

Alanine Grafting of Ion-Beam-Modified Polyethylene

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ABSTRACT: The grafting of a polyethylene (PE) surface layer implanted with 156 keV Xe⁺ ions at fluences of $3 \cdot 10^{13}$ to $1 \cdot 10^{15}$ cm⁻² with alanine was studied with the aim to prepare prospective materials for biological experiments. It was shown by different spectroscopical methods that alanine adds onto double bonds or reacts with radicals created by ion irradiation on the polymer chain. The grafting occurs in the whole ion-damaged polymer layer. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1144–1148, 2000

Key words: ion beam; modification; grafting; alanine; polyethylene.

INTRODUCTION

Polymers find ever-increasing usage in different technological applications, for example, in electronics, optics, and medicine. The surface properties of polymers can be altered, in a controlled way, by irradiation with energetic ions by which polymer electrical conductivity, optical parameters, adhesion, friction, and surface morphology can be affected.¹ The irradiation is accompanied by ionization and excitation of atoms and molecules, which, in turn, lead to the splitting of macromolecules and to the production of free radicals and low mass fragments, some of which can eventually be ejected from the polymer.^{2,3} These processes result in dehydrogenation, production of conjugated double bonds,² macromolecular chain crosslinking, and carbonization, by which new, two- and three-dimensional structures are created.^{2–4}

Thanks to increased free volume and chemical activity, the radiation-modified polymers are exceptionally vulnerable to penetration and incorporation of different agents which may further

modify the polymer properties, for example, electrical conductivity can be affected by introducing suitable donor or acceptor dopants^{5,6} and grafting of the polymer surface with appropriate organics may enhance polymer biocompatibility.^{7,8}

In principle, the grafting of polymers can be accomplished by (a) copolymerization initiated by radiation and/or catalysts, (b) grafting (often radiation-stimulated) onto a modified polymer or copolymer, and (c) grafting onto the sites on the macromolecular chain, which were activated in some way but without radiation. Radiation-initiated copolymerization is a significant well-known method for altering the surface or bulk characteristics of a polymer.⁹ Another possibility of functional-group grafting onto a polymer is a chemical reaction of a doped compound on the polymer's damaged sites (radicals, double bonds) produced by irradiation. In this case, the grafting is realized without further initiation. The latter technique was recently used for the grafting of carboxylic groups onto radiation-modified polyethylene (PE), the biocompatibility of which was studied by an *in vivo* method.¹⁰

It is well known that, in some cases, amino acids increase the biocompatibility of materials. Due to this fact, in this article, the penetration and interaction of alanine with Xe⁺ ion-modified

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PE was studied. Spectroscopic methods were used to find how and to what depth alanine reacts with ion-modified PE film.

EXPERIMENTAL

All the present experiments were performed on 15 μm -thick foils of PE with a molecular weight of $M = 1.8 \times 10^5$ and a density of $\rho = 0.954 \text{ g cm}^{-3}$ (supplied by Chemopetrol, CZ). The foils were irradiated on a Varian 350 D implanter with 156 keV Xe^+ ions at fluences of 3.10^{13} to $1.10^{15} \text{ cm}^{-2}$. According to the calculation with the TRIM (version 91) code,¹¹ the projected range of 156 keV Xe^+ ions in PE should be $R_p = 100 \text{ nm}$. The irradiation was performed at room temperature from both foil sides in order to amplify the optical changes. The ion-beam current density was kept below $50 \mu\text{A m}^{-2}$ to avoid thermal degradation of the samples during the ion implantation. Residual pressure in the implanter target chamber was kept at 10^{-4} Pa . Immediately after the irradiation, a part of the irradiated PE was exposed at room temperature for 12 h to a 2 wt % water solution of alanine [$\text{CH}_3\text{—CH}(\text{NH}_2)\text{—COOH}$]. After doping, the samples were immersed for 2 h in water to rinse out the unbonded alanine and then the samples were dried in a vertical position for 5 h at the temperature of 60°C .

The concentration of conjugated double bonds on the modified PE chain was determined from UV-vis spectra measured using a standard spectrometer.¹⁰ IR spectrometry was carried out using an FTIR spectrometer Nicolet 740. Differential IR spectra were obtained by subtracting the spectra of as-irradiated samples (PE/Xe^+) from those of irradiated and alanine-treated ones ($\text{PE}/\text{Xe}^+/\text{Ala}$). By this procedure, the polymer oxidation by implantation was annulated. The oxygen concentration and its depth profiles in the PE surface layer modified by the ion implantation and chemical doping were determined using a Rutherford backscattering (RBS) technique (2 MeV α -particles, 160° laboratory scattering angle). The concentration of radicals (unpaired electrons) was determined using electron paramagnetic (spin) resonance spectroscopy (EPR) using a Carl-Zeiss device (337 mT magnetic field, 10 mW microwave, room temperature). The number of radicals was determined using the $\text{Mn}^{2+}/\text{ZnS}$ standard.

RESULTS AND DISCUSSION

Ion irradiation leads to dehydrogenation of the PE chain and to production of conjugated double

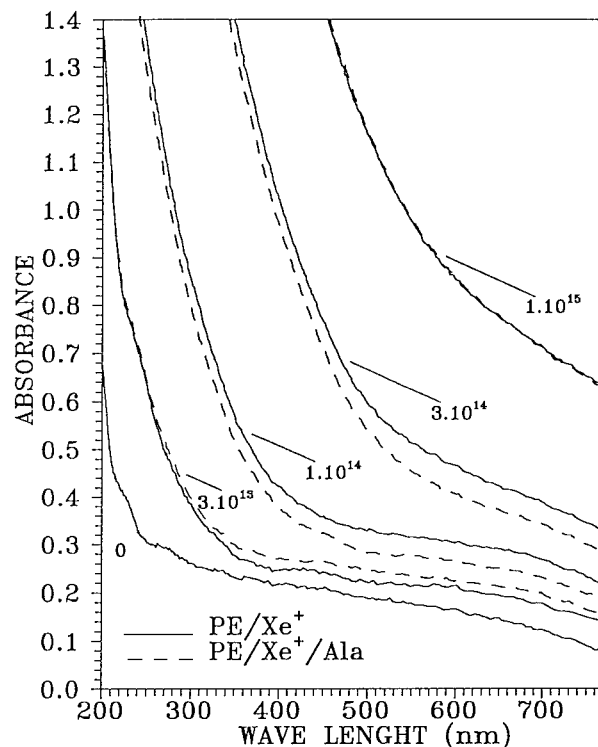


Figure 1 UV-vis spectra of pristine PE and PE, implanted with 156 keV Xe^+ ions at different fluences (PE/Xe^+) and PE implanted and subsequently doped with alanine ($\text{PE}/\text{Xe}^+/\text{Ala}$). The curve numbers indicate the ion fluences in cm^{-2} .

bonds.¹⁰ Their length and concentration can be determined by UV-vis spectroscopy. The UV-vis spectra measured on the as-irradiated PE samples to different ion fluences and the PE samples irradiated and doped with alanine are compared in Figure 1. The irradiation produces conjugated double bonds, of which the concentration and conjugation length are increasing functions of the ion fluence. At the fluences of 1.10^{14} and $3.10^{14} \text{ cm}^{-2}$, the alanine doping results in a significant decrease of the concentration of the conjugated double bonds. The effect is, however, not seen at higher and lower implanted fluences. Decrease of the double-bond concentration after alanine doping is caused by alanine addition onto these bonds. Addition of chlorine onto the double bonds produced by ion implantation in the polymer was already observed earlier in ref. 12.

Structural and compositional changes initiated by ion irradiation and alanine doping were examined by FTIR spectroscopy. Ion irradiation leads to dramatic structural changes of the polymer and creates many reaction products within the

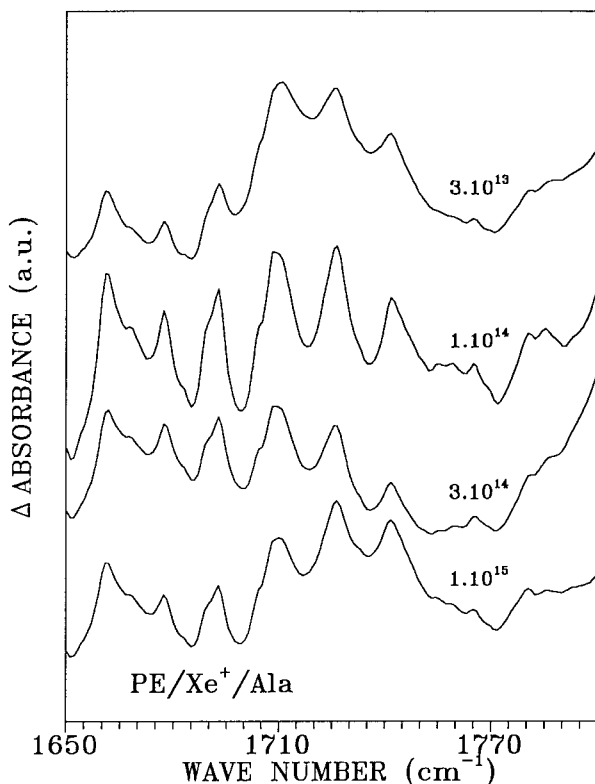


Figure 2 Differential IR spectra in the region of 1650–1800 cm^{-1} obtained by subtracting the IR spectra of as-irradiated PE (PE/Xe⁺) from those of the PE additionally doped with alanine (PE/Xe⁺/Ala). The curve numbers indicate the ion fluences in cm^{-2} .

damaged layer which may eventually be oxidized by ambient oxygen in the implanter.¹⁰

It is seen from Figure 2 that there are pronounced absorption bands in the 1710–1740 cm^{-1} interval, which are characteristic for carbonylic, carboxylic, and esteric groups (e.g., the C=O group from the esteric group absorbs at 1725 cm^{-1}).¹³ One can see that the irradiation to the fluence of $1.10^{14} \text{ cm}^{-2}$ results in the highest concentration of the oxidized structures in PE. It is seen from Figure 3 that the specimen irradiated to the fluence of $1.10^{14} \text{ cm}^{-2}$ exhibits an absorption maximum at 3083 cm^{-1} in the differential spectrum. This maximum is commonly related to the —NH— and/or —NH group in —NH₂. The presence of this group was confirmed also by observation of an absorbance at 540 cm^{-1} . A correlation between Figures 2 and 3 proves the presence of groups characteristic for α -amino acid.

The presence and the concentration depth profile of the incorporated alanine can indirectly be estimated from the oxygen excess in the alanine-

doped samples. The RBS data on the oxygen content in a 600 nm-thick radiation-damaged surface layer of the PE samples irradiated to different fluences are summarized in Table I (left-hand side). The oxygen content in both, as-irradiated and, subsequently, alanine-doped, samples achieves a maximum at the fluence of $1.10^{14} \text{ cm}^{-2}$, and for higher fluences, it declines due to an increasing fraction of crosslinked and carbonized material. These findings are in accord with the FTIR results described above. A significant increase in the oxygen content (by about 40%) after the alanine doping is observed only in the samples irradiated to the fluences of 1.10^{14} and $3.10^{14} \text{ cm}^{-2}$. For lower and higher fluences, no effect is observed (see Table I), probably due to insufficient sensitivity of the RBS method.

An interesting problem is where the alanine is bonded in the radiation-damaged PE layer. From that point of view, the oxygen concentration depth profiles measured by the RBS technique in the PE sample irradiated and the sample subsequently doped with amino acid may be of interest (see Fig. 4). Since the value of $R_p = 100 \text{ nm}$, the profile of

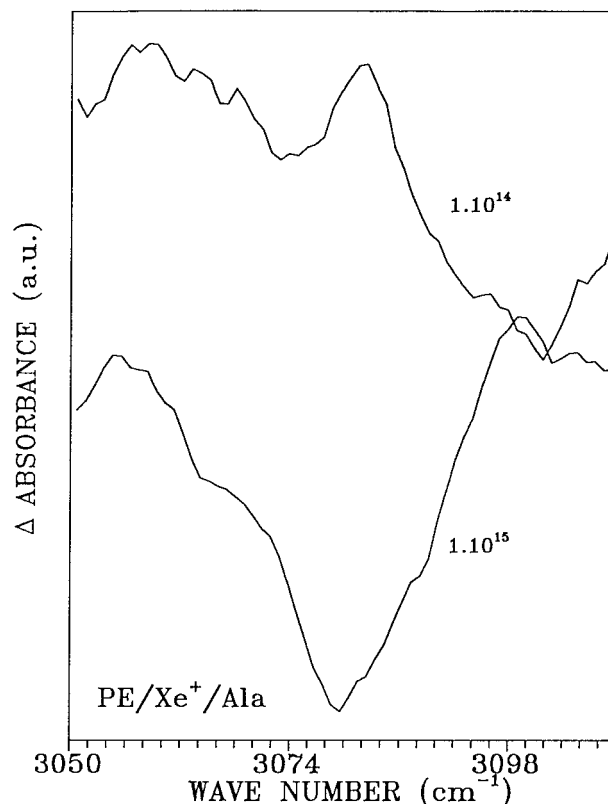


Figure 3 Differential IR spectra as in Figure 2 but in the region of 3050–3110 cm^{-1} .

Table I Dependence of Oxygen Content and Free-Radical Concentration in the PE Surface Layer on the Xe⁺ Ion Fluence

Fluence Xe ⁺ Ions (cm ⁻²)	O Areal Density (× 1.10 ¹⁵ cm ⁻²)		Radical Concentration (× 1.10 ¹⁵ g ⁻¹)	
	PE/Xe ⁺	PE/Xe ⁺ /Ala	PE/Xe ⁺	PE/Xe ⁺ /Ala
3.10 ¹³	63	62	—	—
1.10 ¹⁴	112	145	25.29	5.00
3.10 ¹⁴	75	101	63.71	54.04
1.10 ¹⁵	36	34	618.15	513.45

PE/Xe⁺, As-irradiated Samples; PE/Xe⁺/Ala, Irradiated and Alanine-doped Samples.

incorporated oxygen after irradiation accords with the course of PE damage. It is seen in Figure 4 that alanine is bonded to the whole damaged layer roughly equally. Figure 4 shows the oxygen concentration profile in the sample irradiated at the fluence of 1.10¹⁴ cm⁻², as shown in Table I; after the irradiation at this fluence, the highest oxygen concentration and its highest increase caused by alanine doping was observed by the RBS technique.

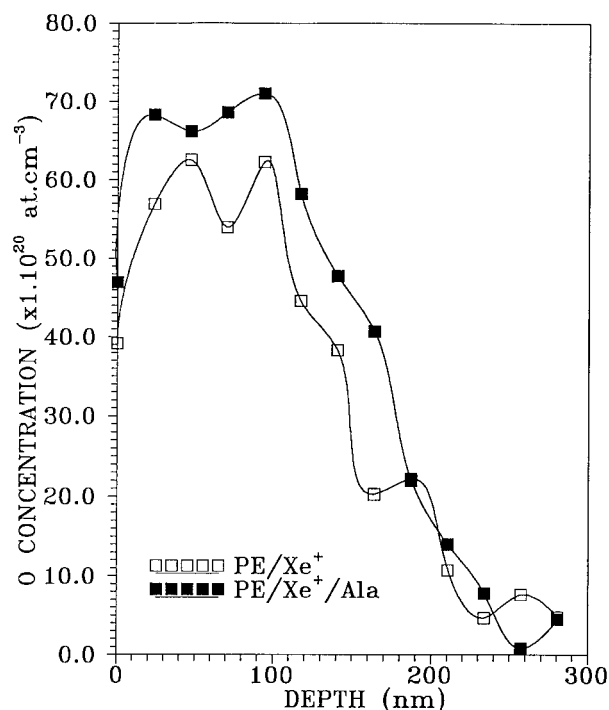


Figure 4 Concentration depth profile of oxygen incorporated into the PE irradiated with Xe⁺ ions at a fluence of 1.10¹⁴ cm⁻² (PE/Xe⁺) and in the PE irradiated at the same fluence and doped with alanine (PE/Xe⁺/Ala).

The dependence of the free-radical concentration in the radiation-damaged layer on the ion fluence is shown in Table I for as-irradiated and, subsequently, alanine-doped samples. With increasing ion fluence, the concentration of free radicals in the ion-modified PE layer increases, as would be expected. The subsequent alanine doping results in a decrease of the number of radicals, which is most pronounced at the fluence of 1.10¹⁴ cm⁻² (the radical concentration at the fluence of 3.10¹³ cm⁻² is below the present EPR sensitivity).

The above results led us to the conclusion that alanine diffuses into the radiation-damaged PE layer, where it is chemically bonded. The resulting alanine depth profile in the layer is roughly homogeneous (see Fig. 4). It is well known that amino acids form ambident ions in water (zwitterions) [CH₃—CH(NH₃⁺)—COO⁻], which are supposed to add especially to double bonds. This hypothesis is in accord with the present results, namely, with the observed decrease of the concentration of conjugated double bonds after the alanine doping (Fig. 1) and the observation of esteric groups in the modified PE (Fig. 2). The radical CH₃—CH(NH[•])—COOH present in the water solution may participate in the alanine bonding in the radiation-modified PE. The limited experimental data obtained in this study, however, are not sufficient for unambiguous identification of the underlying chemical reactions.

CONCLUSIONS

The principal results of this study can be summarized as follows:

- (i) IR spectra proved the presence of oxidized groups and the NH group after alanine doping of modified PE.

- (ii) UV-vis spectroscopy confirmed that alanine adds onto the double bonds.
- (iii) It was observed using EPR spectroscopy that alanine bonds to radicals as well.
- (iv) It was determined by the RBS technique that alanine is bonded to the whole modified PE layer roughly homogeneously.
- (v) Alanine is supposed to bond, above all, to the double bonds (in the form of zwitterions) and on the radicals via the —NH— group.

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