Polymer Bulletin 36, 503–510 (1996)

Polymer Bulletin

Surface modification of polyethylene film by liquid phase photograft polymerization

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Received: 17 October 1995/Revised version: 11 December 1995/Accepted: 13 December 1995

Summary

The surface modification of low-density polyethylene(PE) by liquid phase photograft polymerization with acrylic acid(AA), acrylamide(AM) and glycidyl methacrylate(GMA) was described. The grafting of AA and AM was proved and characterized by electron spectroscopy for chemical analysis(ESCA). It was found that fully hydrophilic surface can be obtained in very short irradiation time. With ESCA and attenuated total reflection infrared spectroscopy(ATR-IR), it can be confirmed that bifunctional monomer GMA was grafted onto the PE film surface. Through further reaction with GMA grafted film, heparin and protamine were immobilized onto the grafted film surface.

Introduction

Polyethylene(PE) is one of the most widely used synthetic polymers. It exhibits inert and hydrophobic surface. But many of its applications require hydrophilic or functionalized surface property while still retaining its bulk properties. Surface modification of PE has been an attractive problem in recent years. The methods for surface modification include chemical oxidation, corona discharge treatment(1), plasma treatment(2), ozonation(3) and photoinitiated graft polymerization(4-6). Among these methods, photoinitiated graft polymerization is particularly suitable for surface modification due to low cost of equipment, easy control of reaction and thin modified layers on the substrate surface.

Photoinitiated graft of vinyl monomers, such as acrylic acid(AA) and acrylamide (AM), has been shown to give PE with increased surface wettability(4,7,8). In addition, polymer surface property can be further improved by grafting with a bifunctional monomer like glycidyl methacrylate(GMA) and its reacting with a wide variety of different compounds with special properties. An example is polymer in medical use, where a heparin layer on the surface will prevent blood coagulation(antithrombogenicity)(6). In this paper, we will present our results of studies on photograft polymerization of AA, AM and GMA onto PE film, and the immobilization of heparin(an anticoagulant) and protamine(an coagulant(9)). To date no report has been found concerning the immobilization of the latter onto PE film by photografting method.

Experimental

Materials: LDPE films ca. 90μm thickness supplied by Beijing Twelfth Plastic Plant were extracted with acetone for two days before use. AA was free from inhibitor by reduced pressure distillation. AM, benzophone(BP) and acetone used were of grade AR.

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Heparin sodium and protamine sulfate, supplied by Beijing BaiTai Biochemistry Technique Company and American Biorganics respectively, were used as received.

Apparatus: The ultraviolet light source used is a 500W high pressure mercury lamp(GGU-500 Shanghai Yaming Light Bulk Factory). A filter which absorbs ultraviolet radiation with wavelength shorter than 310nm is fixed at the bottom of the reactor as an irradiation window. The photografting device is schematically shown in Figure 1.

Photografting and Immobilization: PE films to be grafted were placed on the bottom of the reactor containing a solution of monomer and 0.2M BP in acetone. After placing a piece of glass onto the sample, the reactor was purged with nitrogen for ten minutes, heated in a water bath, and irradiated through the filter window. After irradiation, the grafted film were extracted with acetone in a soxhlet apparatus to remove monomer, initiator and homopolymer formed during grafting. These samples grafted with AA and AM were washed with hot water for three hours. After that all grafted samples were washed with distilled water and then dried at room temperature overnight. Heparin and protamine were immobilized onto the grafted surface by placing the grafted film in a flask with 50ml H_2O and 2g heparin (or 0.1g protamine), stirring for 24 hours at 40°C. After reaction, the film was washed with distilled water for 24 hours.

Measurements: 1) ESCA measurement: The ESCA spectra were recorded on a ES-300 Spectrometer with a Mg Kα X-ray radiation source.

2) Contact angle measurement: The contact angles to water of the modified samples were measured on a CA-D Contact Angle Goniometer at ambient humidity and temperature. The data of '0 degree' means that water droplets can be spread out thoroughly on the sample surface. It cannot be measured exactly with this goniometer in the region of 0~5 degree.

3) ATR analysis: ATR analysis was performed with an FTIR Spectrophotometer BRUKER IFS 113V.

Results and Discussion

Photografting with Acrylic Acid,Acrylamide

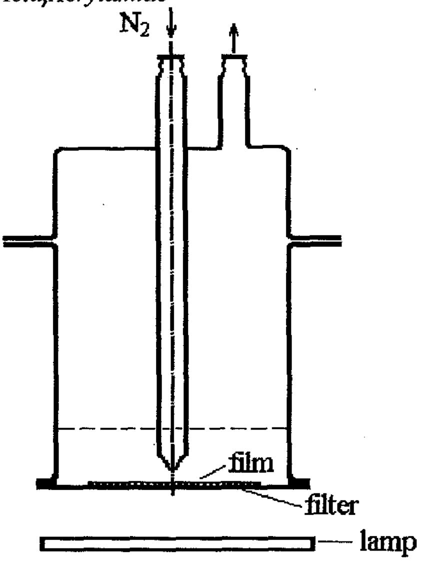

Figure 1 Liquid-phase surface photografting device

Acrylic Acid (AA) and Acrylamide as hydrophilic monomers were photografted onto PE film surfaces to modify their surface hydrophilic property. Detailed chemical information about the outermost layer of the modified PE surfaces was obtained with ESCA spectra. Figure 2 shows the wide scan and C_{1S} peak of ESCA spectra of pure PE and PE grafted with AA and AM. There was a very small peak caused by contamination of pure PE film in the position of O_{1S} peak. As can be seen in the Figure 2, AA and AM were indeed grafted onto the PE film surface. After grafting with AA and AM, wide scan of ESCA measurements on the film surface showed much higher amounts of oxygen, and oxygen and nitrogen,respectively, and the carbon peak of PE film splited into two peaks. For AA grafted film, the binding energy of the left C_{1S} peak is 289ev, which is attributedto the carbon atom with environment of -C(=O)O-. For AM grafted film, the left peak is assigned to C_{1S} 288.2ev (-C(=O)-N). Therefore, it can be further proved that AA and AM were attached to the PE film surface. For polyethylene, its noma l position of carbon atom is at 285.0ev in ESCA spectrum. After graft a monomer with certain electron attractive group on it, a shoulder peak with a higher binding energy must appear beside the normal position, as shown in Figure 3. Theoretically, the intensity of the shoulder peak is proportional to the coverage of grafted polymer onto the surface within certain depth. The area of the shoulder peak over the area of normal C_{1S} peak can be used as a measure of the grafting degree. Taking the accuracy of data process into account, S1 and S2, the area of outmost half parts of the C_{1S} peak respectively, were chosen to calculate the relative grafting degree indicated by R. Then R is equal to S1 over S2.

Figure 4 and 5 show the changes of grafted amount and the corresponding changes of contact angle to water with irradiation time for AA and AM, respectively. As shown in Figure 3, the ratio R in ESCA increased with increasing irradiation time. R reached 0.39 after irradiation for 9 minutes. Since the R of pure poly(acrylic acid) is 0.37, it can be concluded that a full coverage of PE film surface by poly(acrylic acid) can be obtained. The contact angle to water of grafted film surface decreased rapid in the first two minutes of irradiation followed by a slow drop to a pateau value with increasing irradiation time. The two curves of the grafting amount and contact angle showed that the contact angle to

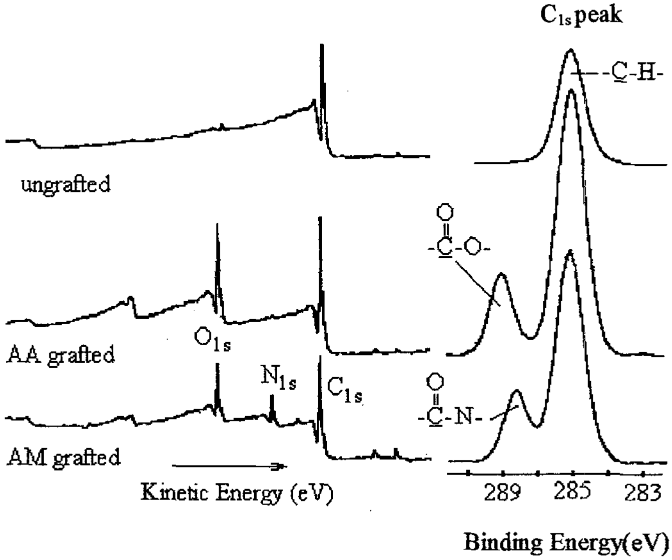

Figure 2 The ESCA spectra of pure PE and PE grafted with AA and AM

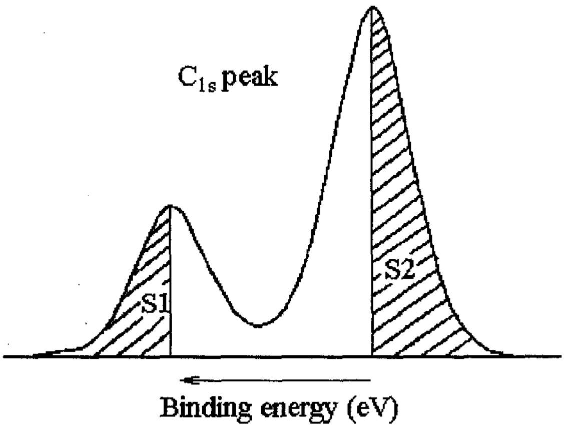

Figure 3 C_{1s} peak of ESCA spectra

water of grafted surface decreased, the hydrophilicity of PE film improved with the increasing grafting amount. Furthermore, the hydrophilicity of PE film can be kept for a long time(such as one year) according to the contact angle measurement since the hydrophilic monomer was attached to the PE film surface through chemical bonding.

In the case of grafting with AM, a similar trend is observed. The graft amount of AM increased and the contact angle to water decreased with increasing irradiation time. In addition, the contact angle after irradiation for 1min, had fallen from 78° to 10°, indicating a substantial modification of the PE film surface which is consistent with the presence of grafted poly(acrylamide). From the results of grafting with AA and AM, it was noticed that in a very short time (2~5 minutes), the remarkable improvement of surfacial hydrophilicity of PE film can be reached. This would be favorable to industry practice of photografting modification.

Photografting with Glycidyl Methacrylate(GMA)

It is well known that the epoxy group can react with a lot of different functional groups. A reactive polymer surface can be formed by introducing such groups onto it.

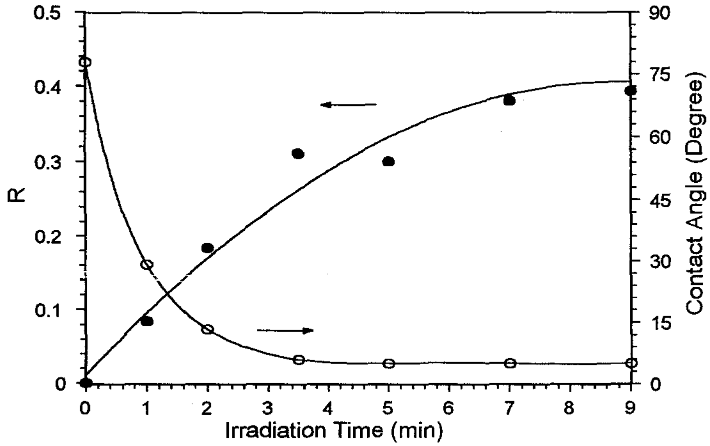

Figure 4 Amount of grafted AA and the contact angle measurements of water at increasing irradiation time

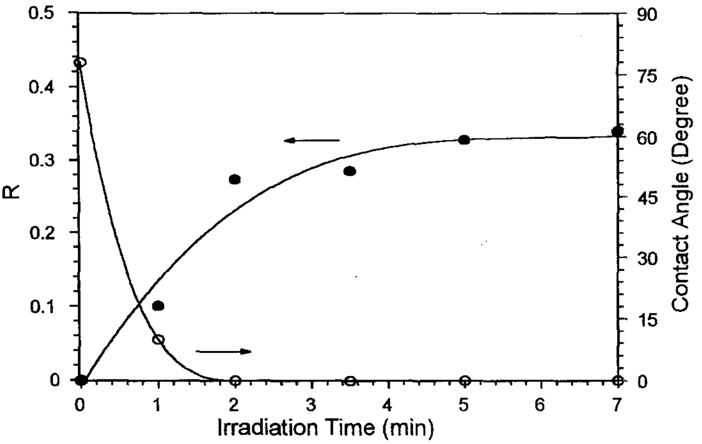

Figure 5 Amount of grafted AM and the contact angle measurements of water at increasing irradiation time

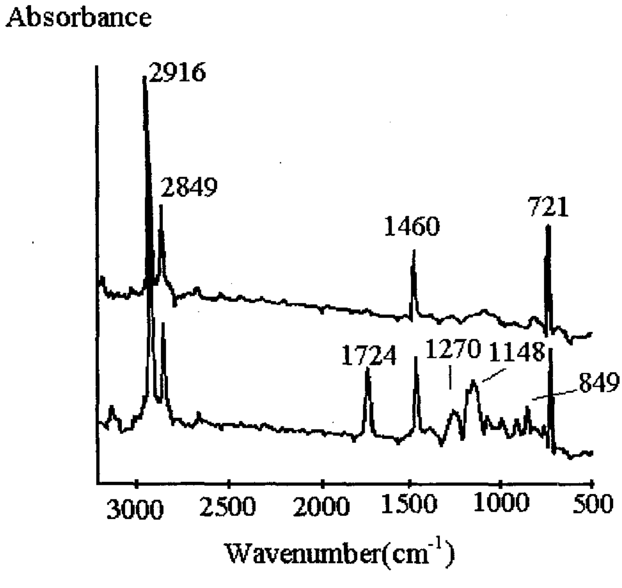

Figure 6 ATR spectra of pure PE and PE grafted with GMA

After some substances are attached to PE surface through reaction with epoxide group, its surface property can be modified furtherly.

The grafting of GMA was confirmed by ATR and ESCA. Figure 6 shows the ATR spectra of pure PE and PE grafted with GMA. As it can be seen, the characteristic bands of glycidyl ethers(1270, 849cm^{-1}) and ester(1724cm^{-1}) appeared in the spectrum of grafted film. The ESCA spectra of pure PE and PE grafted with GMA are displayed in Figure 7. From the wide scan, and C_{1s} and O_{1s} peaks, it can be found that ESCA measurements on the grafted film showed much higher amounts of oxygen. The C_{1s} peak of grafted film have two shoulder peaks in the left of normal carbon peak. As shown in Figure 8, this C_{1s} peak can be resolved by curve fitting with standard peaks$^{(10)}$ into component peaks at binding energies of 285, 286.9 and 289.2eV, corresponding to carbon in $-\underline{C}-H$, $-\underline{C}-O-$,

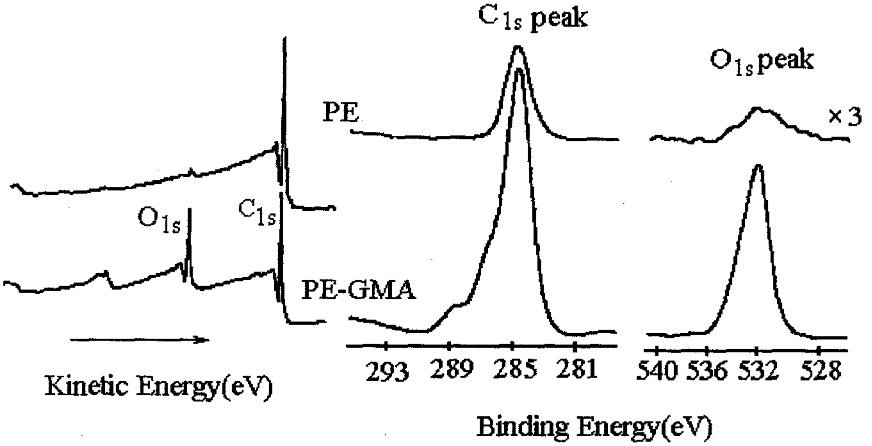

Figure 7 The ESCA spectra of pure PE and PE grafted with GMA

O-$\underline{C}$=O, and the O_{1s} peak can be decomposed into two peaks with binding energies of 532.7 and 534eV respectively. These peaks are assigned as follows: O_{1s} 532.7eV (-C=$\underline{O}$ or -C-$\underline{O}$-) and O_{1s} 534eV(-$\underline{O}$-C=O). Therefore, GMA was indeed grafted onto PE film surface according to the results of ATR and ESCA.

Immobilization of heparin and protamine

Heparin is a polysaccharide and is taken as anticoagulant in medical application. It contains acid, amine and alcohol groups, which can react with epoxy groups. Figure 9 showed that after reaction, traces of sulfur and nitrogen which belong to the characteristic peaks of heparin were detected in ESCA spectra. Heparin was indeed immobilized onto the grafted film surface.

Protamine is a low molecular weight protein rich in lysine, argine and other basic aminoacids. It binds heparin through the electrostatic interaction and neutralizes the anticoagulant activity of heparin in extracorporeal blood circulation. It is desired to immobilize protamine onto the polymer surface to avoid the toxity caused by it and heparin. As can be seen in the ESCA spectrum of Figure 10, protamine was immobilized onto the PE surface. After the reaction with protamine, nitrogen peak which did not present before the reaction with protamine appeared in the ESCA spectra of the grafted film. In one word, biological substance such as heparin and protamine can be attached to the polymer surface for bio-medical use with two-step procedure. The biological activity of immobilized heparin and protamine remains to be investigated.

Conclusion

It was proved by ESCA data that vinyl monomers, such as AA and AM, were surface-photografted onto PE film in solution. The contact angle of the modified surfaces to water decreased remarkably in a very short irradiation time and a fully hydrophilic surface could be obtained.

GMA as a bifunctional monomer was successfully photografted onto PE film surface, as shown by ATR analysis and ESCA measurements. Through the further reaction of GMA with heparin and protamine, heparin and protamine were immobilized onto the grafted film surface. The activity of the immobilized biological substances is subject to further study.

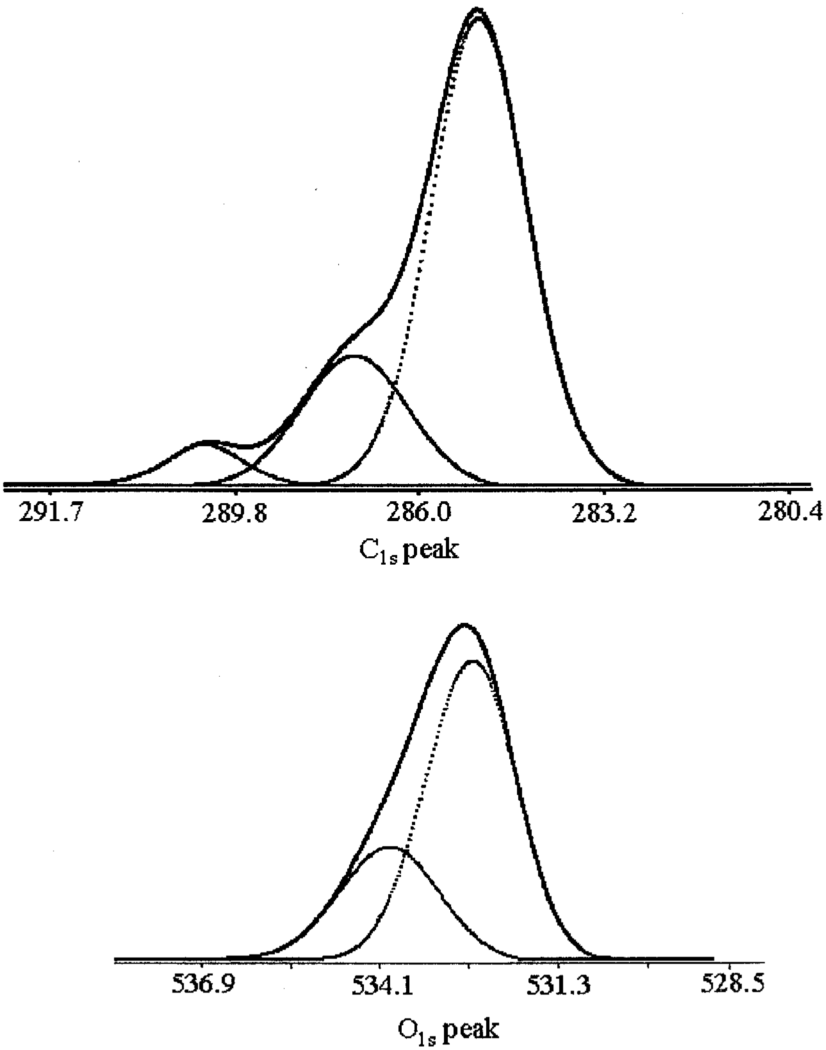

Figure 8 C_{1s} peak and O_{1s} peak of ESCA spectra of PE film grafted with GMA

Acknowledgment

This work was supported by a Fund for Young Scientist from the National Advanced Materials Committee of China (NAMCC). The ESCA analysis was supported by and performed in the United Center of Analysis and Measurement of Zhongguancun Area.

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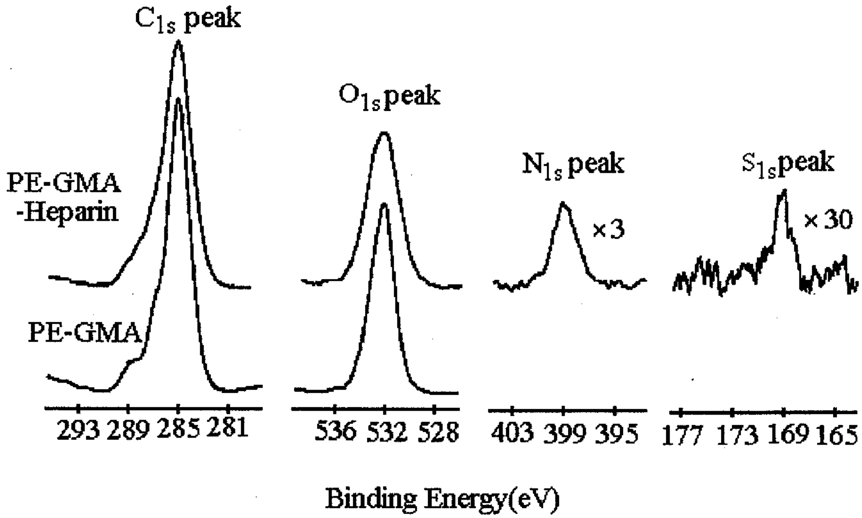

Figure 9 The ESCA spectra of PE grafted with GMA, before and after treatment with heparin

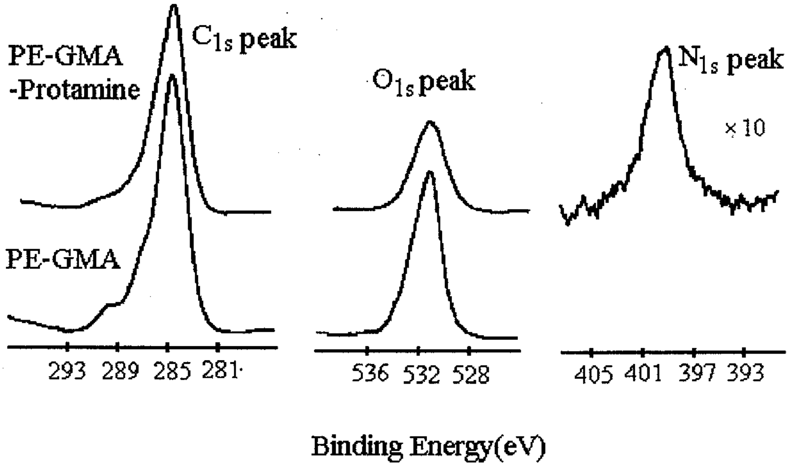

Figure 10 The ESCA spectra of PE grafted with GMA, before and after treatment with protamine

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