The Grafting of Methyl Methacrylate onto Ultrahigh Molecular Weight Polyethylene Fiber by Plasma and UV Treatment

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ABSTRACT: In this study, ultrahigh molecular weight polyethylene (UHMWPE) fibers were treated with a gas plasma of argon for 5 min. The plasma-treated UHMWPE fibers were put into a methyl methacrylate solution with n-hexane or chloroform as the solvent and irradiated with a UV lamp. The UV irradiation time was changed. The surface topography that had a significant change on the fiber was seen by scanning electron microscopy. Infrared spectra (IR) and electron spectroscopy for chemical analysis (ESCA) were also studied to probe the surface atomic chemistry and to identify the functional groups and their relative changes with treatment conditions. The grafting content was estimated by the titration of esterfication method. It was found that the grafting amount for the system with chloroform as the solvent is larger than that for the system with n-hexane as the solvent. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 365–371, 1997

Key words: methyl methacrylate; ultrahigh molecular weight polyethylene; grafting; UV; plasma

INTRODUCTION

As ultrahigh molecular weight polyethylene (UHMWPE) fibers have long linear chains with a high degree of crystallinity and almost 100% orientation in the crystalline regions,[1] they behave as extremely inert. UHMWPE can be used in fiber-reinforced plastics and, due to its backbone, may offer many excellent properties, such as high toughness, excellent chemical resistance, low moisture absorption, and abrasion resistance. Since the current approval of UHMWPE for use in the human body, they are also suitable for biological application.[2]

The disadvantage of UHMWPE fiber is the poor adhesion to the resins, which results from the lack of chemical-bonding sites and the smooth surface of the UHMWPE fiber. To enhance the fiber/matrix adhesion, a number of fiber-surface treatment methods have been developed to plant functionalities on the fiber surface.[3–9]

Fibers treated by cold gas plasma have been studied by several workers.[10–12] The bombardment of fiber surfaces by energetic plasma species always generates active radicals which result in functionalities[13] when they are exposed to ambi-

ent conditions. Employment of cold gas plasmas has been found to significantly improve the adhesion of UHMWPE fibers to epoxy matrices.[3-5] Utilization of this technique also improved bonding with poly(methyl methacrylate)(PMMA).[14]

In addition to plasma treatment, γ-ray and photoirradiation (UV and visible sources) also offer unique possibilities for selective modification of the polymer surface properties without any noticeable changes in the bulk properties of the polymer.[15-17] The effect of plasma treatment on the surface modification for UHMWPE fiber has been reported in the literature[3-9,14]; however, the use of a UV irradiation method to induce graft polymerization of methyl methacrylate (MMA) onto the plasma-treated UHMWPE fiber has never been reported.

In the present study, UHMWPE fibers were surface-treated with Ar plasma to modify and plant functionalities on the surface. Immediately, the plasma-treated UHMWPE fibers were put into an MMA solution with hexane or chloroform as the solvent and irradiated with a UV lamp to obtain the MMA-grafted UHMWPE fibers. Scanning electron microscopy (SEM) was used to characterize the morphology changes of the modified UHMWPE fibers. Infrared spectroscopy (IR) and electron spectroscopy for chemical analysis (ESCA) were also studied to probe the surface atomic chemistry and to identify the functional groups and their relative changes with treatment conditions. The grafting content was estimated by the titration of esterfication method.

EXPERIMENTAL

Materials

The ultrahigh molecular weight polyethylene (UHMWPE) fibers used were Spectra 1000 from Allied Signal Inc. The characteristics of Spectra 1000 given by the manufacturer are listed in Table I. Fibers were washed following the procedures of Hild and Schwartz.[14] Fibers were washed with a 1% solution of tribasic sodium phosphate in distilled water and rinsed in acetone prior to plasma treatments. MMA was distilled to eliminate impurities and kept under nitrogen gas. Chloroform, hexane, and benzoin

ethyl ether were all reagent grade and were used directly.

Gas Plasma

A bell jar-type plasma treatment system PD-2S (Samco Ltd., Japan) was used to create the plasma for fiber treatments. Fibers were exposed to a gas plasma of argon at a power level of 60 W. The chamber was evacuated to < 60 m Torr before the introduction of argon gas. The gas flow rate of argon was kept constant, so that a pressure of 100–120 mTorr was maintained. Fibers were then exposed for 5 min.

Grafting of MMA onto UHMWPE Fiber by UV Irradiation

UHMWPE fibers, which were treated by gas plasma, were immersed into an MMA solution with hexane or chloroform as the solvent and irradiated with a UV lamp without degassing. The radiation wavelength was 2537 Å and the power level was 12,800 microwatts/cm^2. Benzoin ethyl ether was used as the photoinitiator. After photografting, the MMA-grafted UHMWPE (MMA-g-UHMWPE) fibers were extracted with hot methanol for at least 48 h to remove the homopolymer, followed by drying in a vacuum oven.

Identification of MMA-g-UHMWPE Fibers by FTIR, ESCA, Element Analysis, and Scanning Electron Microscopy

UHMWPE and MMA-g-UHMWPE fibers were characterized by a Bio-Rad FTIR spectrometer. An electron spectroscopy for chemical analysis (ESCA) 2110 VG Scientific instrument was used to measure the UHMWPE and MMA-g-UHM-WPE fibers. The UHMWPE fiber was analyzed by an element analyzer (Heraeus CHN-0-RAPID).

Table I   Characterization of Spectra 1000 Fiber

Strength (10^3 psi)	435
Tensil modulus (10^6 psi)	25
Elongation (%)	2.7
Shrinkage at boil (%)	1
Filament size (μ)	27
Density (g/cc)	0.97
Denier/no. filaments	650/120
Melt point (°C)	147

The UHMWPE and MMA-*g*-UHMWPE fibers were plated with chromium, and the morphology of the surfaces were studied by a scanning electron microscope (JEOL, Model JSM-6300).

Titration of Esterfication Method for MMA-*g*-UHMWPE Fiber

To determine the content of MMA grafted onto the UHMWPE fiber, the titration of esterfication method was used. The MMA-*g*-UHMWPE fiber was immersed in a $2N$ $NaOH_{(aq)}$ solution at 80°C for 0.5 h and the fiber was washed with deionized water to remove the residue of NaOH. Following the procedures, the UHMWPE fiber was immersed in $1N$ $HCl_{(aq)}$ for 24 h and washed with deionized water, and then the fiber was immersed in the $NaCl_{(aq)}$ solution for 24 h. Lastly, the pH value of the $NaCl_{(aq)}$ solution was evaluated by a pH meter and the content of MMA grafted onto the UHMWPE fiber was determined. The equation for the above procedures can be shown as follows:
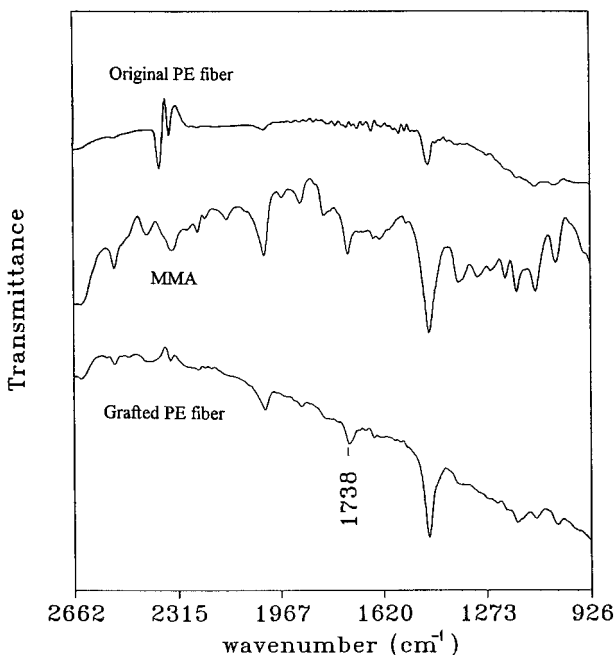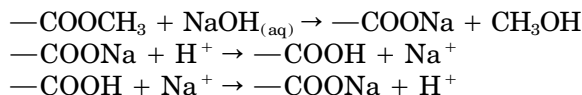
$$—COOCH_3 + NaOH_{(aq)} \rightarrow —COONa + CH_3OH$$
$$—COONa + H^+ \rightarrow —COOH + Na^+$$
$$—COOH + Na^+ \rightarrow —COONa + H^+$$

Figure 1 FTIR spectra of (a) UHMWPE fiber, (b) PMMA, and (c) MMA-*g*-UHMWPE graft fiber.
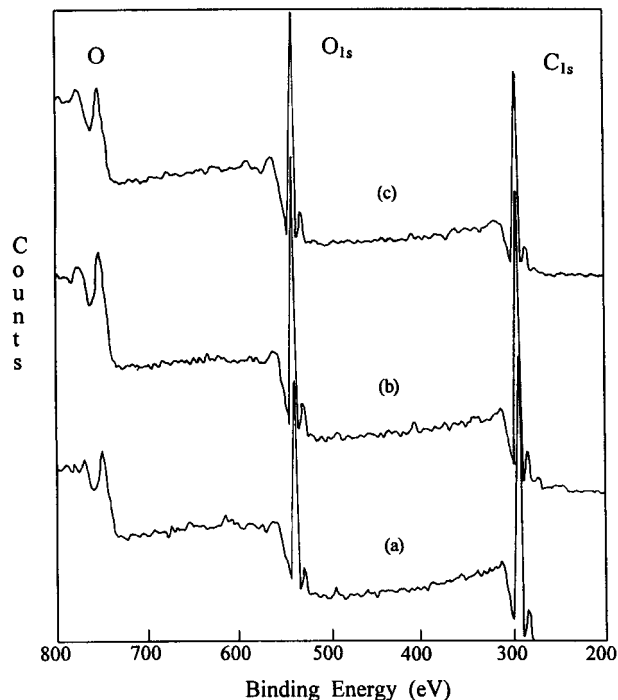

Figure 2 ESCA spectra of (a) UHMWPE fiber, (b) plasma-treated UHMWPE fiber, and (c) MMA-*g*-UHM-WPE graft fiber.

$—COOCH_3$: the ester group of PMMA grafted onto the UHMWPE fiber.

RESULTS AND DISCUSSION

Characterization of MMA-*g*-UHMWPE Fibers by FTIR, ESCA, Element Analysis, and Scanning Electron Microscopy

Shown in Figure 1(a)–(c) are the absorption spectra of the UHMWPE fiber, homo-PMMA, and the MMA-*g*-UHMWPE graft fiber, respectively.

Table II The Relative Ratio of O/C for Various Samples

Sample	O/C
UHMWPE fiber	0.019[a]
UHMWPE fiber	0.319[b]
Plasma-treated UHMWPE fiber	0.329[b]
MMA-*g*-UHMWPE graft fiber	0.407[b,c]

[a] The result by element analysis.
[b] The results by ESCA analysis.
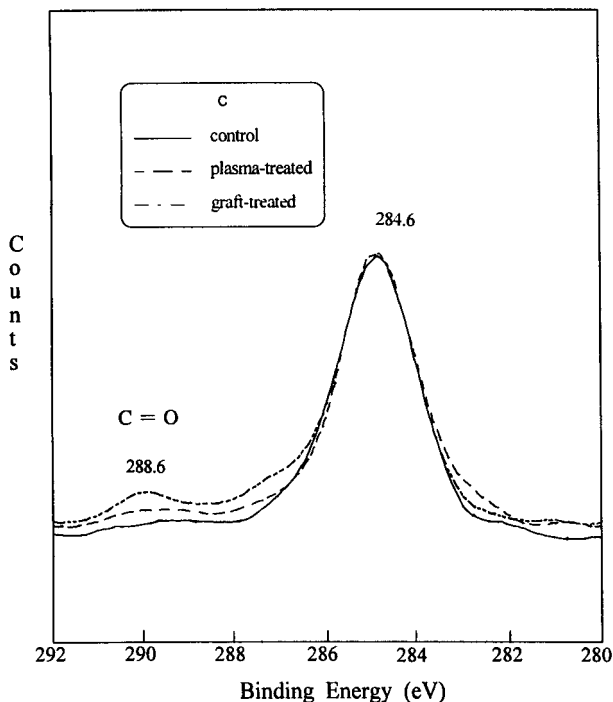[c] The grafting amount of MMA is about 4900 nmol/g.

Figure 3 C_{1S} ESCA spectra for (——) UHMWPE fiber, (– – –) plasma-treated UHMWPE fiber, and (— – —) MMA-g-UHMWPE graft fiber.

In addition to those absorption peaks associated with the UHMWPE fiber, the MMA-g-UHMWPE graft fiber also shows absorption peaks at 1738 cm^{-1} (C=O) and at about 1085–1150 cm^{-1} for the C—O—C group. Since the unreacted MMA and its homopolymer have been extracted with hot methanol, the presence of these absorption bands confirms that the MMA-g-UHMWPE was a graft fiber.

The ESCA spectra of the UHMWPE fiber, plasma-treated UHMWPE fiber, and the MMA-g-UHMWPE graft fiber are shown in Figures 2(a)–

(c), respectively. Table II is the ratio of O/C obtained for each of the UHMWPE fibers, plasma-treated UHMWPE fibers, and MMA-g-UHMWPE graft fibers. A strong peak at 284.6 eV, indicative of carbon–carbon bonds in the fibers, was evident from the C_{1S} spectra for the fiber surface. The other significant peak in Figure 2 was attributed to the peroxide or trapped oxygen on the fiber surface. Since PE is a polymer prepared by the polymerization of an ethylene monomer, it should not contain oxygen in the polymer. But shown in Table II, the O/C ratio obtained by element analysis for the UHMWPE fiber is 0.019. It was also found that the O/C ratio obtained by the ESCA study for the UHMWPE fiber is 0.319, indicating that most of the oxygen atoms come from the attachment of the oxygen atom on the fiber surface. This was not surprising, as other researchers have found loosely bound oxygen contamination on untreated PE films or fiber as revealed by ESCA.[4,14,18] When the UHMWPE fiber was treated by argon plasma, the ratio of O/C is 0.329. The increase of the O/C ratio was due that, during the plasma treatment, free radicals were formed on the surface of the fiber. Oxygen from the atmosphere may have attached to the fiber surface when the fibers were exposed to air, in that argon plasmas introduce oxygen groups (carbonyls, carboxyls, and hydroxyls) onto the surface.[14,18] After the UV treatment of the UHMWPE fiber with the MMA monomer, the O/C ratio increases further. It resulted from the grafting of MMA onto the UHMWPE fiber to obtain the MMA-g-UHMWPE grafted fiber, which is confirmed in Figure 3. There was another peak at 288.6 eV which was assigned to the C=O bond on the fiber surface.
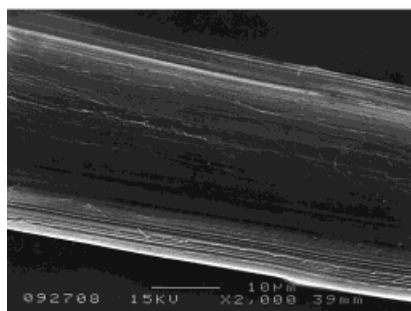
Figure 4(a)–(c) displays the SEM topography of the UHMWPE fiber, the plasma-treated UHMWPE fiber, and the MMA-g-UHMWPE grafted

Table III   The Grafting Amount of MMA onto UHMWPE Fiber Under Various Conditions
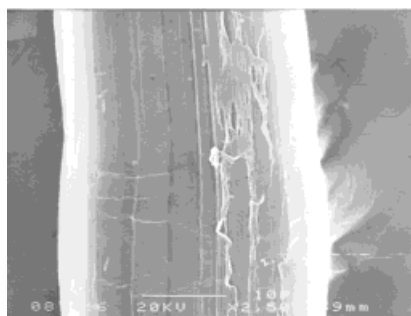
UV Radiation Time (h)	Without Plasma Treatment		With Plasma Treatment	
	In n-Hexane (nmol/g)	In Chloroform (nmol/g)	In n-Hexane (nmol/g)	In Chloroform (nmol/g)
2.5	31 ± 14	410 ± 34	116 ± 20	718 ± 31
3	85 ± 15	856 ± 60	402 ± 23	1304 ± 51
4	131 ± 10	1007 ± 73	414 ± 37	2190 ± 297
5	279 ± 51	1130 ± 36	731 ± 97	2383 ± 300
6	384 ± 24	1445 ± 70	1677 ± 273	4891 ± 277
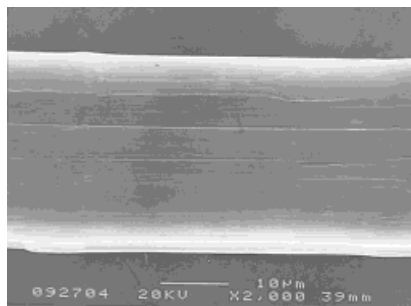
(a)

(b)

(c)

Figure 4 Scanning electron photomicrographs of (a) UHMWPE fiber, (b) plasma-treated UHMWPE fiber, and (c) MMA-*g*-UHMWPE graft fiber.

fiber, respectively. There is a significant difference in the surface topography. There was no surface roughening on the UHMWPE fiber, but the roughening on the plasma-treated UHMWPE fiber and the MMA-*g*-UHMWPE grafted fiber was

found. The presence of PMMA onto the surface was also found.

The Study of the Grafting Amount of MMA onto UHMWPE Fiber

To determine the grafting amount of MMA onto the UHMWPE fiber, the titration of esterfication method was used. The effects of plasma treatment, time of UV irradiation, and the solvent on the grafting amount are shown in Table III. It was found that the MMA monomer could be grafted onto the UHMWPE fiber to obtain the MMA-*g*-UHMWPE graft fiber by UV photografting without plasma treatment. The value of the grafting amount for MMA grafting onto the UHMWPE fiber for the treatment by the plasma and UV photografting method is larger than that without plasma treatment, because there are fewer free radicals induced by the UV irradiation without plasma treatment. As shown in the discussion of the characterization of the fiber by ESCA in this study, during the plasma treatment, free radicals were formed on the surface of the fiber. Oxygen from the atmosphere may have attached to the fiber surface when the fibers were exposed to air, in that argon plasmas introduce oxygen groups (carbonyls, carboxyls, and hydroxyls) onto the surface.[14,18] So, there were more free
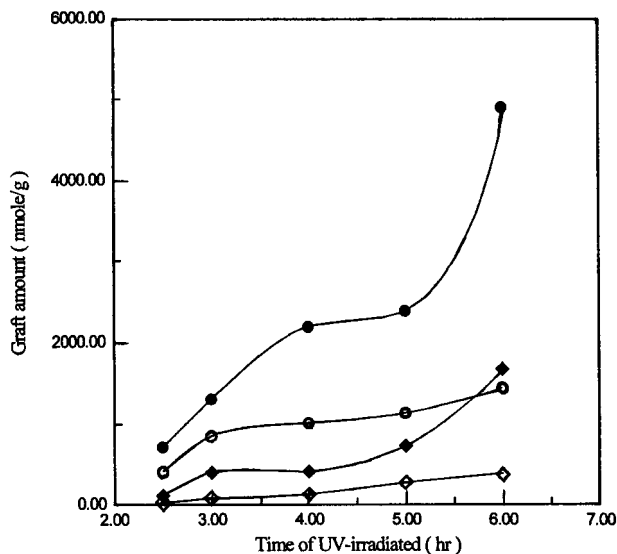

Figure 5 The relationship between graft amount and UV irradiation time for (●) plasma-UV treatment in chloroform, (○) UV treatment in chloroform, (◆) plasma-UV treatment in *n*-hexane, and (◇) UV treatment in *n*-hexane.

Table IV   The Solubility Parameter[21] of Solvents and Polymer

	Solubility Parameter $(\text{cal/cm}^3)^{0.5}$
n-Hexane	14.9
Chloroform	19
PMMA	18.8

radicals on surface to undergo grafting polymerization for MMA grafting onto the UHMWPE fiber by UV photografting with plasma treatment.

As shown in Figure 5, the grafting amount increased with UV irradiation time. When the photografting time was longer than 5 h, the grafting amount increased rapidly for the plasma–UV-treated system. As there are fewer free radicals induced by the UV irradiation without plasma treatment, the increase of the grafting amount is not as significant as in the system treated by the plasma–UV method.

In Figure 5, it is also found that the value of the grafting amount for the system with chloroform as the solvent is higher than that for the system with n-hexane as the solvent. As reported previously,[19,20] the grafting amount of irradiation (or photografting)-induced graft copolymerization is affected by the molecular chain mobility, which is related to the solubility of molecules in the graft-polymerization system. From the values of the solubility parameter in Table IV,[21] chloroform is a good solvent for PMMA; n-hexane is a nonsolvent for PMMA. Under the same conditions, the chain mobility in chloroform is larger than that in n-hexane and the viscosity of the system with chloroform as the solvent is smaller than that of the system with n-hexane as the solvent. As there was competition between the homopolymerization and the grafting polymerization, the MMA monomer in the system with n-hexane as the solvent was trapped in the homopolymer and was homopolymerized before it could diffuse to the surface to undergo graft-copolymerization. This resulted in the value of the grafting amount for the system with n-hexane as the solvent to be lower than that for the system with chloroform as the solvent.

CONCLUSION

The grafting of MMA onto the UHMWPE fiber could be confirmed by FTIR. The absorption peaks are at 1738 cm^{-1} (C=O) and about 1085–1150 cm^{-1} for the C—O—C group of the MMA grafted onto the UHMWPE fiber. It can also be identified by ESCA. A strong peak at 284.6 eV, indicative of carbon–carbon bonds in the fiber, was evident by the C$_{1s}$ spectra for the fiber surface. There was another peak at 288.6 eV which was assigned to the C=O bond on the MMA-g-UHMWPE graft fiber surface. Due to the grafting of MMA onto the UHMWPE fiber, the topography of the modified fiber became rough. The presence of PMMA onto the surface was also found.

By using the titration of esterfication method, the grafting amount of MMA onto the UHMWPE fiber was determined. The grafting amount increased with UV irradiation time. As there are fewer free radicals induced for the system by UV irradiation without plasma pretreatment, the increase of the grafting amount is not as significant as for the system treated by the plasma–UV method. The value of the grafting amount for the system with chloroform is larger than that for the system with n-hexane as the solvent, because the MMA monomer was trapped in the homopolymer and was homopolymerized before it could be diffused to the fiber surface to undergo graft copolymerization.

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