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Solventless Surface Modification of LDPE through Electron Beam Radiation Grafting of 2-Hydroxyethyl Methacrylate

Jalil Morshedian[*1], Mojgan Mirzataheri[2], Rouhollah Bagheri[3], and Mitra Moghadam[3]

(1) Department of plastics; (2) Department of Polymer Science, Iran Polymer & Petrochemical Institute, P.O. Box: 14965/115, Tehran, I.R. Iran
(3) Department of Chemical Engineering, Isfahan University of Technology, Isfahan-84156 I.R. Iran

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ABSTRACT

The electron beam radiation technique has been explored as the latest and most effective means of forming chemically active sites on LDPE surface. In this novel work a solventless grafting of 2-hydroxyethyl methacrylate (HEMA) on to LDPE surface was conducted. Thus prepared active sites were exploited to subsequently solventless graft copolymerization of HEMA onto LDPE by high energy electron beam radiation (10 MeV) at dose range of 10 up to 200 kGy at atmospheric pressure in air. As HEMA could not wet LDPE surface, its synthesized tacky polymer was used for coating and then grafting purposes. LDPE film and sheet surfaces were impregnated with the prepared adhesive and were irradiated. FTIR Spectra showed that the concentration of characteristic bonds of poly(HEMA-*g*-LDPE) (C=O in ester groups, in hydroxyl groups as C-OH, and ether carbon bonds as C-O) increased with increasing irradiation dose, also, the percentage of grafting significantly increased up to 60%. The hydrophilicity of the grafted surface considerably increased compared to that of the ungrafted ones as contact angle measurements showed a 72% decrease. Furthermore, the yields of gel content measurement were investigated and the topology of the surface and cross-section of poly(HEMA-*g*-LDPE) films and sheets was studied by means of SEM. Moreover, the mechanism of achieving up to 70% cross-linked network in solid semi-crystalline LDPE is discussed.

Key Words:
solventless surface grafting;
electron beam;
irradiation;
LDPE;
HEMA.

INTRODUCTION

A great extent of research has been focused on the grafting of hydrophilic monomers onto non-polar polymer surfaces, to improve their biocompatibility, but none of them has been done by electron beam irradiation of HEMA onto LDPE surface in the absence of solvent and additives, as will be reported in this paper.

LDPE is one of the most popular polymer materials with fast growing markets, however its weak mechanical properties at high temperatures as

(*)To whom correspondence should be addressed.
E-mail: J.Morshedian@ippi.ac.ir

well as its inert chemical structure, limit its usage in some applications. But cross-linking and grafting improve its properties and hence its usage. Some surface modification methods have been employed to alter the polymer properties such as flame, corona and plasma treatments, as well as surface grafting [1-5]. Among these methods, surface grafting of selected monomers or polymers has presented better modification of surface nature.

There are several methods of grafting onto the surface of polymers,which are chemical graft polymerization and graft polymerization induced by glow discharge, UV irradiation, and high energy radiation such as x, γ, and β rays [6-12].Among various forms of high energy radiations, electron beam radiation has useful advantages. It is powerful, easily attainable, with high depth electron penetration, wide range of dose rates, and finally high efficiency which is made it appealing, clean, and simple with safe operation [1-3].

Since 1960, HEMA has been widely used for surface graft modification of various polymer substrates, and mostly has been applied for preparing biomedical materials with outstanding biocompatibility and good mechanical properties [13-16]. For instance, Cohn reported grafting of HEMA on LDPE surface in 30% by weight solution at 0.5 Mrad gamma irradiation which was reached a value of 3.13 g/cm^2 grafting [17], while Lei has grafted LDPE surface with HEMA using corona discharge technique, and reported 120 g/cm^2 grafting with 33^o contact angle [4], whereas in present work we managed to obtain 27^o contact angle. Also in grafting of HEMA onto PP film, maximum graft percentage was 18% and minimum degree of contact angle was about 65^o [18].

In this research work, a high energy electron beam (10 MeV) radiation induced grafting of poly(HEMA) onto LDPE film and sheet surfaces was done at doses of 10, 25, 50, 100, 150, and 200 kGy in air without applying solvent or any other chemical additives. Whereas, in all previous works researchers utilized various solvents and chemicals for grafting [19-22]. In this work cross-linking degree, grafting percentage, hydrophilicity and morphology were studied by means of gel content test method, FTIR spectroscopy, contact angle, and scanning electron microscopy, respectively. Not using solvent is a beneficial achievement for environmental protection and cost reduction.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA) with 97% purity was supplied by Merck and used as received. The polymerization initiator, *t*-butyl peroxypivalate, was from Bandar Imam Petrochemical Co. Iran, with 75% purity and kept cool under 5^{o}C until use. The low density polyethylene (LDPE) from Iran Petrochemical Co., grade Lf0200 with d=0.92 g/mL and MFI= 2 g/10 min was used. All washing solvents were reagent grade.

Equipments and Test Methods

Films with thickness of 50 μm were prepared at 130-160^{o}C by film blowing unit of Haake extruder at 45 rpm. Sheets in dimensions of 180 180 2 mm were produced at 150^{o}C under pressure of 170 bars by compression moulding.

10 MeV Electron beam radiation was produced by an electron beam accelerator, Rhodotron TT200, available at Yazd Radiation Processing Centre, Iran (Table 1). Samples were irradiated by irradiation doses of 10, 25, 50, 100, 150, and 200 kGy at room temperature in air. FTIR absorption spectra of the irradiated films were obtained by using a Shimadzu spectrophotometer model 8300. Static contact angle of water on the grafted LDPE surface was measured at 25^{o}C using G10 Kruss contact angle measuring device. Distilled water was used for this measurement and five readings were

Table 1. Rhodotron TT200 electron beam accelerator parameters.

Beam energy	5 and 10 Mev
Beam power at 10 MeV	≅ 70 kW
Beam power at 5 MeV	≅ 35 kW
Energy dispersion at 10 MeV	≅ 300 keV
Scanning range	30-100 cm
Total power consumption	< 300 kW
RF	107.5 MHz
RF power output	200 kW
Electron gun average current	0-10 mA
Resolution	50 μm

averaged.

Surface topography of grafted films and the depth of their grafted layers were studied using Stereoscan electron microscope 360 (SEM) from Cambridge Co., with magnification of 2000.

Grafting Procedure

LDPE film and sheet surfaces were grafted with poly(HEMA) using the electron beam irradiation. This technique can be summarized as follows:

Strips of polyethylene films and sheets were washed with acetone for few minutes and rinsed with distilled water and then dried in oven at 60ºC for some hours and, weighed. Afterwards, their cleaned surface was impregnated with a thin layer of tacky poly(HEMA), which was synthesized by bulk polymerization of HEMA in presence of *t*-butyl peroxypivalate. These prepared samples were directly irradiated by electron beam energy of 10 MeV and exposure doses ranged 10-200 kGy at room temperature in air. Then samples were washed thoroughly in acetone under reflux over a 16 h period in order to remove the ungrafted poly(HEMA) and, followed by drying in a vacuum oven at 50-60ºC for 24 h and weighed again.

Degree of grafting was studied using FTIR analysis, while degree of cross-linking of polyethylene sheets was studied through gel content measurement on extraction by boiling xylene at 140ºC for 16 h according to ASTM D2765-95. For this purpose, three samples were used to determine the average value.

RESULTS AND DISCUSSION

Grafting Degree

Surface modification of LDPE sheet or film by grafting reaction of poly (HEMA) has been demonstrated via FT-IR spectroscopy and contact angle measurements. Moreover SEM investigations have confirmed the grafting reaction of a very tiny amount of polyHEMA onto the surface of polyethylene.

FTIR Absorption spectra of the ungrafted irradiated LDPE and poly(HEMA -grafted-LDPE) films at irradiation dose of 50 kGy are depicted for comparison in Figure 1. The prominent bands of LDPE at 1464,1377, and 719-720 cm^{-1} arising from the -CH_2- group in the PE chain [23], appear almost without modification. The strong absorption at 1725 cm^{-1} (C=O stretching) and the broad multibands at about 1000 to 1300 (sharply at 1150 due to coupling of C-O- stretching and -OH in plane bending) are showed in the spectrum of the poly(HEMA-*g*-LDPE) [4]. This was evident from the LDPE surface that was covered with grafted poly(HEMA).

The intensity absorption at 1464 cm^{-1} due to LDPE decreased and those around 1150, 1725, and 3435 cm^{-1}, due to poly(HEMA) increased as the percentage of HEMA grafting was increased by increasing irradiation doses from 10 to 50 kGy, and that was shown in Figures 2-3.

The effect of irradiation doses on concentrations of ester groups of poly(HEMA-*g*-LDPE) is shown in Figure 4. As shown in this figure the absorption band strength increases with increasing irradiation dose which is the result of increase in grafting.

The absorbance of the ester group(C=O) in stretching mode of poly(HEMA) grafted at 1725 cm^{-1} in FTIR spectrum was used to determine the degree of grafting, which was generally expressed as amount of poly-(HEMA) grafted [4]. So for measuring the graft percentage, the peaks surface ratios were calculated at 1725 and 1464 cm^{-1} that are characteristic bands of poly(HEMA) and LDPE, respectively. These calculations have been plotted versus the radiation doses in Figure 5. It can be seen that the grafting percentage increases with increasing irradiation dose for all the samples, and it reaches a maximum value of 60 % at 200 kGy. The gradual decrease in the slope of the curve

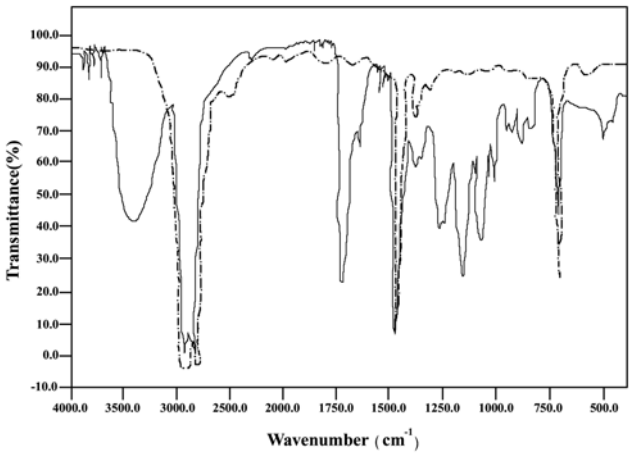

Figure 1. FTIR Spectra of ungrafted irradiated LDPE (dotted curve) and poly (HEMA-*g*-LDPE) (solid curve) films at 50 kGy.

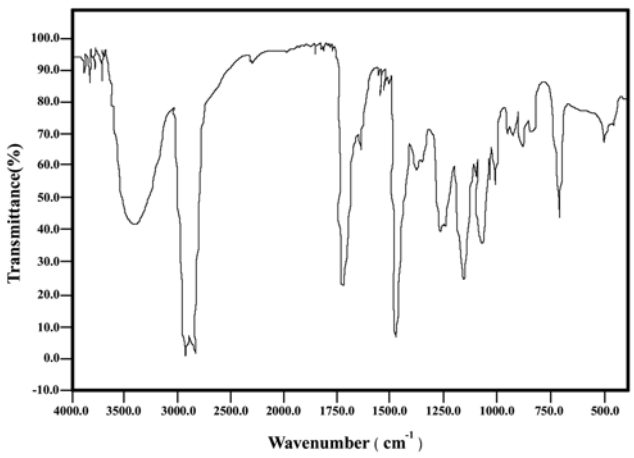

Figure 2. FTIR Spectrum of poly(HEMA-*g*-LDPE) film at 10 kGy.

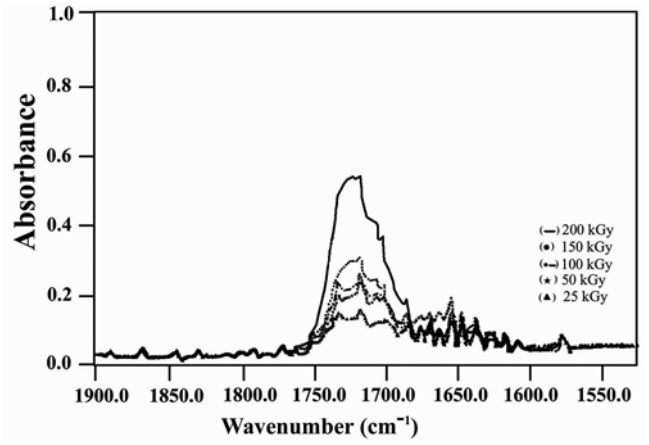

Figure 4. Magnification of ester group absorption in FTIR spectrum of poly(HEMA-*g*-LDPE) at 200, 150, 100, 50, 25 kGy from top to end, respectively.

and leveling off at about 150 kGy could be due to a competition between grafting reaction and breakdown of the part of already grafted poly(HEMA) chain at high irradiation doses.

When LDPE is exposed to high energy electron beam radiation, alkyl radicals are primarily generated throughout its bulk. Then these radicals start to decay by combination reaction of allyl and polyenyl radicals. Oxygen reacts readily with these radicals to form peroxy radicals. So they are converted to peroxides [2]. It is suggested that free radicals on peroxidized LDPE are the most significant initiators for HEMA grafting on LDPE surface [24,25].

It is worth noting that due to a significant difference between solubility parameters of HEMA as a polar molecule and LDPE as an inert non-polar polymer, diffusion and mixing of these materials are not possible. This is the reason why poly(HEMA) is brought in contact with LDPE, immediately segregated droplets of poly(HEMA) are formed on the surface of polyethylene sheet or film due to great interfacial tension between these phases. Grafting of heterogeneous materials has been carried out either by aiding a solvent or impregnating the polymer with great amount of monomer in a closed vessel.

In this work partially polymerized HEMA as a tacky modifier was applied onto the surface of LDPE in films or sheet forms. Thus wetting was achieved by van der Waals forces which existed between polyethylene and poly(HEMA). Still due to a large interaction parameter, diffusion of big molecules of poly(HEMA) into the bulk of polyethylene was not possible. Irradiation could only graft a very thin layer of poly(HEMA) in immediate contact with LDPE surface.

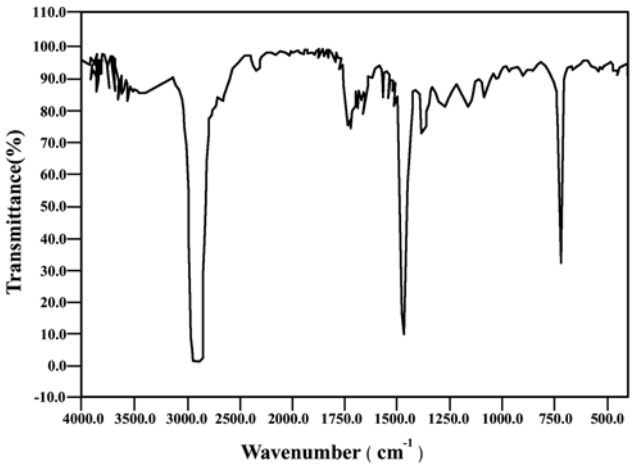

Figure 3. FTIR Spectrum of poly(HEMA-*g*-LDPE) film at 50 kGy.

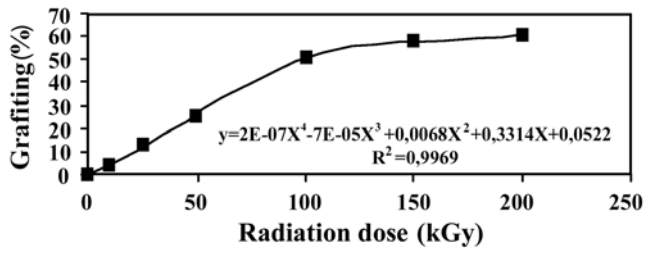

Figure 5. The effect of the irradiation dose on the grafting percentage of poly(HEMA) onto LDPE films (all in same conditions).

Gel Measurement

When poly(HEMA) surface-treated polyethylene sheet or film was exposed to electron beam irradiation, several reactions occurred simultaneously. First of all, polyethylene was cross-linked with a degree, depending on the dosage of irradiation [26].

After irradiation, the bulk of the polyHEMA grafted sheet of cross-linked polyethylene, was used for gel content measurements and its gel content was compared with that of ungrafted cross-linked polyethylene at the same dose. Variations of gel content as a function of irradiation doses for these two samples are shown in Figure 6. It is clear that for both samples gel content increased exponentially with increasing dose and almost levels off at about 150 kGy with 60 to 70% gel content. This type of behaviour was due to governing cross-linking reactions at low doses and severe competition between cross-linking and chain scissioning at higher doses [26]. The bulk gel content of cross-linked polyethylene whose surface was grafted with poly(HEMA) has been found to be slightly higher than the unmodified XLPE at the same doses. This could be accounted to slightly higher heat build up in poly(HEMA) grafted samples which could lead to higher degree of cross-linking. It is worth mentioning that cross-linking via irradiation in solid state occurs merely within the amorphous phase of polyethylene [2, 27].

The previous DSC measurements on this grade of LDPE have shown that its crystallinity was about 50% [28]. Since irradiation is employed at room temperature and the crystalline behaviour is intact, according to above belief, upon gel measurements, all 50% intact crystalline structure must be dissolved in hot xylene. Let us say no gel content above 50% should be obtained, while, 70% gel content for the irradiation of 200 kGy has been observed in this work. This suggests that the crystalline structure is under attack by electron beam and consequently some degree of cross-linking could be occurred in crystalline domain as well.

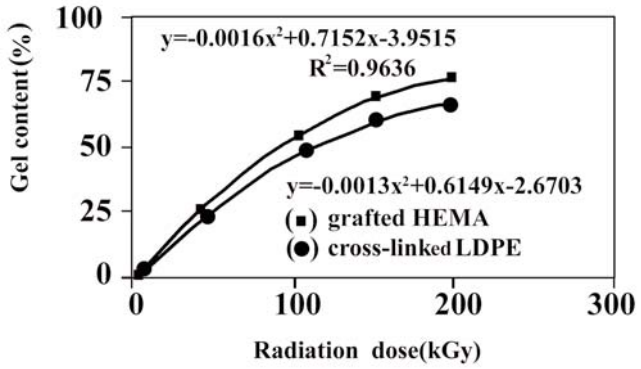

Figure 6. Variation of gel content as a function of the radiation doses for ungrafted crosslinked LDPE and bulk of the surface poly(HEMA-*g*-LDPE) sheet.

Contact Angle (θ)

The measured contact angles (θ) for poly(HEMA-*g*-LDPE) films versus irradiation doses, are shown in Figure 7. It is observed that contact angles decreased with increasing irradiation doses and grafting percentages, respectively. This is indicated that grafting had introduced polarity on prepared samples, so the polar groups of poly(HEMA) on LDPE interacts strongly with water, especially through hydrogen bonding. Therefore, the hydrophilicity of the LDPE film could be remarkably improved by grafting with poly(HEMA) through solventless electron beam grafting, which is more significant with increasing of the degree of grafting.

Scanning Electron Microscopy

SEM Micrographs of samples surfaces before and after grafting are shown in Figures 8 and 9, respectively. It is clear from these figures that LDPE films and sheets surfaces are grafted with a thin layer of poly(HEMA) in the form of a well developed stretched platelet-like circular globules. These continuous and homogeneous grafted phases are scattered onto LDPE surfaces and are increased in both number and size with increasing of the degree of grafting. From these images we could also find the direction of adhesion of tacky poly(HEMA) onto LDPE surfaces. Figure 10 depicts micrograph of cross-section of a modified LDPE sheet surface. Grafting of a thin layer of about 3 micron of poly(HEMA) onto polyethylene surface is clear.

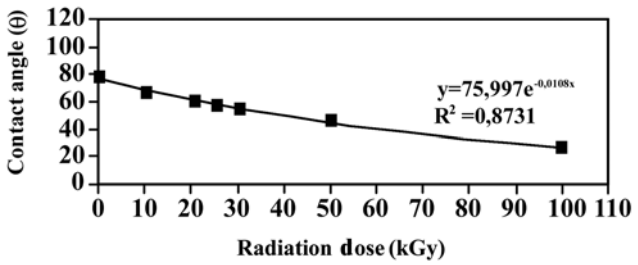

Figure 7. The effect of the irradiation doses on contact angle (θ) of poly(HEMA-*g*-LDPE) films.

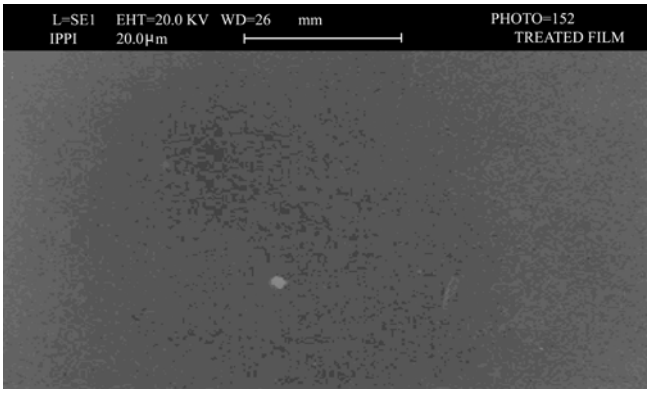

Figure 8. SEM Micrograph of ungrafted LDPE sheet.

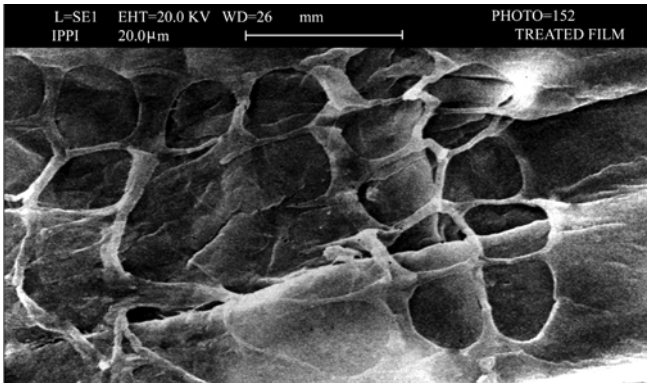

Figure 9. SEM Micrograph of poly(HEMA-*g*-LDPE) sheet at 200 kGy.

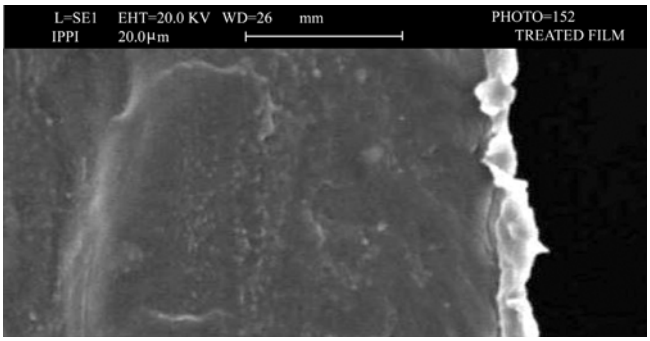

Figure 10. SEM Micrograph of cross sectional poly(HEMA-*g*-LDPE) sheet.

CONCLUSION

The chemically inert surface of LDPE films and sheets can be grafted with poly(HEMA) through electron beam irradiation. We have shown that this surface modification can be done without making use of any solvent or other chemicals, and a thin adhered layer of poly(HEMA) was grafted. To confirm the surface structure of the grafted films, they have been examined by infrared spectrophotometry. After grafting, the spectra show the characteristics bands of both LDPE and poly(HEMA). Several soxhlet extractions did not remove the grafted polymer. Hydrophilicity of poly(HEMA-*g*-LDPE) is remarkably improved, compared to that of ungrafted LDPE. This leads to the conclusion that this grafting as a thin layer is covalently bonded to the surface as is shown in cross-section SEM micrographs. Cross-linking and grafting occurred simultaneously and increased with increasing doses of irradiation and both reached an equilibrium value at higher doses, where 70% gel content and 72% decrease in contact angle were achieved.

Furthermore, it is concluded that cross-linking of LDPE by electron beam irradiation occurs to some extent within its crystalline domain as well.

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