Comparative Ozonization of LDPE and HDPE and Grafting of Some Monomers to Elaborate New Ion Exchange Membranes

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ABSTRACT: A comparative study of the ozonization of low density polyethylene (LDPE) and high density polyethylene (HDPE) was carried out. A grafting study of acrylic acid (AA), *N*,*N*-dimethylamino-2-ethylmethacrylate (MADAME) and vinyl phosphonic acid (VPA) on LDPE and HDPE was performed in mass and solution. The ozonized polyethylene and the grafting polymers were characterized by IR spectroscopy and elementary analysis. Ion exchange membranes were prepared from grafted copolymers and characterized by the exchange capacity and electrical resistance. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4423–4429, 2006

Key words: ozonization; LDPE; HDPE; grafting; copolymers; membranes; characterization

INTRODUCTION

Recent technological improvements in the manufacture of ion exchange membranes (IEM) have led to the many practical applications of these membranes in industry. The IEM, which was conceived for brackish water desalting, now has many further applications.

These membranes may be prepared in several ways—by chemical, photochemical, radiochemical, and mechanical techniques.[1–9] Ozonization grafting is one of the most suitable methods. This technique has the advantage with respect to oxidation by atmospheric oxygen, of yielding relatively stable peroxide groups that are used to graft monomers for subsequent polymerization.

Ozonization is an interesting way to prepare graft copolymers, having been developed for many years for different applications, such as semipermeable membranes, adhesion promoters, emulsifying agents, biomaterials, compatibilizers of copolymers, and textile fiber modifications.[10–18]

In this work, a comparative study of the ozonization of low density polyethylene (LDPE) and high density polyethylene (HDPE) was carried out, to synthesize IEM having good physicochemical properties. The synthesis has been realized by the ozone activation of LDPE and HDPE followed by mass grafting or grafting in solution of some monomers.

While, acrylic acid (AA) and *N*,*N*-dimethylamino-2-ethylmethacrylate (MADAME) have been mainly used as monomers to obtain IEM by ozonization of polyethylene (PE), a few studies on the grafting of vinyl-phosphonic acid (VPA) onto ozonized PE have been reported.[17]

EXPERIMENTAL

Ozonization of LDPE and HDPE

Fifty grams of polyethylene (PE), low-density powdered polyethylene (LDPE) and high-density powdered polyethylene (HDPE) were ozonized separately in a fluidized bed at 50°C for 1 h. The ozone was generated using a standard ozone generator (Trailigaz-type). The oxidation was started by bubbling the O_3/O_2 gas mixture through the PE. The ozone power generator was fixed at 300 W and the air/ozone gas flow to 700 L/h.

Titration of the ozonized LDPE and HDPE by 2,2-diphenyl-1-picrylhydrazyl

The peroxides and hydroperoxides titration by 2,2-diphenyl-1-picrylhydrazyl (DPPH) have been already

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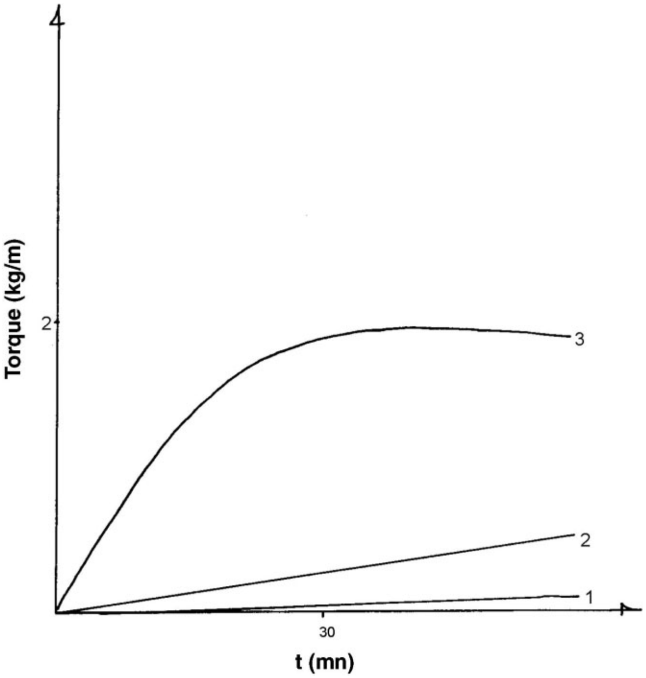

Figure 1 Torque evolution of mixture versus time. Nonozonized HDPE + AA (1), ozonized HDPE (2), ozonized HDPE + AA (3).

described in another study.[11] A predetermined amount of ozonized PE (LDPE or HDPE) is introduced into a container connected with an argon entry and containing the DPPH solution in xylene. After oxygen elimination and heating at 110°C, the DPPH excess is titrated by colorimetry at 520 nm.

Grafting and characterization of copolymers

Mass grafting

Copolymerization was carried out by mass grafting (MG) into a mixing apparatus (Brabender type). We proceeded to a separate grafting of acrylic acid (AA), *N*,*N*-dimethylamino-2-ethylmethacrylate (MADAME) and vinyl-phosphonic acid (VPA) on the ozonized PE (LDPE or HDPE).

The PE was preliminary swollen in the monomer for 1 h. Fifty grams was then introduced into a batch mixer cell preheated to 110°C for AA and MADAME and to 140°C for VPA. The torque was recorded, indicating the evolution of the reaction. The change of the torque (Fig. 1) observed in the case of ozonized swollen PE indicates a large variation of the rheological properties of the product and consequently the formation of the copolymer.

After copolymerization, the product was recovered, pulverized, and precipitated by a solvent of the homopolymer and nonsolvent of the grafted copolymer to eliminate the homopolymer and unreacted monomer. The solvents used for polyacrylic acid, polyvinyl phosphonic acid and MADAME are water, methanol, and acetone, respectively. Then the copolymer was dried at 50°C for 24 h.

Grafting in solution

The grafting in solution (GS) was particularly used in the case of VPA copolymerized with AA or acrylonitrile (AN) on the ozonized PE.

A predetermined amount of PE (LDPE or HDPE) was introduced into the reactor together with a mixture of monomers and solvent. Nitrogen as inert gas was passed through the solution to remove oxygen. Then the reactor was sealed and transferred to a waterbath at a predetermined temperature. The grafted copolymers were treated with water, acetone, and ether to remove homopolymers and unreacted monomers.

Determination of grafting rates

The grafting rates of AA and VPA were determined by elementary analysis of oxygen, and that of MADAME by elementary analysis of nitrogen.

The grafting rate was also estimated in the case of VPA from the infrared spectrum determined by a 510P Nicolet FTIR spectrophotometer. The height ratio of the characteristic band of VPA (P—OH) and of the PE (CH2) leads to the grafting rate.

Preparation and characterization of membranes

The cation and anion exchange membranes were prepared by pressing a known amount of copolymer between two metallic blocks of a press preheated at 150°C.

Before measurement, pretreatment was carried out to remove impurities from the membrane phase. Membranes were immersed in aqueous hydrochloric acid or aqueous sodium hydroxide (1 h), distilled water (2 h), and aqueous sodium hydroxide or hydrochloric acid (1 h) at room temperature.

Exchange capacities of the cation and anion exchange membranes were determined by pH titration.[19]

The electrical resistance of the membrane equilibrated with a solution of NaCl was measured using a Rhone-Poulenc clip cell.[20] The electrodes were platinized-platinum discs. The solution into which the clip cell dips was carefully thermostated. The membrane resistance is the difference between the measured values of the electrical resistance with the membrane and without it.

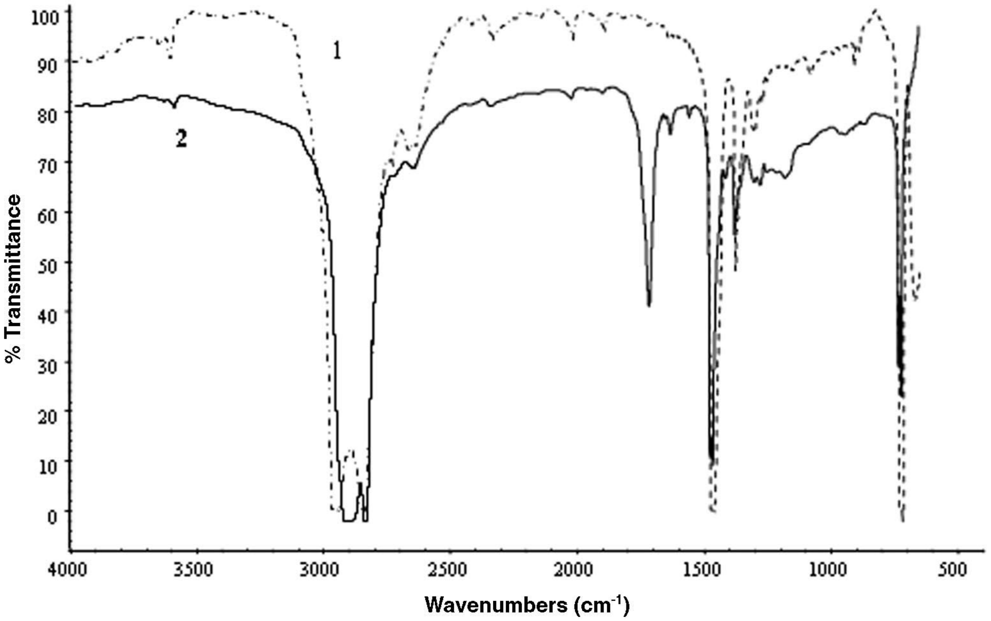

Figure 2 IR Spectrum of nonozonized (1) and ozonized LDPE (2).

RESULTS AND DISCUSSION

Ozonization and titration of peroxides and hydroperoxides of the ozonized LDPE and HDPE by DPPH

Activation of PE (LDPE or HDPE) was produced by a reaction of ozone onto the powdered PE in a fluidized bed-heated reactor.

Experimental conditions have been optimized in another study.[11] The ozonization of polymers is well known and usually leads to the formation of peroxides and hydroperoxides functions on the polymer backbone, according to the reactions proposed by Kefelli et al.:[21]

$$RH + O_3 \rightarrow ROO^{\cdot} + HO^{\cdot}$$

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$$

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$$

$$ROO^{\cdot} + R^{\cdot} \rightarrow ROOR$$

The analysis of ozonized PE (LDPE and HDPE) by IR spectroscopy shows a large band at 1720 cm^{-1} (C=O) which does not exist in the IR spectrum of nonozonized LDPE (Fig. 2) and HDPE (Fig. 3). This band is more important in the case of LDPE than for HDPE because of its high crystallinity.

The titration of the ozonized PE was carried out by DPPH. DPPH is a stable radical which can react with radicals coming from the thermal decomposition of the ozonized LDPE or HDPE. The amount of reacted DPPH with peroxides and hydroperoxides is given by the following formula:[11]

$$N_o = \frac{(\mathrm{Abs}_0 - \mathrm{Abs}_1)V}{m\varepsilon 1000} \qquad (11)$$

where ε is 1.06.10^4 mol^{-1} l cm^{-1} calculated from the standardized curve, m the weight (g) of ozonized PE (LDPE or HDPE) added to the DPPH solution, V the volume of the DPPH solution, Abs$_0$ the absorbance of DPPH without ozonized LDPE or HDPE, Abs$_1$ the absorbance of the DPPH solution with ozonized LDPE or HDPE, and N_o is given in mol equivalent per gram of the ozonized LDPE or HDPE. The amount of per-

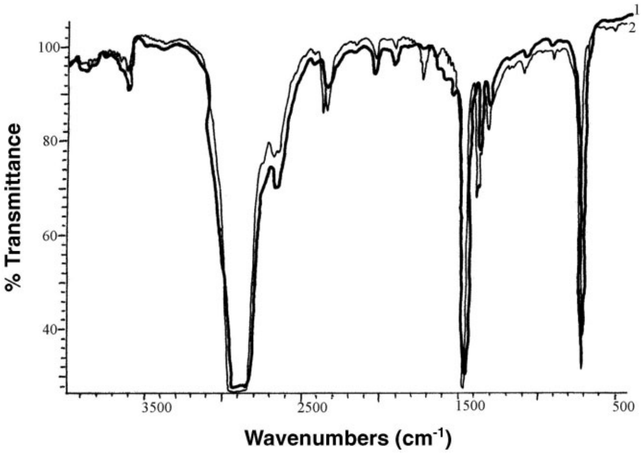

Figure 3 IR Spectrum of nonozonized (1) and ozonized HDPE (2).

TABLE I
Quantitative Characterization of Ozonized LDPE and HDPE

Ozonized PE	N ROOR (10^2 meq/g)	Height ratio of carbonyl band (%)
LDPE	3.40	69
HDPE	2.44	13

oxides and hydroperoxides is given by the following formula:

$$N = N_o/2$$

One molecule of peroxide or hydroperoxide reacts with two DPPH. Table I gives the results of the titration of peroxides and hydroperoxides in the case of LDPE and HDPE.

This table shows that in the same conditions of ozonization more initiating groups were obtained in the case of the LDPE than in the case of the HDPE. This can be due to the high rate of crystallinity of HDPE such as its rigidity and chemical resistance, which limits the creation of a significant number of peroxides and hydroperoxides sites. This is in agreement with the values of the height of the carbonyl bands (Table I) in the case of LDPE and HDPE.

Grafting reaction

The grafting reaction was performed in bulk and in solution, after introducing known amounts of ozonized PE (LDPE or HDPE) and monomer. The GS was especially realized in the case of VPA because of its less reactivity compared to that of the other monomers. Moreover a few studies have been reported on the grafting of VPA on the ozonized PE.[17]

The macroradicals provided by thermal decomposition of peroxides and hydroperoxides initiate the grafting reaction leading to the formation of copolymers and homopolymers.

$$\mathrm{ROOR} \rightarrow 2\mathrm{RO}^{\cdot}$$

$$\mathrm{ROOH} \rightarrow \mathrm{RO}^{\cdot} + \mathbf{HO}^{\cdot}$$

$$\mathrm{RO}^{\cdot} + n\mathrm{M} \rightarrow \mathrm{RO}\text{—}(\mathrm{M})^{\cdot}_{n}$$

$$\mathrm{HO}^{\cdot} + n\mathrm{M} \rightarrow \mathrm{HO}\text{—}(\mathrm{M})^{\cdot}_{n}$$

Mass grafting

A separate grafting of AA, MADAME, and VPA were carried out on the ozonized LDPE or HDPE.

A satisfactory grafting of AA and MADAME on LDPE and HDPE were obtained at 110°C. No grafting of VPA on LDPE occurs even at temperatures up to 110°C. A satisfactory grafting of VPA on HDPE was obtained at 140°C.

Grafting in solution

Because of the difficulties to graft VPA by MG, especially on LDPE, we proceeded to GS. No grafting was obtained when VPA was used alone. So, to increase its reactivity, the VPA grafting was coupled with AA or AN.

After copolymerization, and in all cases of grafting, the product was recovered and purified to eliminate the homopolymer as has been described in the experimental part.

Analysis of graft copolymers

The elementary analysis of O and N in the copolymers makes it possible to estimate the grafting yields of monomers on PE (LDPE and HDPE). The oxygen content of ozonized PE (LDPE and HDPE) is not considered in the calculation. The grafting yields were calculated from the following formula:

$$\%\ \mathrm{AA} = \frac{\%\ \mathrm{O}M_{\mathrm{AA}}}{32}$$

$$\%\ \mathrm{MADAME} = \frac{\%\ \mathrm{N}M_{\mathrm{MADAME}}}{14}$$

$$\%\ \mathrm{VPA} = \frac{\%\ \mathrm{O}M_{\mathrm{VPA}}}{48}$$

TABLE II
Weight Grafting Content of Grafted Monomers (Mass Grafting)

PE	Product	O (%)	N (%)	AA (%)	MADAME (%)	VPA (%)
LDPE	P_{AA}	9.4	–	21.2	–	–
	P_{MADAME}	–	2.5	–	28.1	–
HDPE	P_{AA}	6.5	–	14.6	–	–
	P_{MADAME}	–	2.0	–	22.4	–
	P_{VPA}	7.0	–	–	–	15.7

TABLE III
Weight Grafting Content of Grafted VPA Estimated from the Height Ratio of P—OH Band

	MG of VPA		GS of VPA			
	In the absence of water		In presence of water			
Copolymers	Height ratio (%)	VPA (%)	Height ratio (%)	Estimated VPA (%)	Height ratio (%)	Estimated VPA (%)
HDPE-*g*-VPA	55.0	15.7	–	–	–	–
LDPE-*g*-(AN-*co*-VPA)	–	–	24.0	6.8	14.0	4.0
LDPE-*g*-(AA-*co*-VPA)	–	–	9.0	2.6	7.0	2.0

M_{AA}, M_{MADAME} and M_{VPA} are the molecular weights of the corresponding monomers. All these results are reported in Table II.

The analysis of the results obtained (Table II) shows that, in the case of LDPE, we obtained higher grafting rates of AA, MADAME comparatively to HDPE. This is due to the number of more important peroxides groups in the LDPE. In addition, the rate of crystallinity raised for HDPE hinders the monomer diffusibility.

The synthesized copolymers have been analyzed by FTIR spectroscopy especially in the case of VPA to estimate the percentage of VPA grafting on ozonized PE (Table III).

The IR spectrum of the copolymer HDPE-*g*-VPA, resulting from MG (Fig. 4), shows a characteristic band of P—OH function at 937 cm^{-1}. This confirms the grafting of VPA on HDPE.

The spectrum of the copolymer LDPE-*g*-(AN-*co*-VPA) resulting from GS shows the appearance of two bands in both cases: with water and without it (Fig. 5). One located at 937 cm^{-1}, corresponding to the vibration of the —P—OH function, and the other band located at 2242 cm^{-1}, which corresponds to the nitrile (CN) function. This proves the grafting of the copolymer AN-*co*-VPA on the LDPE.

The examination of the IR spectrum of LDPE-*g*-(AA-*co*-VPA) shows the appearance of two bands in both cases—with water and without it (Fig. 6).

One located at 937 cm^{-1} which corresponds to the —P—OH function. The other located at approximately 1713 cm^{-1} which characterizes the —C═O function of the carboxylic acid. These results prove the grafting of the copolymer AA-*co*-VPA on the LDPE.

These results prove that the grafting of VPA in solution must be performed by copolymerization with another more reactive monomer, which initiates the grafting and consequently facilitates the grafting of VPA monomers.

Table III shows the grafting rate of VPA copolymerized with AN and AA in the presence and absence of water. It is noted that the rates of grafting of VPA on the ozonized LDPE in solution are higher with AN when compared with that obtained with AA. This can be explained among others by the strongest AA reactivity to the detriment of the VPA. In the same way, we obtained in both cases of copolymer (AN and AA) a higher rate of VPA grafting in the absence of water than in the presence of this last. This can be attributed to the increase in the concentration of the monomer around the peroxides sites that leads to a more important grafting. Moreover, this increase in the grafting

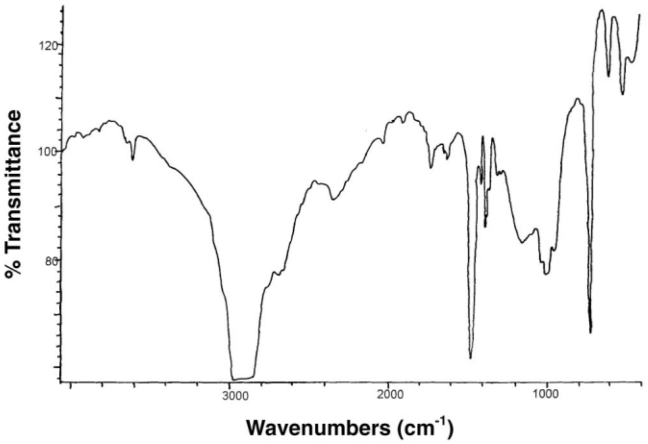

Figure 4 IR Spectrum of HDPE-*g*-VPA.

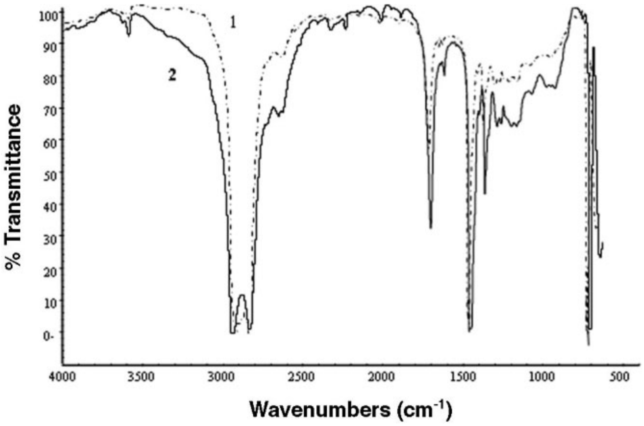

Figure 5 IR Spectrum of LDPE-*g*-(AN-*co*-VPA) in the presence of water (1) and in the absence of water (2).

rates in the absence of water is markedly noticed in the case of the grafting of VPA in the presence of AN. This can be explained, among others, by the enhancement of the grafting of VPA initiated by a grafting of a significant number of CN groups at higher concentration.

Characterization of membranes

The characterization of the synthesized membranes consists of determining some physicochemical properties to examine whether they fit the requirement of the ion exchange membranes (IEM)—low electrical resistance, relatively high exchange capacities, and good mechanical and chemical resistance. We determined the following parameters: exchange capacity and electrical resistance.

Table IV gives the values of the exchange capacities and the electrical resistances for the synthesized membranes. The exchange capacity is the number of milliequivalent of ions that the membrane can exchange (in meq of ions per gram of membrane). They were determined by pH titration. Table IV gives the values of the measured exchange capacities. These values show that in the case of LDPE, regardless of the way of grafting, we obtained membranes with higher exchange capacities than in the case of HDPE. This is in agreement with the grafting rates of the monomers, which are more important for LDPE. The highest value of exchange capacity is obtained in the case of MG of AA on ozonized LDPE. However, the lowest one is obtained in the case of GS of VPA copolymerized with AN.

The electrical resistances of the synthesized membranes are reported in Table IV. These values are relatively low, especially for the membranes made from AA and MADAME by MG, regardless of the type of PE. The membranes made from VPA have relatively high electrical resistance, except those obtained by copolymerization with AA, which improves its electrical properties. In the case of LDPE-*g*-(AN-*co*-VPA), we have obtained a higher electrical resistance. This is in agreement with the low amount of ionogenic groups in the membrane, given by the value of exchange capacity.

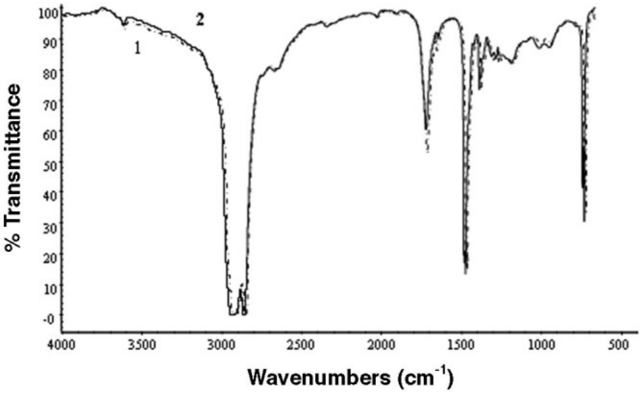

Figure 6 IR Spectrum of LDPE-*g*-(AA-*co*-VPA) in the presence of water (1) and in the absence of water (2).

TABLE IV
Exchange Capacities and Electrical Resistances of the Synthesized Membranes (IEMs)

PE	Exchange capacity (meq/g)	Electrical resistance (Ω cm^2)
LDPE		
LDPE-*g*-AA (MG)	3.0	2.0
LDPE-*g*-MAD (MG)	2.8	3.5
LDPE-*g*-(AN-*co*-VPA) (GS)	1.2	8.2
LDPE-*g*-(AA-*co*-VPA) (GS)	2.8	3.2
HDPE		
HDPE-*g*-AA (MG)	1.8	5.4
HDPE-*g*- MAD (MG)	1.0	7.0
HDPE-*g*-VPA (MG)	2.6	6.2

From this physicochemical characterization, we can classify the best electro-chemical properties of the synthesized membranes in the following order:

LDPE-*g*-AA (MG) > LDPE-*g*-(AA-*co*-VPA) (GS) > LDPE-*g*-MAD (MG) > HDPE-*g*-AA (MG) > HDPE-*g*-MAD (MG) > HDPE-*g*-VPA (MG) > LDPE-*g*-(AN-*co*-VPA) (GS).

CONCLUSIONS

A comparative study of the ozonization of LDPE and HDPE was performed. The ozonization was more successful in the case of LDPE than in the case of HDPE. The numbers of hydroperoxide and peroxide groups obtained with LDPE are more important than in the case of HDPE.

The MG of AA and MADAME was carried out successfully for LDPE and HDPE. The grafting of VPA was limited to MG of HDPE. The VPA grafting was improved in solution by copolymerizing it with AN and AA on ozonized LDPE.

Relatively satisfactory IEM were obtained from LDPE grafted with AA, MADAME in mass and LDPE grafted with VPA copolymerized with AA in solution.

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