Graft Copolymerization of Polyethylene Glycol Methacrylate onto Polyethylene Film and Its Blood Compatibility

OH HYUN KWON,[1] YOUNG CHANG NHO,[2] KI DONG PARK,[3] YOUNG HA KIM[3]

[1] Department of Industrial Chemistry, College of Engineering, Hanyang University, Seoul 133-791, Korea

[2] Radioisotopes–Radiation Application Team, Korea Atomic Energy Research Institute, Taejon 305-606, Korea

[3] Division of Polymer, Korea Institute of Science and Technology, Seoul 130-650, Korea

Received 10 February 1998; accepted 5 August 1998

ABSTRACT: In an attempt to produce surfaces that show low levels of adsorption of protein and adhesion of platelets, different molecular weights of polyethylene glycol methacrylate (PEG-MA) were grafted onto polyethylene film by a preirradiation grafting process. The extent of grafting was found to be dependent on the storage condition of the irradiated polyethylene film, the preirradiated dose, reaction time and temperature, molecular weight of PEG-MA, and the type of solvent. The grafting yield was found to decrease rapidly with storage time for irradiated polyethylene film stored at room temperature. On the other hand, the grafting yield in the irradiated polyethylene stored at −130°C remained nearly constant up to 20 days after irradiation. The grafting yield decreased with an increased PEG-MA molecular weight. Human plasma protein was adsorbed onto control and PEG-MA-grafted polyethylene film surfaces, and the relative adsorbed amount of proteins on the surfaces was evaluated by electron spectroscopy for chemical analysis. The adsorbed protein and platelet adhesion on the polyethylene film surface decreased rapidly with the grafting yield. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 631–641, 1999

Key words: polyethylene glycol methacrylate; polyethylene film; grafting; blood compatibility

INTRODUCTION

One of the main problems of using biomaterials has been surface-induced thrombus formation, which is initiated by the adsorption of certain plasma proteins and the adhesion of platelets. Appropriate surface modification of existing biomaterials possessing the desired physical properties is beneficial in improving biocompatibility without altering the bulk properties of the biomaterials. The surface modification method can be grouped into three general categories: physical adsorption, grafting coupling, and grafting polymerization.

The biocompatibility of polymer materials contacting with blood is known to be related to the adsorption of plasma proteins and activation of platelets.[1–3] Polyethylene oxide (PEO) is more and more regarded as a polymer with interesting blood compatibility. The low affinity of PEO for proteins and other blood components has stimulated many investigators to study the interactions of blood and biomaterials based on PEO. Brinkman and colleagues[4] tried to improve the blood compatibility of

Correspondence to: Y. C. Nho.

Journal of Applied Polymer Science, Vol. 71, 631–641 (1999)
 CCC 0021-8995/99/040631-11

Table I Structure of PEG-MA

	PEO2-MA	PEO4/5-MA	PEO7/9-MA
Ethylene oxide no.	2	4–5	7–9
Molecular weight	163–173	261–283	387–468

a commercial copolyether urethane by grafting PEO using a chemical initiator. Vulic and colleagues[5] investigated a three-block copolymer consisting of a hydrophobic block of polystyrene, a hydrophilic spacer block of PEO, and covalently bonded heparin as a bioactive block. Bergstrom and colleagues[6] showed that fibrinogen adsorption is significantly reduced by coating polystyrene with either linear or branched polyethylene glycol with a molecular weight of 1,500 to 20,000.

The grafting method needs free radicals or peroxides to modify the surface of polymers. The production of these initiation species are possible by UV,[7,8] plasma,[9,10] radiation,[11–13] and chemicals. Radiation-induced grafting is one of the effective methods because of its rapid and uniform creation of active radical sites on the existing polymer matrix. Synthesizing blood-compatible materials by radiation has often used γ-rays or electron beams to graft hydrophilic monomers onto substrates. The methods of achieving grafting reactions using radiation include simultaneous irradiation of the backbone polymer in the presence of the monomer and preirradiation.

Hayashi and colleagues[14] evaluated the effects of preirradiation doses in air and grafting percentage on the antithrombogenicity to clarify the optimal preparative conditions for polyethylene radiation-grafted with acrylamide in terms of surface antithrombogenicity. Songh and Ray[15] examined the compatibility of chitosan grafted with 2-hydroxyethyl methacrylate using γ-radiation.

In this study, in an attempt to produce surfaces that show low levels of adsorption of protein and adhesion of cells, polyethylene glycol methacrylate of different molecular weights was grafted onto polyethylene film by the preirradiation grafting process.

EXPERIMENTAL

Materials

Commercial polyethylene film of 100 μm thickness (Hanjung Chemical Co.) was used as a substrate for the grafting reaction. Polyethylene glycol methacrylate (PEG-MA) was supplied by the Nippon Oil & Fats Co. PEG-MA, with different PEO repeat units, was used without further treatment. Other chemicals were reagent grades. The polyethylene film was cut into 3 $\times$ 5 cm pieces and ultrasonically cleaned twice in methanol (MeOH) for 1 h each time, and dried in a vacuum oven. The structure of PEG-MA used in this experiment is shown in Table I.

Grafting Procedure

The γ-ray irradiations from Co-60 sources were conducted at an exposure rate of 5.9 kGy h^{-1} in the presence of air to a total dose of 40–120 kGy. The irradiated polyethylene films were stored in a refrigerator kept at -130°C until the grafting reaction was performed. The grafting experiment was conducted in a pyrex ampoule having a vacuum cock. Solvent as a diluent was added first, followed by PEG-MA. Polyethylene film (3 $\times$ 5 cm) was immersed in the pyrex ampoule containing 40 mL PEG-MA solution and purged by bubbling nitrogen for 20 min. The grafting reaction was conducted by placing the ampoules in a water bath set at the relevant temperature. After the grafting reaction, grafted films were taken out from the monomer solution in a glass ampoule and washed with methanol and distilled water to remove the remaining homopolymer. The degree of grafting was determined by the following:

$$\text{Degree of grafting } (\%) = \frac{W_g - W_o}{W_o} \times 100$$

where W_g and W_o are the weights of the grafted and starting polyethylene film, respectively. The grafted polyethylene films were verified by Fourier transform infrared spectroscopy in the attenuated total reflectance mode (FTIR-ATR) and electron spectroscopy for chemical analysis (ESCA). A Nicolet model 205 spectrophotometer (USA), with a nominal 45° attenuated total reflectance, was used to examine the grafting onto poly-

ethylene by irradiation. ESCA for examining the grafting and adsorption of protein on polyethylene film was conducted with a V. G. SCIENTIFIC ESCALAB MK II spectrometer using MgKα X-ray radiation at 1253.6 eV operating at 10^{-9} mbar and photoelectron takeoff angles of 60°. The control and polyethylene samples were cut to form 6-mm disks, and then they were introduced into the UHV spectrometer chamber. MgKα radiation was used with the analyzer operating at a constant bandpass energy of 20 eV. The spectrometer was calibrated by assuming the binding energy of the Au $4f_{7/2}$ line to be 83.9 eV, with respect to the Fermi level. Survey scans (0–1,200 eV) were recorded for each sample to obtain a qualitative elemental analysis.

Determination of Peroxide

For the irradiated samples, the amount of peroxide formed around the surface was quantified with 1,1-diphenyl-2-picrylhydrzyl (DPPH).[13] The polyethylene samples stored at room temperature for 10 days after irradiation were dipped into a DPPH/toluene solution (1×10^{-4} mol L^{-1}) at 70°C for 3 h to decompose the peroxides formed on and near the polyethylene surfaces. The DPPH molecules consumed were measured from the difference in transmittance between the control and irradiated polyethylene samples at 520 nm using a UV spectrophotometer (Cesil Instruments, CE 292).

Contact Angle Measurement

The PEG-MA-grafted polyethylene surfaces were characterized by water contact angle measurements using an optical contact angle goniometer (Erma Optical Ltd., Japan). The water contact angle for each polyethylene sample was measured by a sessile drop method five times with the sample length at the room temperature. Drops of purified water (3 μL) were deposited onto the PEG-MA-grafted polyethylene surface, and the direct microscopic measurement of the contact angles for polyethylene stored at room temperature during the 3 min after deposition was done with a goniometer. Water sessile drops were deposited from the glass syringe onto the sample surfaces, and the contact angle was measured after a defined period of time to allow the establishment of equilibrium.

Platelet Adhesion

Human blood from healthy volunteers was collected with a polypropylene syringe containing a 3.8% sodium citrate solution. Platelet-rich plasma (PRP) having a 2.43×10^5 cell μL^{-1} concentration was obtained by centrifuging human blood at 2,300 rpm for 4 min at 4°C. Control and grafted polyethylene films were hydrated by placing them in phosphate-buffered saline (PBS; pH 7.4)-filled polystyrene (24 wall vials five times for 10 min). Each rehydrated film was transferred into a PRP prewarmed to 37°C for 30 min. After incubation at 37°C, the samples were washed carefully with PBS to remove weakly adhered platelets. Platelets adherent on the films that remained adhered to the polyethylene surfaces were fixed with a 2.5% glutaraldehyde in PBS for 10 min at room temperature. The platelets fixed on the surfaces were dehydrated in an ethanol-grade series (50, 60, 70, 80, 90, and 100%) for 10 min after each was washed with PBS, and allowed to dry on a clean hood at room temperature. The platelets attached to the polyethylene samples were examined by a scanning electron microscope (SEM; JSM-840A, JEOL Co., Japan) with a tilt angle of 45° after gold deposition in a vacuum.

Plasma Protein Adsorption

Human plasma protein (Sigma Chemical Co., St. Louis, MO) was diluted with PBS to make a 1% solution. The control and grafted polyethylene film hydrated in PBS five times at 37°C was placed in contact with the above solution in 24 polystyrene wall vials at the same temperature for 1 h. The samples were washed with PBS, after incubation, and then washed with purified water to remove unadsorbed proteins. After vacuum-drying, the change in protein adsorption of the control and PEG-MA-grafted polyethylene surfaces were investigated by ESCA. The changes in the nitrogen 1-s peaks from the X-ray photoelectron spectroscopy survey scan spectra were examined as described.

Calcination Time

Human blood was centrifuged at 4,000 rpm for 5 min at 4°C to obtain platelet-poor plasma (PPP). PPP (0.5 mL) prewarmed to 37°C was added to each sample. All samples before the test were hydrated five times in saline water at 37°C for 10 min. The reaction was initiated by a further 0.1 mL addition of 0.1*M* calcium chloride to each sample. The calcination time was examined when blood on the sample did not flow while the sample was tilted to 30°.

RESULTS AND DISCUSSION

It is known that proteins are complex macromolecules with molecular weights ranging from thousands to millions and that they adsorb onto practically all interfaces during the first few minutes of blood or biological fluid exposure.[16] Generally, the adsorption process results in the activation of coagulation and subsequent thrombus formation. Various efforts have been concentrated on minimizing or controlling protein adsorption. Surfaces that have minimal protein adsorption may be important in many applications, such as dialysis membranes for separation processes in blood, oxygenators, and contact lenses. Although a large amount of work to improve the blood compatibility of polymeric materials has been performed, the results are still not very conclusive.

Among the hydrophilic materials, a particularly effective polymer for protein-resistant surfaces seems to be PEO, due to its unique solution and surface properties in water. PEO surfaces have been introduced by physical adsorption of high-molecular weight PEO or various PEO-containing block copolymers onto hydrophobic polymeric substrates. This process may be a simple and rapid means of introducing PEO surfaces, if the PEO-containing copolymers can be adsorbed strongly onto the surfaces. However, it is difficult to get the immobilized polymers to remain permanently on the surface. Another process of introducing a permanent PEO surface is to use covalent binding of PEO or PEO derivatives onto polymeric substrates. However, this method is possible if only the surface has chemically active functional groups that can couple with PEO derivatives. This limits the application of this technique to certain biomaterials. One of the effective methods is to use radiation to produce PEO groups on the polymer surface.

It is known that the free radicals created by irradiation in solid polymers may be immobilized and remain trapped for a considerable length of time.[17] In the preirradiation process, the polymeric material is irradiated and, subsequently, the deaerated monomer is contacted with the irradiated polymer. Grafting is induced by macroradicals trapped in the irradiated polymer. Virtually little homopolymers are 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 trapped radicals. The main factor governing the trapping of radicals is the physical state of the irradiated polymer. In the case of rubbery and noncrystalline polymers, the mobility of radicals is fairly significant; and their survival time after irradiation is not so long, compared with polymers having high crystallinity. The usefulness of the grafting method depends largely on the crystallinity of the polymer, and also the relative reaction rates of monomers with trapped radicals and thermal decay of radicals at the temperature required for grafting.

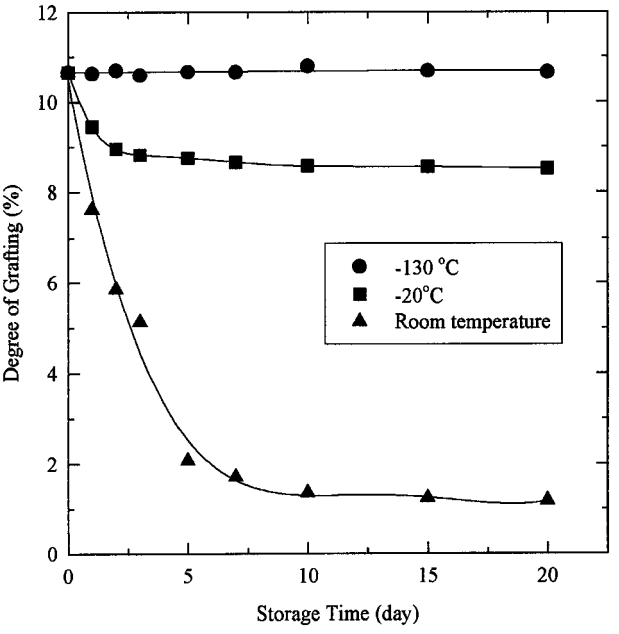

Figure 1 Effect of storage temperature and time on the grafting of PEO4/5-MA onto 120 kGy preirradiated polyethylene in 30 vol % PEG-MA MeOH/THF (2/1) solution at 30°C for 3 h.

The life time of the trapped free radical depends on the temperature of storage because it can affect the mobility of polymer radicals. The relation between the grafting reaction, and storage time and temperature is valuable in the viewpoint of practical application.

The polyethylene films were stored at various storage conditions for certain time periods immediately after irradiation. Figure 1 shows the effect of storage temperature and time on the grafting of PEG-MA onto polyethylene film preirradiated to a total dose of 120 kGy. The grafting yield of the irradiated polyethylene film stored at room temperature was found to decrease rapidly with storage time. The grafting yield of the irradiated polyethylene stored at −20°C decreased slightly with

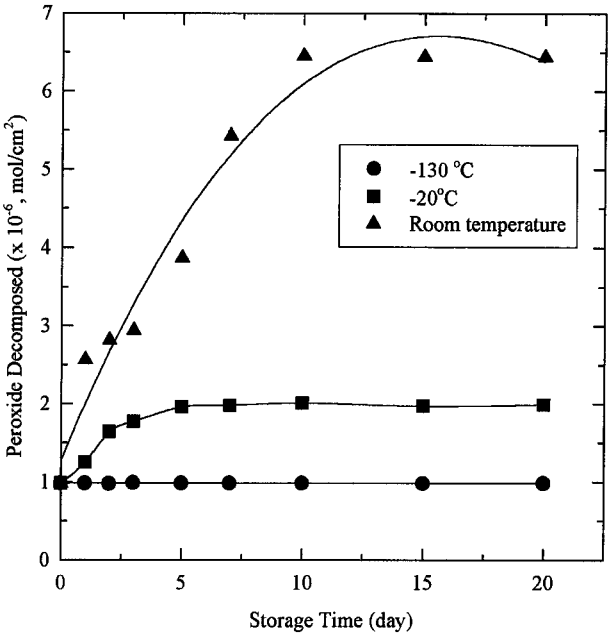

Figure 2 Effect of storage temperature and time on the decomposition of peroxides.

storage time. On the other hand, the grafting yield in the irradiated polyethylene stored at −130°C remained nearly constant up to 20 days after irradiation. The reason why the grafting yield was not changed even after 20 days' storage at −130°C can be attributable to the decrease in the termination of free radicals, which comes from the comparatively high crystallinity of polyethylene and the restriction of chain segmental motion at extremely low temperatures. Termination of various active sites increased with an increased storage temperature of the irradiated polymer.

Figure 2 shows the effect of storage temperature and time on the formation of peroxides on polyethylene films that was irradiated to a total dose of 120 kGy. The DPPH technique was used to evaluate the concentration of peroxide formed on the irradiated polyethylene sheet by counting the quantity of DPPH consumed from the reaction of peroxide radicals with DPPH. The decomposed peroxide concentration was calculated from the DPPH consumption as a function of the reaction time at 70°C for polyethylene films irradiated by γ-rays. It was shown that the peroxides at room temperature increased rapidly with storage time until 10 days and then leveled off. On the other hand, the peroxide extent stored at −130°C did not change until 20 days after irradiation. When organic polymers are subjected to ionizing radiation, the trapped radicals, capable of initiating graft copolymerization reactions, are generally formed. The trapped radicals at room temperature are easily oxidized to form peroxide in the presence of air, because the chain segmental motion of polyethylene is comparatively active. Termination of various active sites increases with increasing storage temperature of irradiated polymers. On the other hand, the polyethylene radicals at extremely low temperatures do not almost change owing to the restriction of chain segmental motion.

Figure 3 shows the effect of reaction time on the grafting of PEG-MA onto polyethylene, which was irradiated at 40, 80, and 120 kGy. The grafting yield increased in proportion to the reaction time up to ~ 5 h and then leveled off.

The reaction temperature is one of the important factors controlling the grafting. As shown in Figure 4, 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 reactions at particularly low reaction temperatures can be attributable to the trapped radicals. On the other hand, it is possible that the reactive sites on the backbone polymer can be generated by the decomposition of hydroperoxide or diperoxide at high temperatures, leading to the grafting reaction.

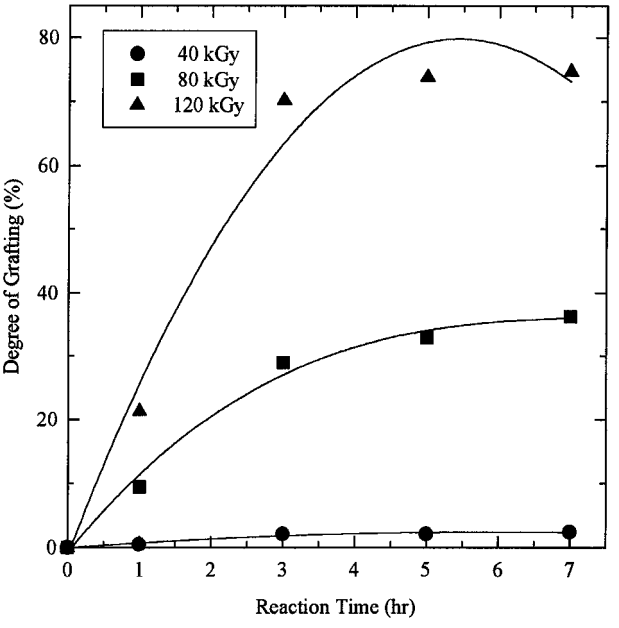

Figure 3 Effect of reaction time on the grafting of PEO4/5-MA onto irradiated polyethylene in 30 vol % PEG-MA MeOH/THF (2/1) solution at 70°C.

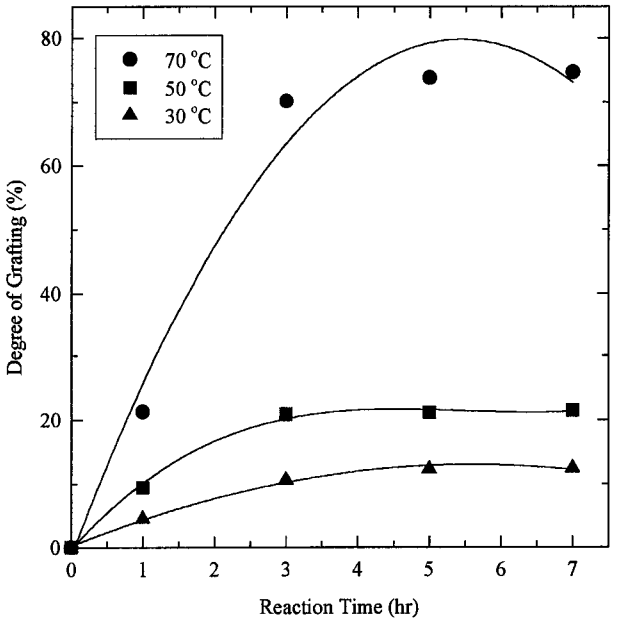

Figure 4 Effect of reaction time on the grafting of PEO4/5-MA onto 120 kGy irradiated polyethylene in 30 vol % PEG-MA MeOH/THF (2/1) solution.

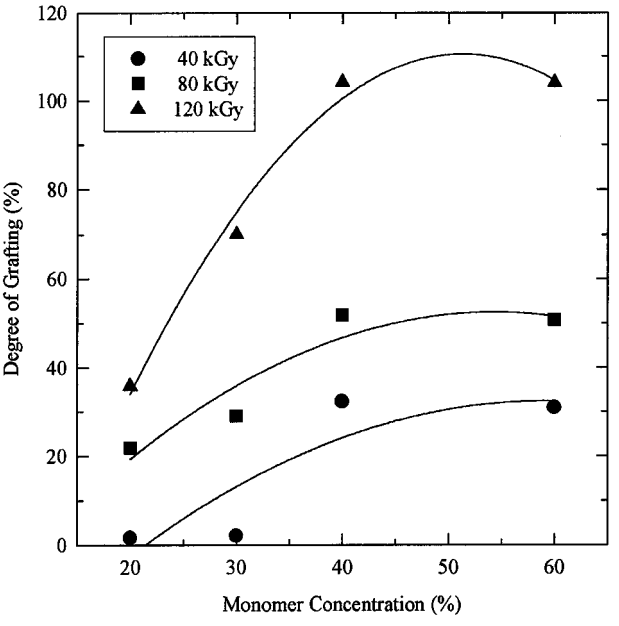

Figure 6 Effect of monomer concentration and irradiation dose on the grafting of PEO4/5-MA onto preirradiated polyethylene in MeOH/THF (2/1) solution at 70°C for 3 h.

Figure 5 shows the relation of PEG-MA molecular weight with grafting yield. The grafting yield decreased with an increased molecular weight of PEG-MA. In the case of high molecular weight PEG-MA, the decrease in grafting yield may be due to the steric effect of the long polyether chain. As the ether chain increases in length, there is an increased probability that the vinyl group becomes shielded by the coil of the PEG group. The vinyl group may therefore be less accessible to radical attack.

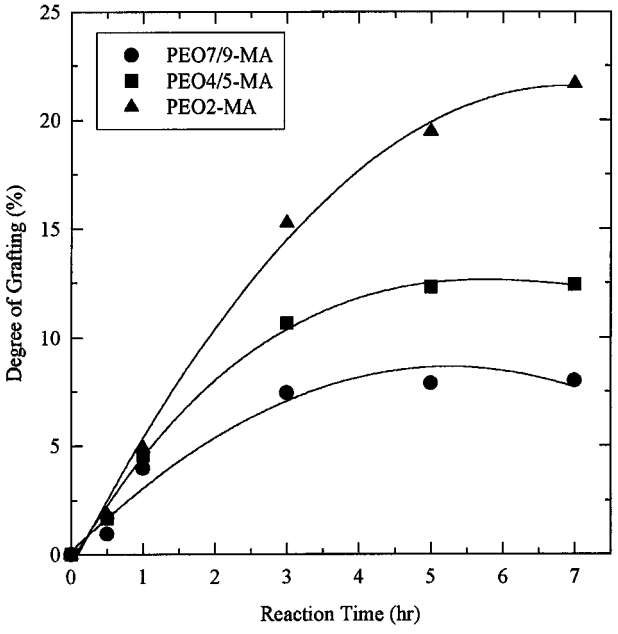

Figure 5 Effect of reaction time on the grafting of PEG-MA onto 120 kGy irradiated polyethylene in 30 vol % PEG-MA MeOH/THF (2/1) solution at 30°C.

Figure 6 shows the effect of monomer concentration on the grafting yields at various irradiation doses of 40, 80, and 120 kGy. The maximum peak occurred at ~ 40% monomer concentration, then did not change despite the increase in monomer concentration.

The role of solvents is one of the most important variables that influence the grafting yield. It is known that the components in the grafting solution that wet and swell the polymer substrate assist the grafting reaction. In order for the grafting in the grafting solution to be effective, the preirradiated polymer must be in contact with a homogeneous solution. Therefore, a solvent should be chosen that first of all will dissolve monomers. The effect of the composition of tetrahydrofuran (THF) and MeOH on the grafting yield is shown in Figure 7. When the composition of THF and MeOH was 40 : 60, the maximum grafting yield was obtained.

The contact angle of water droplets in air on various samples was examined to establish the

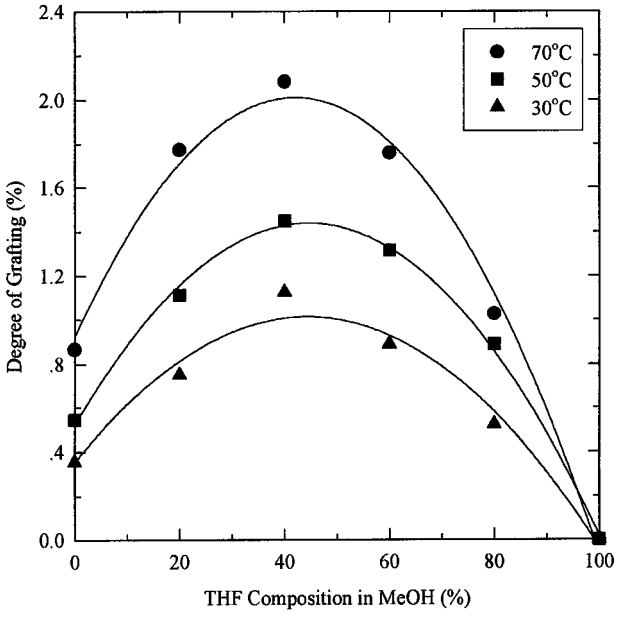

Figure 7 Effect of THF composition in MeOH on the grafting of PEO4/5-MA onto 40 kGy irradiated polyethylene in 30 vol % PEG-MA for 3 h.

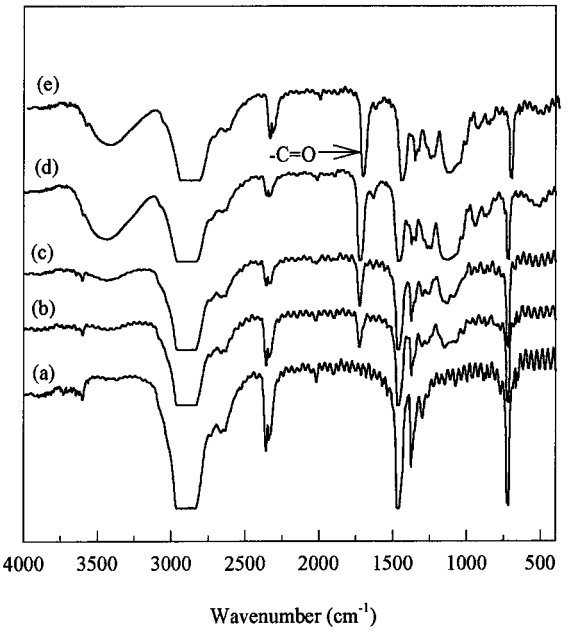

Figure 9 FTIR-ATR spectra of (a) control, (b) 0.153%, (c) 1.082%, (d) 3.435%, and (e) 10.405% of PEO4/5-MA-grafted polyethylene surfaces.

relationship between the degree of grafting and the hydrophilicity. It is clear from Figure 8 that the contact angle of the grafted polyethylene film was appreciably lower than that of the ungrafted polyethylene, and the angle decreased with the increasing extent of grafting due to the hydrophilicity of grafted polyethylene. The film grafted with PEO4/5-MA has a low-contact angle, compared with PEO2-MA and PEO7/9-MA at the same grafting yield.

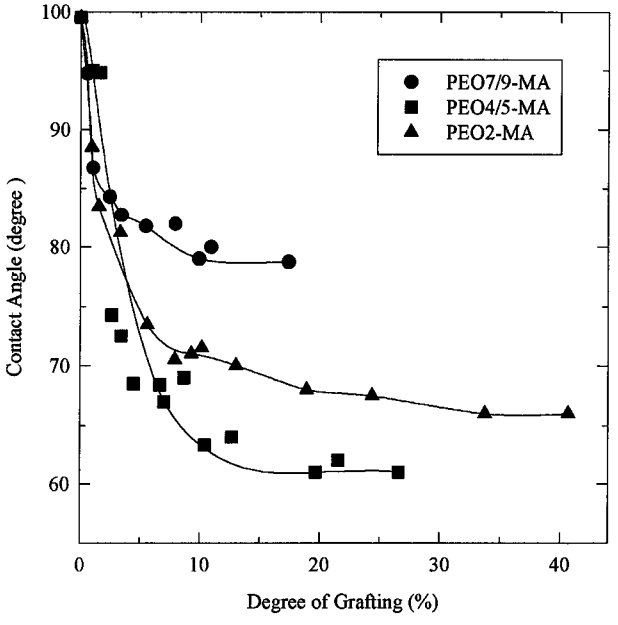

Figure 8 Changes in water contact angle with the grafting of PEG-MA onto irradiated polyethylene.

Changes in the chemical structure of PEO4/5-MA-grafted polyethylene films with the grafting yield were examined by FTIR-ATR and survey scan spectra with an X-ray photoelectron spectrometer. Figure 9 shows the FTIR-ATR spectra of control and PEO4/5-MA-grafted polyethylene film surfaces with the grafting yield. With increased grafting yields, the stretching peaks of the carbonyl group (—C═O) at 1,730 cm^{-1} and ether carbon band (—C—O, 1,130–1,160 cm^{-1}) increased, whereas the C—H bending peaks at 1,465 cm^{-1} decreased with the grafting yield. The polyethylene film surfaces of different grafting yields were studied by measuring the survey scan spectra with an X-ray photoelectron spectrometer. Figure 10 shows the ESCA survey scan spectra of polyethylene film surfaces for control and PEO4/5-MA-grafted polyethylene. As shown in Figure 10, the grafted polyethylene had oxygen (O-1s : 537.0 eV) peaks, as well as carbon (C-1s : 284.6 eV) peaks, with there being no oxygen peak for ungrafted polyethylene. The oxygen peak of polyethylene with increased grafting yield increased more and more due to increasing carbonyl groups on polyethylene surfaces. From these re-

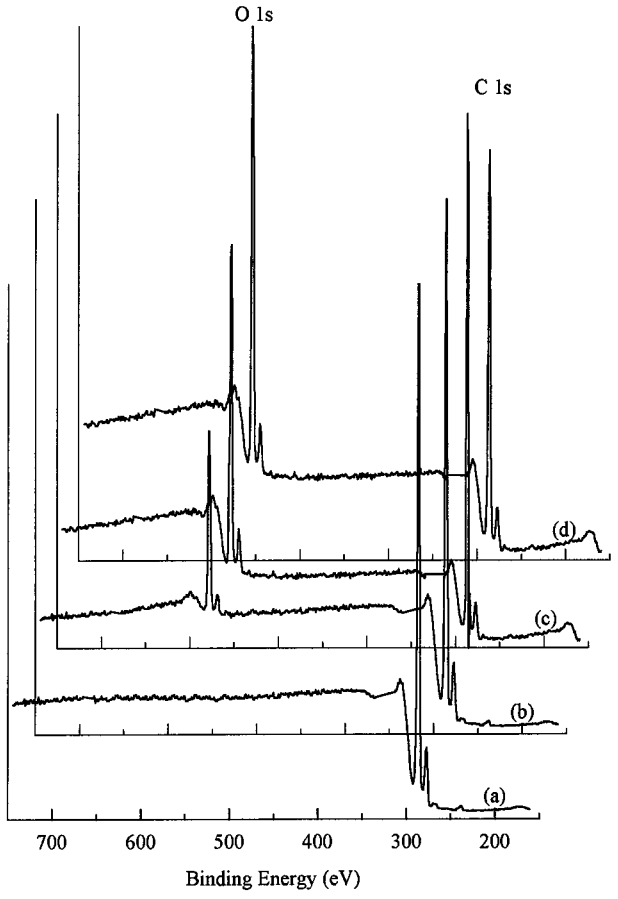

Figure 10 ESCA survey scan spectra of (a) control, (b) 0.03%, (c) 6.66%, and (d) 12.67% of PEO4/5-MA-grafted polyethylene surfaces.

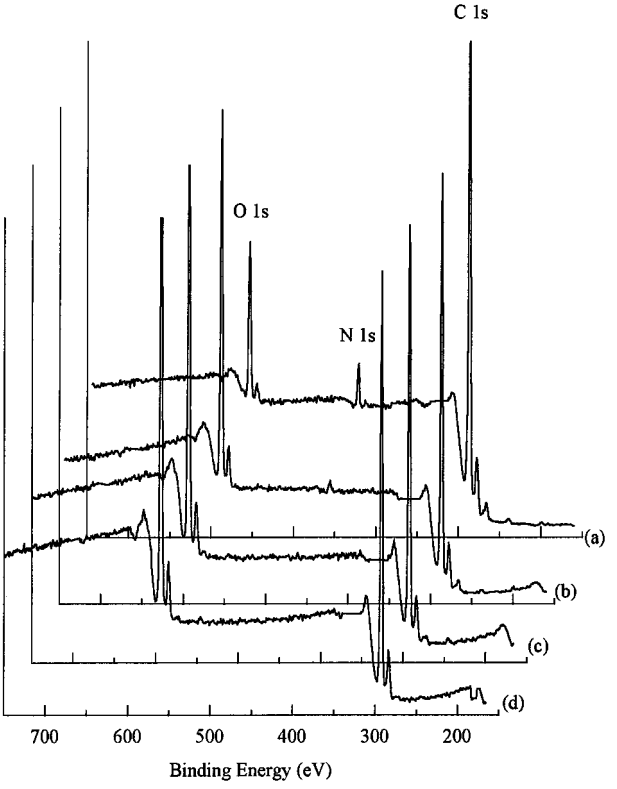

Figure 11 ESCA survey scan spectra of (a) control, (b) 0.03%, (c) 6.66%, and (d) 12.67% of PEO4/5-MA-grafted polyethylene surfaces after plasma protein adsorption.

sults, it could be concluded that grafting layer was produced on polyethylene film surfaces. The atomic percentage calculated from the ESCA survey scan spectra and its ratio is shown in Table II.

Human plasma protein was adsorbed onto control and PEG-MA-grafted polyethylene film surfaces, and the relative adsorbed amount of proteins on the surfaces was evaluated by ESCA. The nitrogen peak from the peptide bonds was used as an indicator of surface protein adsorption. Figure 11 shows an ESCA survey scan spectra of control and PEO4/5-MA-grafted polyethylene after plasma protein adsorption. The nitrogen peak (N-1s : 399.3 eV) from the control polyethylene surface was much

Table II ESCA of Control and PEO4/5-MA-Grafted Polyethylene Film Surfaces

Polyethylene		Atomic %[a] Carbon	Atomic %[a] Oxygen	Ratio[b] —C—O—/—C—C—
	Control	99.998	0.002	0.024
	0.03	70.746	29.254	0.802
Grafting (%)	6.66	68.524	31.476	0.885
	12.67	66.556	33.444	0.942
	15.45	64.790	35.210	0.951

[a] Analyzed from survey scan spectra.
[b] Analyzed from C-1s core-level spectra.

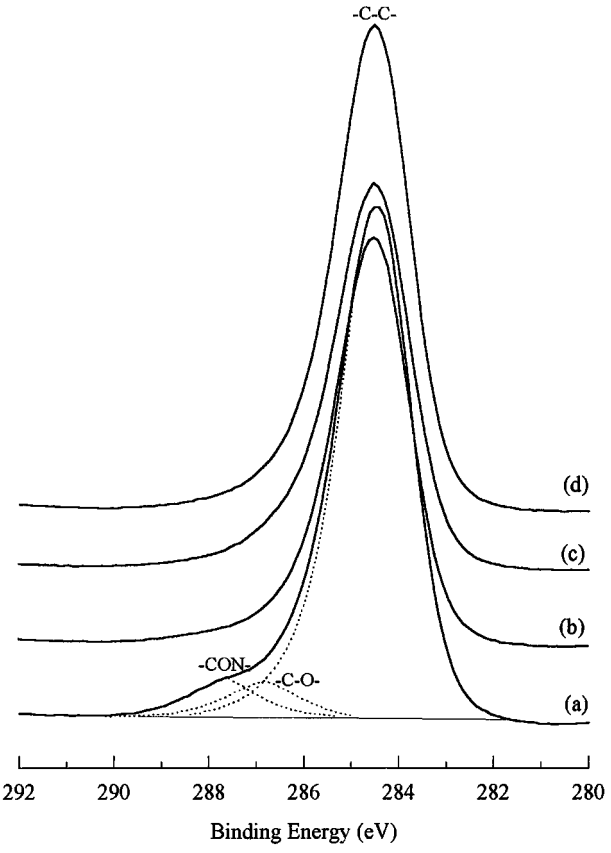

Figure 12 ESCA C-1s core-level spectra of (a) control, (b) 0.03%, (c) 6.66%, and (d) 12.67% of PEO4/5-MA-grafted polyethylene surfaces after plasma protein adsorption.

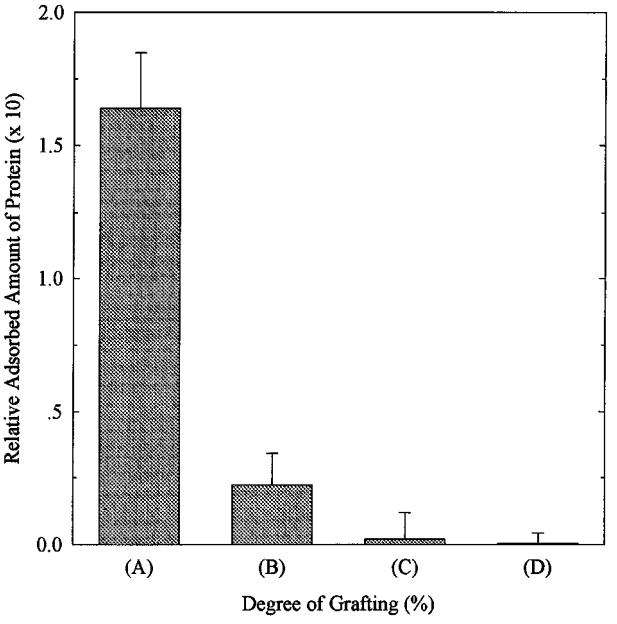

Figure 13 Relative adsorbed amount of plasma proteins on (a) 0.03%, (B) 6.66%, (C) 12.67%, and (D) 15.45% of PEO4/5-MA-grafted polyethylene surfaces.

higher than the PEO4/5-MA-grafted polyethylene surface, indicating the larger amount of protein adsorption on the control surface. It may be explained that this is due to the hydrophobic interaction of protein molecules with the hydrophobic polyethylene film surface. In the case of a PEO4/5-MA-grafted polyethylene surface, the nitrogen peaks decreased with increased grafting yields.

The reason why the PEO chain length increased with the increasing grafting yield can be attributable to the increase in PEO density of the polyethylene surface, that gradually reduced protein adsorption. Figure 12 shows an ESCA survey scan spectra analyzed from C-1s core-level spectra of control and PEO4/5-MA-grafted polyethylene film surfaces after protein adsorption. The atomic percent calculated from this result and its ratio are shown in Table III. Figure 13 compares

Table III ESCA of Control and PEO4/5-MA-Grafted Polyethylene Film Surfaces after Protein Adsorption

Polyethylene		Atomic %[a]			Ratio[b]
		Carbon	Oxygen	Nitrogen	N—C═O/C—O
Grafting (%)	Control	82.082	12.279	5.639	0.943
	0.03	67.290	31.786	0.924	0.212
	6.66	67.054	32.821	0.125	0.103
	12.67	64.788	35.201	0.011	0.054
	15.45	64.088	35.910	0.002	0.021

[a] Analyzed from survey scan spectra.
[b] Analyzed from C-1s core-level spectra.

the relative adsorbed amount of plasma proteins on the PEO4/5-MA-grafted polyethylene surfaces. It was determined as follows:

$$\text{Relative adsorbed amount of proteins} = \frac{\text{N\% of PEG-MA-grafted surface}}{\text{N\% of control surface}}$$

As shown in Figure 13, the polyethylene surfaces showed less protein adsorption with the grafting yield, and the maxima occurred at 15.45% grafting yield.

For the blood antithrombogenicity, 0.5 mL of PPP with 0.1 mL of 0.1*M* calcium chloride was added to the control and PEO4/5-MA-grafted polyethylene sample with the different grafting yields at room temperature. As shown in Figure 14, it was shown that the plasma recalcification time increased rapidly with grafting yields up to 15.45% and then leveled off. This is probably due to the hydrophobic interaction of the protein mol-

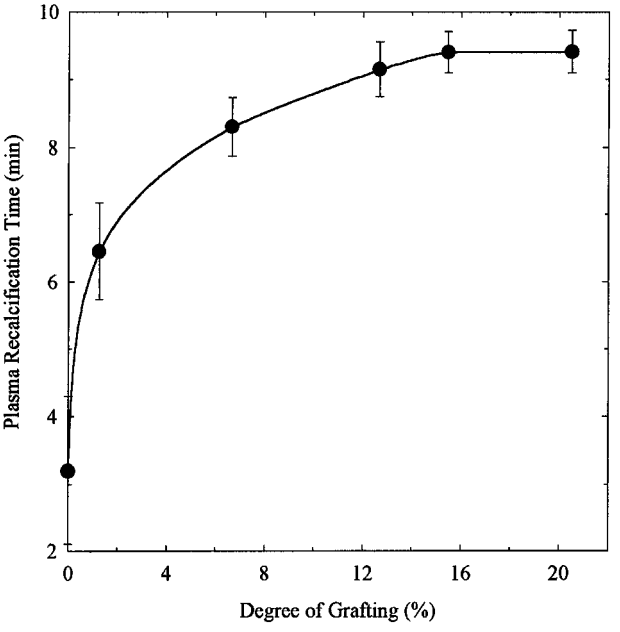

Figure 14 Plasma recalcification time of PEO4/5-MA-grafted polyethylene with the grafting yield.

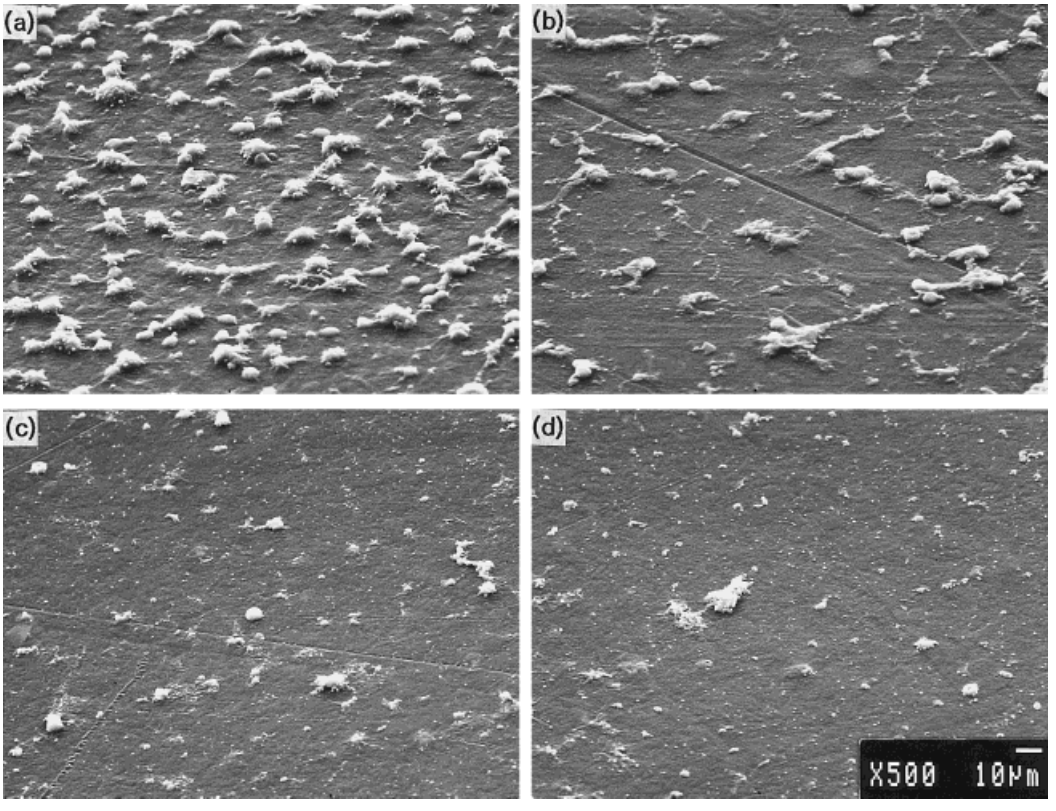

Figure 15 SEM photographs of (a) control, (b) 0.03%, (c) 1.26%, and 6.66% of PEO4/5-MA-grafted polyethylene surfaces after platelet adhesion.

ecules with the PEO chain length on polyethylene film surfaces (as described in Fig. 11).

For the platelets adhered to the polyethylene surfaces, the control and PEG-MA-grafted samples with the grafting yield were observed using SEM. As shown in Figure 15, the platelet adhesion on the polyethylene film surface decreased rapidly with the grafting yield. From these studies, it was found that a PEG-MA-grafted surface has biocompatible properties, such as its low interfacial free energy, hydrophilicity, high surface mobility, and steric stabilization effect.

CONCLUSIONS

In this study, the effects of protein adsorption and platelet adhesion on polyethylene films after being grafted were examined. The extent of grafting was found to be dependent on the storage condition of the irradiated polyethylene film, the preirradiated dose, grafting reaction time and temperature, PEG-MA molecular weight, and grafting solvent type. The grafting yield of the irradiated polyethylene film stored at room temperature and −20°C was decreased with storage time; however, for the irradiated polyethylene film stored at −130°C, the grafting yield was nearly constant up to 20 days after irradiation. The water contact angle of the grafted polyethylene film was lower than that of the ungrafted polyethylene film and decreased with an increased grafting yield due to the hydrophilicity of grafting layer. Human plasma protein was adsorbed onto control and PEG-MA-grafted polyethylene film surfaces, and the relative adsorbed amount of proteins on the surfaces was evaluated by ESCA. The adsorbed protein and platelet adhesion on the polyethylene film surface decreased rapidly with the grafting yield.

REFERENCES

1. Andrade, J. D.; Hlady, V. Adv Polym Sci 1986, 79, 1.
2. Amiji, M.; Park, K. Biomaterials 1992, 13, 682.
3. Ikeda, Y.; Kohinzo, S.; Yamashita, S. J Mater Sci: Mater Med 1991, 2, 110.
4. Brinkman, E.; Poot, A.; Van der Does, L.; Bantjes, A. Biomaterials 1990, 11, 200.
5. Vulic, I.; Okano, T.; Vandergaag, F. J.; Kim, S. W.; Feien, J. J Mater Sci Mater Med 1993, 4, 448.
6. Bergstrom, K.; Osterberg, E.; Holmber, L.; Hoffman, A.; Schuman, T.; Kozlowski, A.; Harris, J. M. J Biomater Sci Polym Ed 1994, 6, 123.
7. Nho, Y. C.; Dworjanyn, P. A.; Garnett, J. L. J Polym Chem: Chem Ed 1992, 30, 1219.
8. Dworjanyn, P. A.; Garnett, J. L. J Polym Chem: Polym Lett 1988, 26, 135.
9. Lee, Y. M.; Shim, J. K. J Appl Polym Sci 1996, 61, 1245.
10. Suzuki, M.; Kishida, A.; Iwata, H.; Ikada, Y. Macromolecules 1986, 19, 1804.
11. Nho, Y. C.; Dworjanyn, P. A.; Garnett, J. L. J Polym Chem: Chem Ed 1993, 31, 1621.
12. Nho, Y. C.; Sugo, T.; Tsuneda, S.; Makuuchi, K. J Appl Polym Sci 1994, 51, 1269.
13. Dworjanyn, P. A.; Garnett, J. L.; Khan, M. A.; Maojun, X.; Qian, M. P.; Nho, Y. C. Rad Phys Chem 1993, 42, 31.
14. Hayashi, K.; Hukumura, H.; Yamamoto, M.; Yamashita, I. Kobunshi Ronbunshu 1987, 44, 681.
15. Songh, D. K.; Ray, A. R. J Appl Polym Sci 1994, 53, 1115.
16. Vroman, L. Blood, Natural History Press, New York, 1967.
17. Mukherjee, A. K.; Gupta, B. D. J Macromol Sci-Chem 1983, A19, 1069.