remove any effects due to noise variables. The results were analyzed statistically by the ANOVA method with Qualitek-4 software.¹⁸

ANOVA

The signal-to-noise (S/N) ratio was used for statistical analysis. The S/N ratio is a general term used to measure the sensitivity-to-noise factors or variables. It takes a different form depending on the type of quality characteristics. The response being considered for the purpose of optimization in a Taguchi experimental design is called a *quality characteristic*. Some of the variables influence the quality characteristics or the response of the products. These variables can be classified into the following three categories: signal, noise, and control factors. *Signal factors* are the variables set by the user or the operator to express the intended value for the response of the products. The designer cannot control the *noise factors*, and therefore, they influence the quality of the products. The *control factors* are the designing factors used to optimize the product's quality.¹⁷

To determine the best values of the variables, an objective function should be optimized. The task of finding what adjustments are meaningful in a partic-

ular problem and determining the right S/N ratio is not always easy.

Two types of S/N ratio, which were used in our previous study,¹⁴ are smaller-the-better- and larger-the-better-type problems. In smaller-the-better-type problem, the quality characteristic (response) is continuous and positive; this means that it can take any value from zero to infinity. Its most desired value is zero. Such problems are characterized by the absence of a scaling factor or any other adjustment factors. As there is no adjustment factor in these problems, it should simply minimize the quality loss function without any adjustment. Minimizing the loss function is equivalent to maximizing the objective function (S/N) defined by the following equation:

$$S/N = y_i = -10 \log_{10}(\text{Mean square of responses})$$

$$= -10 \log_{10} \left[\frac{1}{n} \sum_{i=1}^n x_i^2 \right] \quad (3)$$

where x_i is the value of the response factor, y_i is the new S/N response or quality characteristic, and n is the number of replications. The S/N ratio merely measures the effect of noises.¹⁷ However, in the larger-the-better-type problem, the quality characteristic should be as large as possible. This problem can be transformed into a smaller-the-better-type problem by consideration of the reciprocal of the quality characteristics:

TABLE III
Designed Experiments with the L₁₆ Taguchi Standard Array

Test	Level				
	Dose (kGy)	Grafting temperature (°C)	Etching	Grafting time (h)	Monomer concentration (vol %)
1	5	50	Yes	0.5	30
2	5	55	Yes	1	40
3	5	60	No	3	50
4	5	70	No	5	60
5	10	50	Yes	5	50
6	10	55	Yes	3	60
7	10	60	No	1	30
8	10	70	No	0.5	40
9	20	50	No	1	60
10	20	55	No	0.5	50
11	20	60	Yes	5	40
12	20	70	Yes	3	30
13	30	50	No	3	40
14	30	55	No	5	30
15	30	60	Yes	0.5	60
16	30	70	Yes	1	50

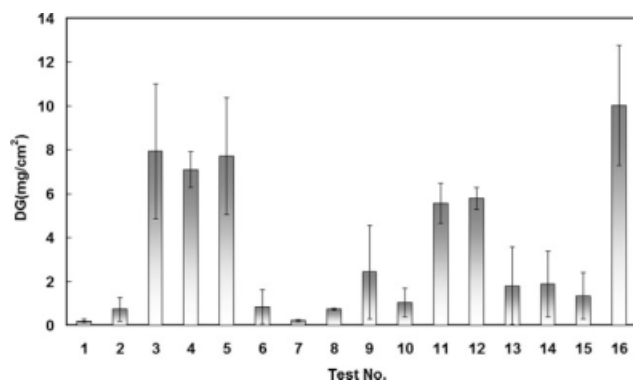


Figure 1 Comparison of the average DG values (mg/cm²) of different samples of L₁₆ Taguchi experiments grafted in MMA monomer and a methanol solution containing $1.5 \times 10^{-4}M$ FeSO₄·7H₂O and 0.05M H₂SO₄.

$$S/N = y_i = -10 \log_{10}(\text{Mean square of responses})$$

$$= -10 \log \left[\frac{1}{n} \sum_{i=1}^n 1/(x_i^2) \right] \quad (4)$$

The percentage contribution of the variables (P_i) to the objective function is calculated as follows:¹⁷

$$P_i = (S'_i/S_T) \times 100 \quad (5)$$

$$S'_i = S_i - (V_{\text{Error}} \times f_i) \quad (6)$$

where S'_i is the pure sum of squares, S_i is the total sum of squares of the variables, S_T is the total sum of squares, V_{Error} is the variance of the errors, and f_i is the degree of freedom of the variables. In this study, the larger-the-better criterion was used for statistical analysis.

DG

The DG of sheets was calculated with eq. (1). The average and standard deviation of DG for three replications of L₁₆ Taguchi experiments are presented in Figure 1. To analyze the data, the S/N analysis was used. The ANOVA results and the efficient values

for different variables are presented in Table IV to examine the effect of these factors on DG. The effect or percentage contribution of different variables on the objective function was calculated from the ANOVA method with eqs. (4)–(6). The efficient values for different variables were concluded from the variation of each objective function versus different levels of the designed variables with the larger-the-better criterion for designed objective function in this study. The efficient conditions included high levels of irradiation dose, grafting temperature, grafting time, monomer concentration, and application of chromic acid etching; all of these increased DG. According to the ANOVA results (Table IV), the grafting time, grafting temperature, and monomer concentration, respectively, were the most effective variables on DG.

Characterization

The changes in the chemical structure of the MMA-g-UHMWPE films were examined by FTIR spectroscopy. As shown in Figure 2, in the grafted UHMWPEs, the peaks corresponding to the ether (1130–1160 cm⁻¹) and carbonyl (1730 cm⁻¹) groups were detected in the grafted samples because of the presence of grafted MMA units on the UHMWPE substrate.

To investigate the interfacial bonding strength of MMA-g-UHMWPE and PMMA bone cement, tensile bonding strength tests were carried out. The average and standard deviation values for three replications of L₁₆ Taguchi experiments are presented in Figure 3. The ANOVA results and the efficient values for different variables are presented in Table IV to examine the effect of these factors on bonding strength. The same procedure of DG was used for bonding strength to find the percentage contribution and the efficient levels of different variables. The efficient conditions included high levels of grafting temperature, grafting time, monomer concentration, and application of chromic acid etching; all of these increased bonding strength. The ANOVA results of bonding strength (Table IV) showed that, except for

TABLE IV
Contributions (%) of the Various Grafting Variables to the DG and Bonding Strength and Their Efficient Levels

Variable	Objective function			
	DG		Bonding strength	
	Contribution (%)	Efficient level	Contribution (%)	Efficient level
Dose (kGy)	4.145	20	2.367	5
Grafting temperature (°C)	30.405	70	1.335	70
Etching	0.289	yes	8.143	yes
Grafting time (h.)	37.097	5	3.831	5
Monomer concentration (vol %)	22.748	50	15.415	60
Error	5.280	—	68.909	—

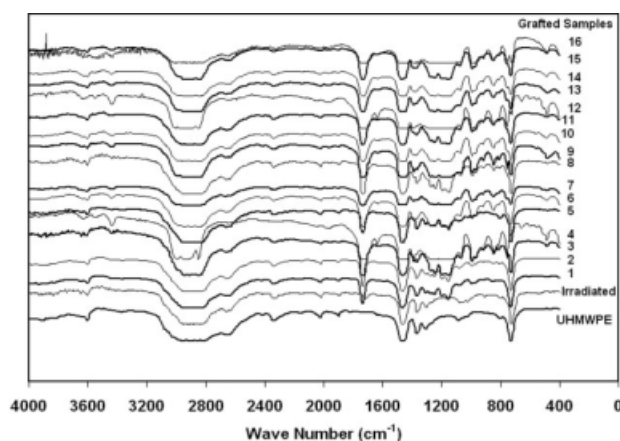


Figure 2 FTIR spectra of the initial UHMWPE, irradiated UHMWPE, and various MMA-g-UHMWPE films with thicknesses of 100 μm in MMA monomer and a methanol solution containing $1.5 \times 10^{-4}\text{M}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.05M H_2SO_4 .

monomer concentration and etching, the other factors did not have a significant effect on the bonding strength. Actually, the bonding strength depends on the interfacial properties of two adjoining materials and is only affected by the factors that influence the surface of the samples. As γ rays diffuse deeply into a polymer and alter its bulk properties, the grafting of the MMA monomer to UHMWPE was carried out on both the UHMWPE surface and bulk; thus, the selected variables for interfacial bonding strength studies did not significantly affect this objective function, and the error showed the dominant contribution. The morphological studies confirmed this idea.

The variation of bonding strength versus DG of the samples is presented in Figure 4. As shown in this figure, the data were scattered, and it was difficult to construct a direct correlation between the

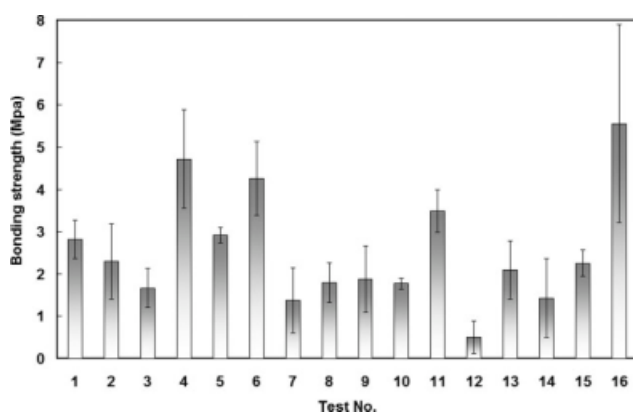


Figure 3 Comparison of the average interfacial bonding strength (MPa) of different samples of L_{16} Taguchi experiments grafted in MMA monomer and a methanol solution containing $1.5 \times 10^{-4}\text{M}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.05M H_2SO_4 .

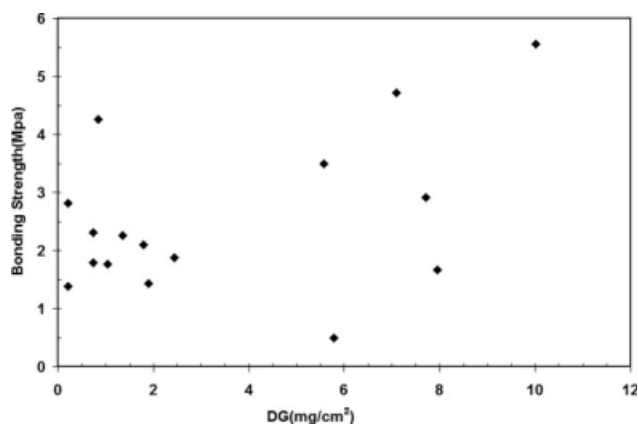


Figure 4 Variation of the interfacial bonding strength with DG.

interfacial bonding strength and DG, but a roughly increasing trend of bonding strength with DG was observed.

The SEM micrographs of the surface stained with OsO_4 of the initial UHMWPE ($\text{DG} = 0$) and samples 13 ($\text{DG} = 2 \text{ mg/cm}^2$), 14 ($\text{DG} = 2.1 \text{ mg/cm}^2$), and 16 ($\text{DG} = 10 \text{ mg/cm}^2$) are shown in Figure 5. These figures show that with increasing DG of the grafted sample, the MMA-g-UHMWPE rich phase increased on the surface; this confirmed the high interfacial bonding strength of sample 16. As mentioned in our previous work,¹³ the dominant adhesion mechanisms were the mechanical interlocking and chemical bonding between the MMA-g-UHMWPE units and PMMA chains in the bone cement.

SEM micrographs from cryogenic-fractured (in liquid nitrogen) and OsO_4 -stained cross sections are shown in Figure 6, typically, for samples 4 and 10. This figure shows that sample 4 had an MMA-g-UHMWPE rich phase near the surface; this confirmed its higher DG and interfacial bonding strength compared to the sample 10.

The effect of MMA irradiation grafting on the thermal properties of the UHMWPE matrix is summarized in Table III. The grafting of MMA units onto UHMWPE resulted in a lower crystallinity but delayed crystallization slightly, as evidenced by the decrease in the crystallization temperatures. To investigate these findings further, the nonisothermal crystallization exotherms of UHMWPE and the MMA-g-UHMWPE samples were recorded. The relative degree of crystallinity as a function of temperature was obtained by integration of the exothermal peaks and transformed into a timescale with T_0 considered as the initial temperature at the start of crystallization (time $t = 0$). Representative plots of the relative degree of crystallinity as a function of time [$X(t)$; eq. (7)] for UHMWPE, irradiated UHMWPE, and MMA-g-UHMWPE samples 1–4 are shown in

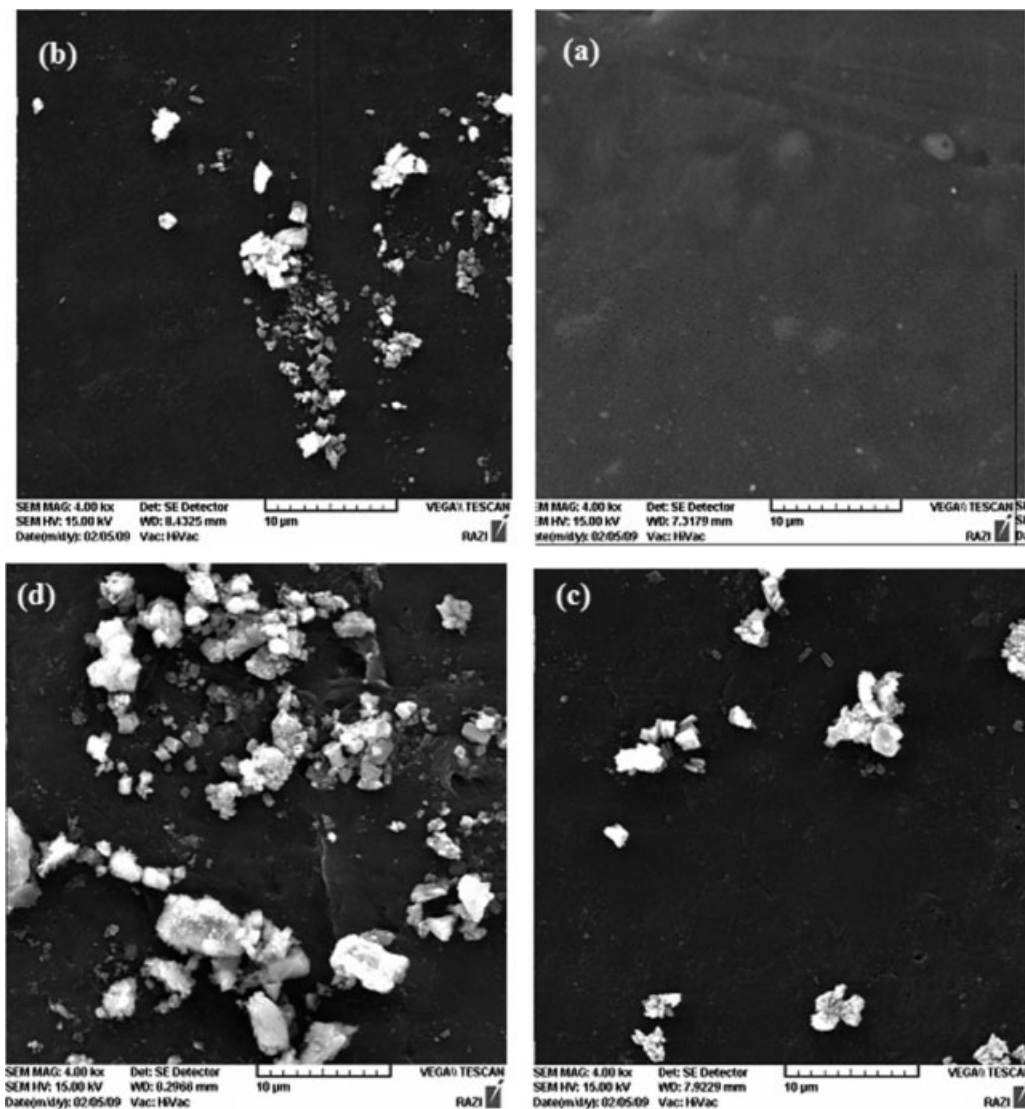


Figure 5 SEM micrographs of surfaces stained with OsO_4 : (a) initial UHMWPE ($\text{DG} = 0$), (b) sample 13 ($\text{DG} = 2 \text{ mg/cm}^2$), (c) sample 14 ($\text{DG} = 2.1 \text{ mg/cm}^2$), and (d) sample 16 ($\text{DG} = 10 \text{ mg/cm}^2$).

Figure 7. Similar trends were observed for the other samples:

$$X(t) = \frac{\int_0^t \frac{dH_t}{dt} dt}{\int_0^{t_f} \frac{dH_t}{dt} dt} \quad (7)$$

where H_t represents the enthalpy and t_f is the time at the end of crystallization.^{12,16} Calculations of the crystallization half-time confirmed that the crystallization process proceeded at a higher rate for the MMA-g-UHMWPE samples than for the initial UHMWPE (Table V). On the basis of these results, it was clear that the crystallization of the grafted samples was slightly accelerated; this suggested that the MMA-g-UHMWPE units act as nucleating agents for the crystallization of UHMWPE. Furthermore, the ultimate crystallinities of the grafted samples

were generally lower than that of the initial UHMWPE. In the grafted samples, the MMA-g-UHMWPE chains could not enter the crystalline structure of the UHMWPE lamellas, and hence, in these samples, the total crystallinity decreased.

CONCLUSIONS

In this study, we tried to achieve efficient conditions of the graft copolymerization MMA onto UHMWPE using a Taguchi experimental design method. The irradiation dose, grafting temperature, etching, grafting time, and monomer concentration were considered the main variables. The FTIR results show the presence of ether and carbonyl groups in the grafted films. The efficient conditions for DG included high levels of irradiation dose, grafting temperature, grafting time, monomer concentration, and application of

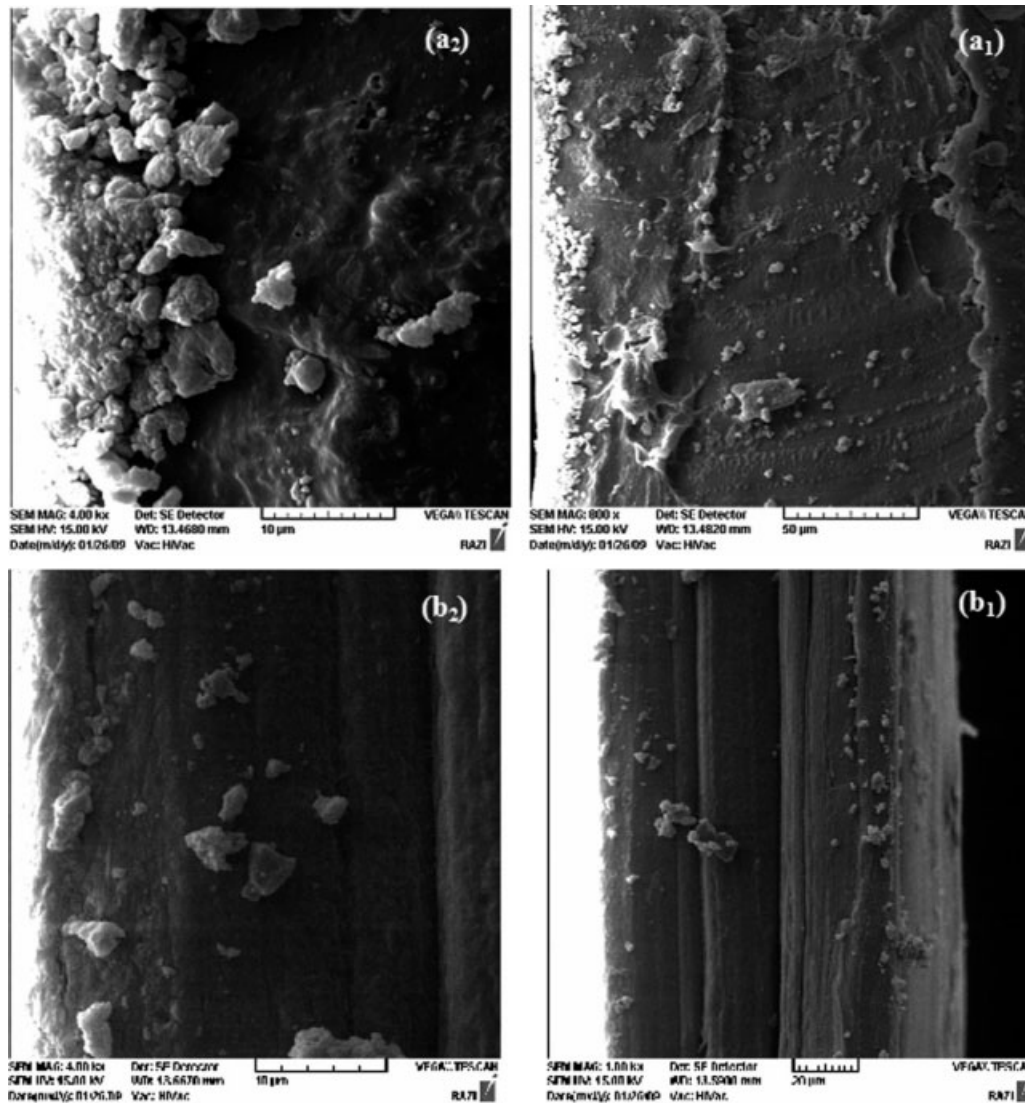


Figure 6 SEM micrographs of the surfaces fractured in liquid nitrogen and stained with OsO_4 with different magnifications: (a) sample 4 ($\text{DG} = 7 \text{ mg/cm}^2$) and (b) sample 10 ($\text{DG} = 1 \text{ mg/cm}^2$).

chromic acid etching. The ANOVA results of bonding strength show that, except for the monomer concentration and etching, the other factors did not affect the bonding strength. As γ rays diffused deeply into the polymer and altered its bulk properties, the grafting of the MMA monomer onto UHMWPE was carried out on both the UHMWPE surface and bulk; thus, the selected variables for interfacial bonding strength studies were not affected significantly. In this objective function the error was dominant.

SEM micrographs of the grafted samples showed that with increasing DG of the grafted sample, the MMA-g-UHMWPE rich phase increased on the surface; this confirmed the high interfacial bonding strength in these samples compared to the initial UHMWPE sample. We suggest that the dominant adhesion mechanisms were the mechanical interlocking and chemical bonding between the MMA-g-

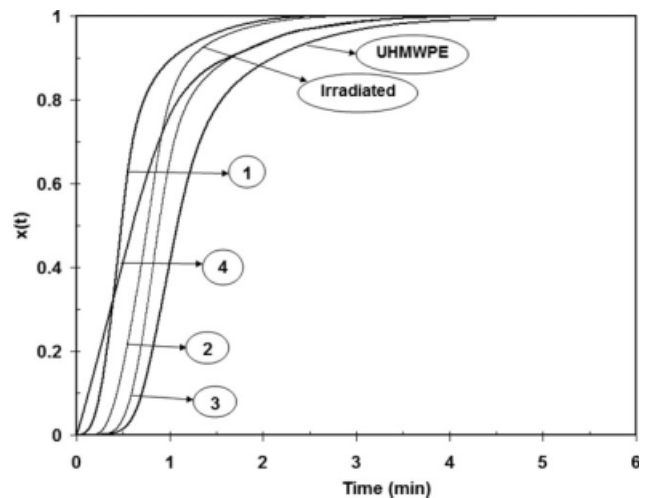


Figure 7 Development of the relative crystallinity with time for the nonisothermal crystallization of UHMWPE, irradiated UHMWPE, and MMA-g-UHMWPE samples 1–4.

TABLE V
Thermal Properties, $t_{1/2}$ Values, and Ultimate Crystallinity Values Obtained from the Nonisothermal Crystallization Experiments with the UHMWPE and MMA-g-UHMWPE Samples

Sample	X_c (%)	T_m (°C)	$T_{m(\text{onset})}$ (°C)	T_c (°C)	$T_{c(\text{onset})}$ (°C)	$t_{1/2}$ (s)
Neat UHMWPE	53.5	136.1	125.4	115.5	120.0	64.97
Irradiated UHMWPE	39.2	134.5	123.3	111.7	118.0	45.60
MMA-g-UHMWPE	1	42.5	128.1	117.3	113.0	29.10
	2	32.4	128.8	115.6	112.4	45.84
	3	21.3	127.1	119.7	111.8	52.86
	4	21.2	133.7	122.0	106.8	36.0
	5	44.6	130.8	118.2	111.5	38.04
	6	46.2	128.5	116.8	112.1	37.98
	7	34.2	128.0	116.6	111.8	34.56
	8	38.9	128.6	118.5	111.6	42.90
	9	29.5	127.7	116.2	112.2	37.38
	10	36.7	129.9	117.4	111.2	41.3
	11	35.9	129.0	119.5	112.8	41.4
	12	22.4	134.6	119.0	108.2	37.0
	13	39.9	129.2	121.7	113.5	43.73
	14	32.1	127.8	117.4	112.9	41.40
	15	42.0	127.7	116.0	112.3	43.74
	16	21.1	127.5	118.0	112.4	35.82

$t_{1/2}$ = crystallization half-time; T_c = crystallization temperature; $T_{c(\text{onset})}$ = onset crystallization temperature; T_m = melting temperature; $T_{m(\text{onset})}$ = onset melting temperature.

UHMWPE units and PMMA chains in the bone cement.

The grafting of MMA units onto UHMWPE resulted in lower crystallinity but delayed crystallization slightly. The results of crystallization half-time confirmed that the crystallization process proceeded at a higher rate for the MMA-g-UHMWPE samples compared to the initial UHMWPE. The crystallization of the grafted samples was slightly accelerated; this suggested that the MMA-g-UHMWPE units acted as nucleating agents for the crystallization of UHMWPE. Furthermore, the ultimate crystallinity of the grafted samples was generally lower than that of the initial UHMWPE.

References

1. Kwon, O. H.; Nho, Y. C. *J Appl Polym Sci* 2002, 86, 2348.
2. Kwon, O. H.; Nho, Y. C.; Lee, Y. M. *J Mater Sci: Mater Med* 2000, 11, 593.
3. Oosterom, R.; Ahmed, T. J.; Poullis, J. A.; Bersee, H. E. N. *Med Eng Phys* 2006, 28, 323.
4. Zhao, J.; Feng, Y.; Chen, X. F. *J Appl Polym Sci* 2003, 89, 811.
5. Fu, Z. S.; Xu, J. T.; Jiang, G. X.; Zhang, Y. Z.; Fan, Z. Q. *J Appl Polym Sci* 2005, 98, 195.
6. Kang, P. H.; Nho, Y. C. *Radiat Phys Chem* 2001, 60, 79.
7. Ishigaki, I.; Sugo, T.; Senoo, K.; Okada, T.; Okamoto, J.; Machi, S. *J Appl Polym Sci* 1982, 27, 1033.
8. Ishigaki, I.; Sugo, T.; Senoo, K.; Okada, T.; Okamoto, J.; Machi, S. *J Appl Polym Sci* 1982, 27, 1043.
9. Wang, J.; Liang, G.; Zhao, W.; Lu, S.; Zhang, Z. *Appl Surf Sci* 2006, 253, 668.
10. Cho, E. H.; Lee, S. G.; Kim, J. K. *Curr Appl Phys* 2005, 5, 475.
11. Rezaei, M.; Ebrahimi, N. G.; Kontopoulou, M. *J Appl Polym Sci* 2006, 99, 2344.
12. Rezaei, M.; Shirzad, A.; Ebrahimi, N. G.; Kontopoulou, M. *J Appl Polym Sci* 2006, 99, 2352.
13. Kalteh, H. G.; Rezaei, M.; Sheikh, N.; Abbasi, F. *J Appl Polym Sci* 2008, 108, 1086.
14. Rezaei, M.; Shirzad, A.; Ebrahimi, N. G. *Iran Polym J* 2006, 15, 3.
15. Wu, S. *Polymer Interface and Adhesion*; Marcel Decker: New York, 1982; Chapters 5 and 9.
16. Parasnis, N. C.; Ramani, K. *J Therm Anal Calorim* 1999, 55, 709.
17. Phadke, M. S. *Quality Engineering Using Robust Design*; Prentice-Hall International: New York, 1989.
18. Roy, K. R. *A Primer on the Taguchi Method*; Competitive Manufacturing Series; Van Nostrand Reinhold: New York, 1990.