

Maleic Acid Grafting on Low Density Polyethylene

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ABSTRACT: Grafting of maleic acid (MAc) on low density polyethylene (LDPE) was carried out using γ -irradiation technique. Preactivation method was used for grafting and a maximum grafting of 2.4% was obtained. Grafted polymer (LDPE-g-MAc) was characterized by chemical method, Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Thermo-Gravimetric Analysis (TGA), Melt Flow Index (MFI), Tensile Property Measurement, Particle Size Analysis, and Hot Stage Optical Microscopy. Presence of carbonyl peak of high intensity, high acid

value, and low melt flow index value confirmed grafting of MAc on LDPE. A marginal change in thermal and mechanical properties of LDPE was observed after grafting. Change in crystallization behavior of LDPE has been noticed after grafting. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2802–2807, 2004

Key words: polyethylene; graft copolymers; mechanical properties; radiation

INTRODUCTION

Polyethylenes are of high commercial interest due to characteristics such as easy availability, low cost, and a wide range of physical and chemical properties. However, their use in polymer blends of technological interest has been limited due to their typical non-polar character. To overcome this deficiency and to facilitate compatibilization with polar polymers, polyethylenes have been chemically modified through functionalization. This process introduces polar groups onto the polymer main chain as pendant units or short-chain branching.¹ It can be achieved by copolymerization of new monomers or by modification or blending of existing polymers.²

Grafting of preformed polymer is an important method for preparation of polymers with suitable functional groups.³ Grafting involves covalent coupling of species, usually monomers or chain extenders, onto an existing polymer backbone. Reactive sites for grafting can be generated by mechanical processing, by chemical initiation, by photochemical activation (UV-radiation), and by high-energy radiation (electron beam or gamma radiation). Grafting processes may be carried out under simultaneous treatment conditions, with all components being present during creation of reactive sites. Alternatively, grafting can be performed via preactivation process. Reactive sites are generated in the absence of the modifying species, but subsequently exposed to modifying spe-

cies under some predetermined and controlled condition.⁴ Recently, other methods have been developed such as atom transfer radical polymerization (ATRP)^{5,6} or “living” radical polymerization.^{7,8} These methods allow controlling the length of grafts since they act more efficiently on the kinetics of the chain growth.

Maleic anhydride (MAN) is one of the most widely used vinyl monomers for graft modification of polyolefins. It has been grafted to polyethylene by mechanical, free radical, ionic, and radiation techniques.⁹ The reason for use of MAN as monomer for graft modification can be attributed to the chemical reactivity of the anhydride functionality. Rangnathan et al.¹⁰ reported that performance of MAN graft modified polymers in adhesion and compatibilization can be expected to depend on the chemical nature and microstructure of graft. Gaylord and coworkers^{11–13} reported formation of single and oligomeric grafts during grafting of MAN onto polyolefins. In addition to these grafts, bridges consisting of single and oligomeric MAN units between polymer chains were proposed. Formation of free poly(maleic anhydride) was also observed, which could be reduced by using additives that suppressed formation of homopolymer.

Considerable studies have been carried out on MAN^{9–14} grafting of polyethylene, but the authors have not come across any reported work where maleic acid (MAc) has been taken as starting material for grafting on low density polyethylene (LDPE). It is reported¹⁵ that introduction of the highly polar MAc improves adhesion of coatings. Aim of the present work is to introduce polar groups in polyethylene

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matrix by grafting MAC using γ -radiation to avoid the additional step of hydrolysis of MAN to MAC.

EXPERIMENTAL

Materials

LDPE powder obtained from IPCL (Vadodara, India) has a density of 0.93, average particle size of 267 μm , and melting point of 103°C. LDPE powder was sieved in laboratory, and powder having particle size less than 200 μm was used for grafting. MAC monomer used in the study, having 99.5% purity and melting point 136–141°C, was supplied by S. D. Fine Chem (Mumbai, India) and was used as received. Chemical reagents used for titration were of AR grade and used without further purification.

Grafting of MAC on LDPE

LDPE powder of less than 200 μm particle size, 100 g, was exposed under atmospheric conditions at different levels of radiation in γ -radiation chamber using Co-60 as source. Immediately after irradiation, powder was transferred to three-necked flask containing 350 mL aq. MAC solution (10% w/v). The reaction mixture was maintained at 80–90°C for 3½ h under nitrogen atmosphere. Irradiated powders were agitated continuously by using magnetic stirrer. After completion of reaction, the powder was separated by filtration, transferred to hot distilled water, and stirred for about 30 min and filtered. Powder was washed thoroughly with hot water to remove any free MAC. Grafted LDPE powder (LDPE-g-MAC) was dried under reduced pressure at 80°C for 16 h before characterization.

Characterization

Acid value and percent grafting

Acid value and percent grafting were determined by titrating grafted product. 0.5 g of grafted sample was suspended in 25 mL of 0.1N NaOH solution (aq.). Reaction mixture was stirred for 30 min and then it was kept for 24 h. Solid from mixture was removed by filtration. It was washed several times with distilled water and washings were added to filtrate. Unreacted NaOH was determined by titrating the filtrate and blank against 0.1N HCl solution, using phenolphthalein as indicator. Acid value (AV) and percent grafting were calculated using the following equations:

$$\text{Acid value (AV)} = \frac{56.1 \times (V_b - V_s) \times N_{\text{HCl}}}{W} \quad (1)$$

Where V_b : Titer value for blank, ml

V_s : Titer value for sample, ml

N_{HCl} : Normality of hydrochloric acid

W: Weight of the sample

$$\text{Percent grafting} = \frac{E_{\text{MAC}} \times 100}{E_g - E_{\text{MAC}}} \quad (2)$$

Where E_{MAC} = Equivalent weight of MAC

E_g = Equivalent weight of grafted LDPE

Melt flow index

Melt Flow Index measurements were carried out as per ASTM D-1238, using Tinius Olsen Meltflow Indexer (Model MP600; Willow Grove, PA). As melting points of LDPE and LDPE-g-MAC are 103 and 105°C respectively, measurements were carried out at 113°C.

Infrared spectroscopy

LDPE, irradiated LDPE, and grafted LDPE samples were converted into thin films by hot pressing at 130°C and were directly mounted on the frame of spectrophotometer. FTIR spectra of films having identical thickness were recorded by employing a Perkin-Elmer spectrophotometer (Model 1600 series; Beaconsfield, Holland). FTIR spectra were also recorded for LDPE films directly irradiated and grafted.

Thermal properties

Melting points of polymeric powders were determined by using a differential scanning calorimeter (TA Instruments, Model Q 100; New Castle, DE). DSC measurement was carried out with a ramp of 10°C/min maintained during heating scan under nitrogen atmosphere. Cooling scan was performed at a rate of 1°C/min after holding the sample at 110°C for 30 min. Thermal decomposition temperature was studied by Thermo-Gravimetric analyzer (TA Instruments, Model Hi-Res. TGA 2950) at a heating rate of 10°C/min under nitrogen atmosphere to a temperature of 800°C.

Particle size analysis

Particle size analysis was carried out on Mastersizer-2000 of Malvern Instruments (Worcestershire, UK) by dispersing small quantity of powder in aqueous and nonaqueous medium in presence of dispersing agent.

Hot stage microscopy

Crystallization behavior of LDPE and LDPE-g-MAC was studied by taking optical micrographs on a hot

TABLE I
Extent of Maleic Acid Grafting on to LDPE

Radiation dose, kGy	Extent of grafting (± 0.1), wt %
2	0.7
5	1.3
10	1.5
15	1.9
30	2.0
60	2.4
90	2.4

TABLE II
Acid Value and Melt Flow Index of LDPE Samples

Polymer	Acid value, mg of KOH/g	Melt Flow Index g / 10 min (113 °C, 2.16 kg)
LDPE	0.6	2.633
Irradiated LDPE, Dose 30 kGy	0.6	1.710
LDPE-g-MAC, Dose 30 kGy	23.0	1.096

stage microscope (Leica Model DMLD; Beaconsfield, Holland). In this experiment, samples were heated from room temperature to 130°C at a heating rate of 20°C/min to get clear melt. Cooling scan was performed at a rate of 5°C/min after holding the sample at 130°C for 2 min. Cooling was continued until a temperature of 107°C was reached, and the sample was maintained at this temperature for 10 min to facilitate the crystal growth. After this temperature no change in crystallization was observed.

WAXS analysis

The WAXS measurement was done by X-ray wide angle goniometer (M/S Philips, Holland) at 50kV, 120mA using the scan range of 5–35°. The samples were prepared by melting followed by controlled cooling at 1°/min.

Mechanical properties

Tensile strengths of LDPE and LDPE-g-MAC films were determined using a Universal Tensile Testing instrument (INSTRON Model 1123; Buckinghamshire, UK) as per ASTM standard.¹⁶ The free films were prepared by hot pressing LDPE and LDPE-g-MAC at 130°C. For each radiation level, ten samples were

tested and average of five maximum values have been reported as tensile strength.

RESULTS AND DISCUSSION

Due to irradiation, free radicals are generated in LDPE powders.^{4,17} Some of the radicals present in powders participate in grafting on LDPE. In this study, an attempt was made to graft MAC directly to avoid the additional step of hydrolysis of MAN to MAC as done in conventional methods.^{9–14} LDPE-g-MAC thus obtained was characterized by various techniques.

Table I shows variation in percent grafting at different radiation doses. As expected, extent of grafting increased with radiation dose. Grafting of 2.4 weight % was observed for 60 kGy dose and no further increase in extent of grafting was observed with increase in radiation dose. Percent grafting is very low compared to other monomers. This is due to low homopolymerizability of MAC.

Figure 1 shows FTIR spectrum of LDPE, irradiated LDPE, and LDPE-g-MAC. LDPE (spectrum a) has very small peak at 1714 cm^{-1} corresponding to carboxyl group. Irradiated LDPE (spectrum b) and LDPE-g-MAC (spectrum c) have sharp peaks at 1714 cm^{-1} indicating presence of carboxyl group. However, intensity of peak for LDPE-g-MAC is higher compared to

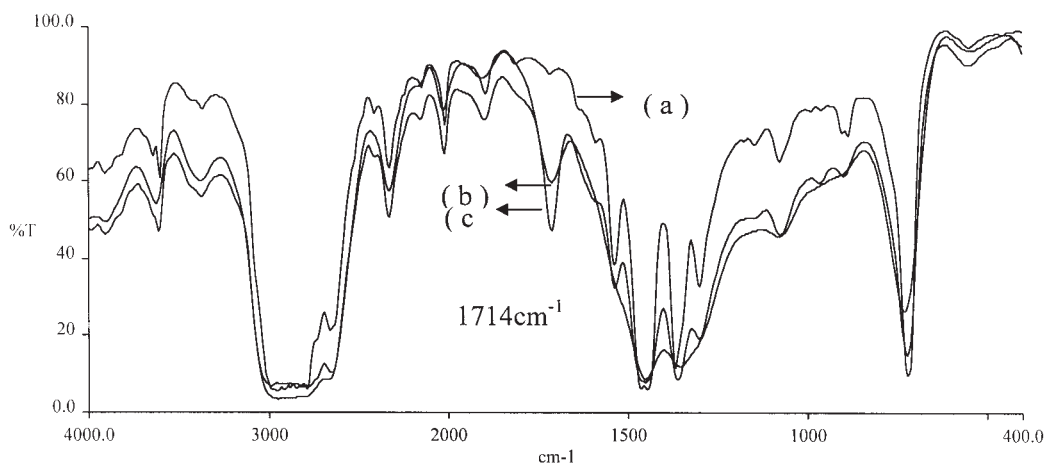


Figure 1 FTIR spectra of (a) LDPE; (b) irradiated LDPE, Dose 30 kGy; and (c) LDPE-g-MAC, Dose 30 kGy.

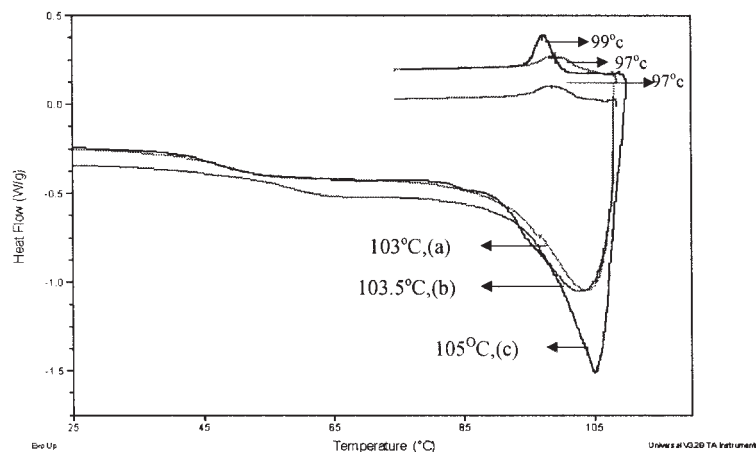


Figure 2 DSC curves of (a) LDPE; (b) irradiated LDPE, Dose 30 kGy; and (c) LDPE-g-MAC, Dose 30 kGy.

that of irradiated LDPE. It has been reported in literature¹⁸ that exposure of LDPE to γ -radiation in air leads to formation of carbonyl groups due to oxidation.

To ascertain the observation that peak appearing at 1714 cm^{-1} in spectrum of LDPE-g-MAC is due to grafting of MAC, acid values of LDPE, irradiated LDPE, and LDPE-g-MAC were determined. Higher acid value of LDPE-g-MAC (Table II) compared to LDPE and irradiated LDPE indicated grafting of MAC onto LDPE. Lower value of melt flow index (MFI) (Table II) for LDPE-g-MAC can be attributed primarily to hydrogen bonding due to presence of grafted MAC units. Increase in molecular weight cannot be ruled out in this case.

DSC curves in Figure 2 show melting points of LDPE and LDPE-g-MAC at 103°C and 105°C , respectively. This change in melting point after grafting can be attributed to presence of polar carboxyl groups. However, the effect is small as the grafting level is

very low. Cooling thermogram shows crystallization peak for LDPE at 97°C , whereas for LDPE-g-MAC, peak appeared at 99°C . The downward shift of crystallization peak for LDPE-g-MAC can be attributed to hindrance by polar groups generated due to grafting of MAC. However, the effect is very small due to very low concentration of MAC in grafted LDPE chains. To verify the effect of irradiation, LDPE was exposed to γ -radiation in identical conditions. The cooling thermogram of irradiated LDPE shows crystallization peak at 97°C , which is the same as that for LDPE. Similarly, the melting point of irradiated LDPE was also found to be close to LDPE. Since the radiation dose of 30 kGy is not very high, the effect of irradiation on melting point and crystallization behavior of LDPE is at minimum level.

Figure 3 shows TGA thermogram of LDPE and LDPE-g-MAC. Initial decomposition temperature (IDT) of LDPE is observed to be at 411°C , whereas that of LDPE-g-MAC is seen at 410°C . It shows there is not much effect

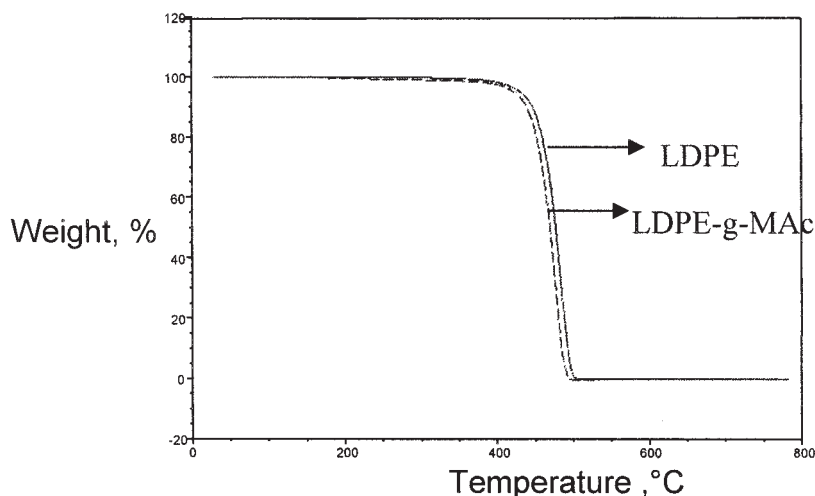


Figure 3 TGA curves of LDPE and LDPE-g-MAC, Dose 30 kGy.

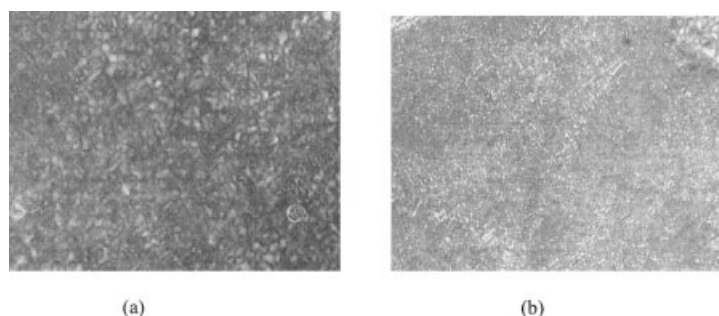


Figure 4 Hot stage optical micrographs of (a) LDPE; and (b) LDPE-g-MAC, Dose 30 kGy (400 X).

in degradation behavior of LDPE due to grafting by MAC. Low grafting is not expected to change much of the thermal degradation behavior.

Particle size analysis carried out in aqueous medium shows increase in size of LDPE from $187\mu\text{m}$ to $192\mu\text{m}$ after grafting. This increase in particle size is mainly due to presence of polar COOH group on the surface, which leads to swelling of the grafted material in aqueous medium. This increase in particle size was not observed when analysis was carried out in non-aqueous medium.

Crystallization behavior of LDPE and LDPE-g-MAC can be seen in optical micrographs presented in Figure 4 (a) and (b). The samples were annealed at temperature above melting point before commencing cooling scan. Slow cooling enabled crystallization of both samples. It can be seen that the crystal growth in LDPE sample at 107°C is quite prominent and crystal size is also good. In the case of LDPE-g-MAC, there is crystal growth at the same temperature. However, the crystal size is very small compared to LDPE. This may be due to reduced stacking in the case of LDPE-g-MAC. It is

obvious that presence of MAC has induced some hydrogen bonding in grafted LDPE and due to this reason only fine crystals resulted. The hindrance due to MAC has also been observed in DSC study.

Figure 5 shows the WAXS spectra for LDPE as well as LDPE-g-MAC samples. It can be seen that the peak intensity of LDPE-g-MAC is lower than that of LDPE. The crystal size calculated from these spectra are 14.8 nm for LDPE and 12.8 nm for LDPE-g-MAC, respectively.

Tensile strength of LDPE and LDPE-g-MAC, at different radiation levels, are presented in Figure 6. It is observed that there is not much change in tensile strength of LDPE, before and after grafting, because the grafting level is very small. Further, there is no appreciable degradation of LDPE due to radiation exposure.

CONCLUSION

MAC was grafted to LDPE by preactivation method using γ -radiation. The dose was varied to achieve

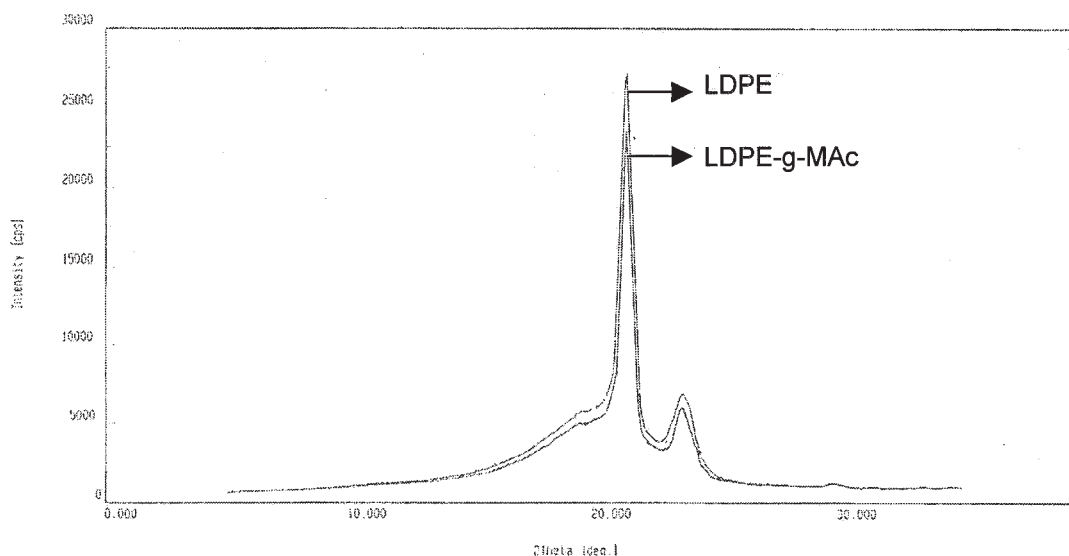


Figure 5 WAXS spectra of LDPE and LDPE-g-MAC, Dose 30 kGy.

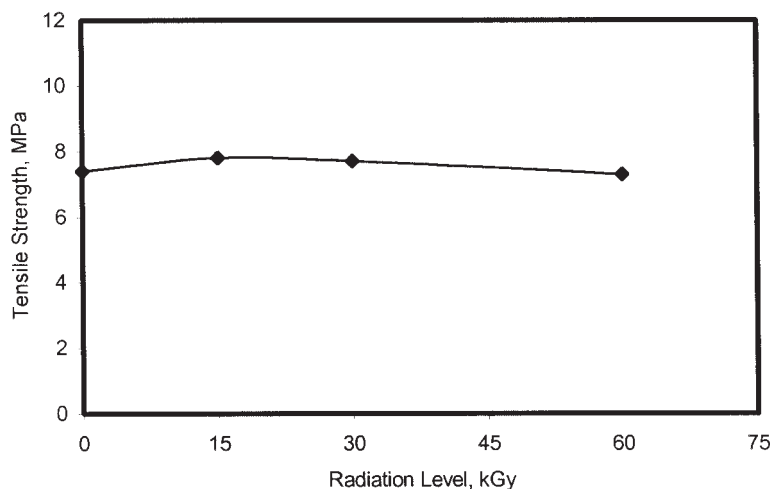


Figure 6 Tensile Strength of LDPE-g-MAc with varying radiation doses.

different levels of grafting. Maximum grafting of 2.4% was achieved at 60 kGy dose. Grafted LDPE has shown modified properties compared to LDPE. FTIR has shown generation of carboxyl group in grafted LDPE, which led to an acid value of 23. Grafting has not affected thermal and mechanical properties of LDPE to an appreciable extent. However, a noticeable change in crystallization behavior has been observed after grafting. Reduced crystalline growth of grafted mass was observed in optical microscope, and size of LDPE-g-MAc obtained from WAXS spectra is 12.8 nm as compared to 14.8 nm for LDPE.

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