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Synthesis and characterization of new graft copolymers based on ozonized polyethylene: Comparative approach between mass and solution grafting

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Abstract

New graft copolymers were developed from low-density polyethylene (LDPE) and high-density polyethylene (HDPE) following an initial ozonation step to introduce reactive functional groups onto the polymer backbone. Among the two polymers, LDPE demonstrated superior susceptibility to ozonation, making it the preferred substrate for subsequent grafting. Grafting was then performed primarily on ozonized LDPE using various functional monomers, including acrylic acid (AA), 4-vinylpyridine (4VP), acrylonitrile (AN), chloromethylstyrene (CMS), as well as copolymers such as AA–vinylphosphonic acid (AA-co-VPA) and AN–vinylphosphonic acid (AN-co-VPA). Grafting was carried out using both solution and melt techniques. The resulting materials were characterized by elemental analysis and Fourier transform infrared (FT-IR) spectroscopy, confirming the incorporation of heteroatoms and the presence of characteristic functional groups. Grafting performed in solution consistently yielded higher efficiencies compared to melt grafting, likely due to improved monomer diffusion and enhanced reactivity of active sites. These graft copolymers exhibit significantly enhanced surface hydrophilicity due to the increased surface polarity and functional group diversity, positioning them as promising candidates for applications in water purification membranes, ion exchange resins, sensors, biomedical devices, and composite materials requiring enhanced interfacial interactions.

1. Introduction

Polyethylene (PE) is a widely used polymer due to its good mechanical properties, chemical resistance, and low cost [1]. Nevertheless, its non-polar nature and chemical inertness severely limit its ability to be functionalized and to adhere to other materials, which restricts its use in more demanding technical applications [2]. As a result, chemical modification of PE is essential to expand its application range. In particular, grafting functional groups onto the PE backbone improves both its compatibility with other substances and its overall performance [3]. In response to the limitations of unmodified polyethylene, various functionalization methods have been explored to introduce polar groups into its structure. Among these, ozonation stands out for its efficiency and environmentally friendly nature. This technique enables the generation of reactive sites such as peroxide, carbonyl, and hydroxyl groups along the polymer chains without the need for harsh chemical agents [4–6]. These activated groups can subsequently initiate grafting reactions with functional monomers. The functionalization of polyethylene through the grafting of polar monomers has been the subject of extensive research aimed at over-coming its chemical inertness. This modification notably enhances adhesion, compatibility with other materials, and surface wettability [7]. Among the available approaches, ozonation proves to be a promising and environmentally friendly method [8]. It generates oxygen-containing groups (carbonyl, hydroxyl, and peroxide) along the polymer chain, which are capable of initiating radical grafting reactions with various functional monomers [9,10]. However, the choice of grafting method strongly influences the efficiency of the process and the final structure of the material. Two common approaches are used: mass grafting (often via reactive extrusion) and solution grafting [10,11]. Mass grafting, performed in the melt state, is particularly suited for industrial processes since it does not require the use of solvents. However, it demands strict control of temperature and shear conditions to prevent thermal degradation of the polymer [12]. On the other hand, solution grafting is performed under milder conditions and offers better control over grafting efficiency, but it remains limited due to the use of solvents and the difficulties related to scaling up [13]. It therefore appears crucial to compare these approaches in order to better understand their respective effects on the final properties of the grafted material.

In this context, the work of Zouahri *et al.* [14,15], conducted a series of studies on polyethylene functionalization by ozonation followed by grafting of polar monomers. They first compared the behavior of LDPE and HDPE under ozonation, demonstrating that LDPE, due to its more amorphous structure, exhibited higher grafting reactivity. They then evaluated solution grafting on ozonized HDPE, which allowed better control over the chemical structure and a more homogeneous dispersion of functional groups. These studies highlighted the decisive influence of the type of high-density polyethylene and the grafting

process on the final properties of the resulting biomaterials [14,15]. While existing research has mainly focused on HDPE, the case of ozonized LDPE remains poorly explored from a comparative perspective. Due to its more amorphous structure and increased reactivity, LDPE is, however, an ideal candidate to evaluate the influence of the grafting process on the final properties of the material. This observation underlines the need for further investigation of this polymer within the framework of radical grafting following ozonation. This study has scientific relevance by comparatively exploring two grafting methods on ozonized low-density polyethylene, a subject that remains largely unaddressed. It enables a better understanding of the influence of the process on the structure and properties of the copolymers. From an industrial standpoint, the results may guide the choice of the most efficient method to develop functional materials suited for technical applications such as packaging, coatings, composites, or compatibility of recycled materials.

The present work first focuses on the activation of polyethylene (PE) by ozone. In a second step, various monomers will be grafted onto the prepared LDPE. The monomers used include acrylic acid (AA), 4-vinylpyridine (4VP), acrylonitrile (AN), chloromethylstyrene (CMS), acrylic acid–vinylphosphonic acid copolymer (AA-co-VPA), and acrylonitrile–vinylphosphonic acid copolymer (AN-co-VPA). Finally, the success of the grafting process and the key parameters influencing the efficiency of the reactions will be thoroughly discussed in the concluding section of this article.

2. Experimental

2.1 Materials

High-density polyethylene (HDPE, Stamylan HD 6621) and low-density polyethylene (LDPE, BD 1922Z) were supplied by DSM Engineering Plastics (Geleen, Netherlands). Prior to use, the powdered polyethylene was sieved to obtain a uniform particle size distribution. Acrylic acid (AA), vinyl phosphonic acid (VPA), acrylonitrile (AN), and chloromethylstyrene (CMS) were purchased from Aldrich (Merck KGaA, Darmstadt, Germany) and used as received. Xylene (analytical grade) was used as solvent for 2,2-Diphenyl-1-pcrylhydrazyl (DPPH) analysis and grafting reactions.

2.2 Activation of polyethylene by ozonation

Polyethylene activation was carried out using a Trailigaz-type ozonizer following previously described procedures [16,17]. Approximately 2 g of PE powder were placed in a glass reactor, and ozone was introduced under controlled conditions consisting of an ozone concentration of 15 $mg \cdot L^{-1}$, an air flow rate of 2 $L \cdot min^{-1}$, and a temperature of 30°C during 30 min. During ozonation, various oxygen-containing functional groups such as hydroperoxides (–OOH), peroxides (–O–O–), hydroxyl groups (–OH), and carbonyl groups (C=O) were incorporated onto the polymer surface, thereby increasing its chemical reactivity and facilitating subsequent grafting reactions. At the end of the treatment, residual ozone was eliminated by purging the polyethylene with an air stream for 2 h.

2.3 Experimental conditions of ozonation

Ozonation was carried out using a Trailigaz-type ozonizer, according to a previously described method [16,17]. All reaction parameters, including ozone concentration (15 $mg \cdot L^{-1}$), air flow rate (2 $L \cdot min^{-1}$), and temperature (T=30°C), were adjustable on the ozone generator. LDPE and HDPE samples were ozonated separately under these controlled conditions. Residual ozone was removed by purging the polyethylene with an air stream for 2 h after the reaction.

2.4 Determination of ozonized PE

The quantification of ozonized PE was carried out by introducing approximately 20 mg to 25 mg of ozonized PE into a flask equipped with an argon inlet and containing a DPPH solution in 25 mL of xylene at a concentration of 0.067 $g \cdot L^{-1}$ or 17×10^{-5} $mol \cdot L^{-1}$. The oxygen in the flask was removed by passing an argon stream for 15 min. The mixture was then immersed in an oil bath heated to 110°C for 15 min.

After cooling, the PE, which is insoluble in cold xylene, settled at the bottom of the flask, and the excess DPPH was measured in the supernatant by colorimetry at 520 nm. This allows the calculation of the amount of DPPH consumed, which corresponds to the radicals produced from the ozonized PE.

2.5 Preparation of grafted copolymers

Graft copolymers were obtained from ozonized polyethylene (LDPE and HDPE) using two distinct methods: the mass method and the solution method. The experimental parameters were adjusted according to the peroxide and hydroperoxide composition of the polyethylene, determined by iodometric titration and spectroscopy. For ozonized LDPE, rich in peroxides (65%), the amount of monomer used was slightly lower (~0.9 g) to limit homopolymer formation. The reaction was carried out in solution in 10 mL of toluene, under a nitrogen atmosphere for 35 min, at a temperature of 80°C to 90°C for 1 h, with moderate stirring (300 rpm). For ozonized HDPE, containing more hydroperoxides (58%), the amount of monomer was slightly increased (~1.35 g), with 15 mL of toluene, under N_2, at 110°C for 3 h. After reaction, the copolymers were rapidly cooled under N_2, washed hot with xylene (80°C for LDPE and HDPE) to remove any homopolymer, then filtered and dried in a vacuum oven at 60°C to 70°C for 24 h.

The grafting yields were subsequently calculated using established stoichiometric relationships correlating the measured elemental percentages to the theoretical content of each monomer. The corresponding formulas, as detailed in Table 1, incorporate the molecular weights of the individual monomers acrylic acid (AA), vinyl phosphonic acid (VPA), acrylonitrile (AN), and chloromethylstyrene (CMS)and account for the atomic masses of their characteristic elements. This methodology enables a precise quantification of the monomer incorporation efficiency into the polymer matrix, providing insight into the effectiveness of the grafting processes under the applied experimental conditions. The M_{AA}, M_{AN}, M_{CMS}, M_{VPA} are the molecular weights of the corresponding monomers.

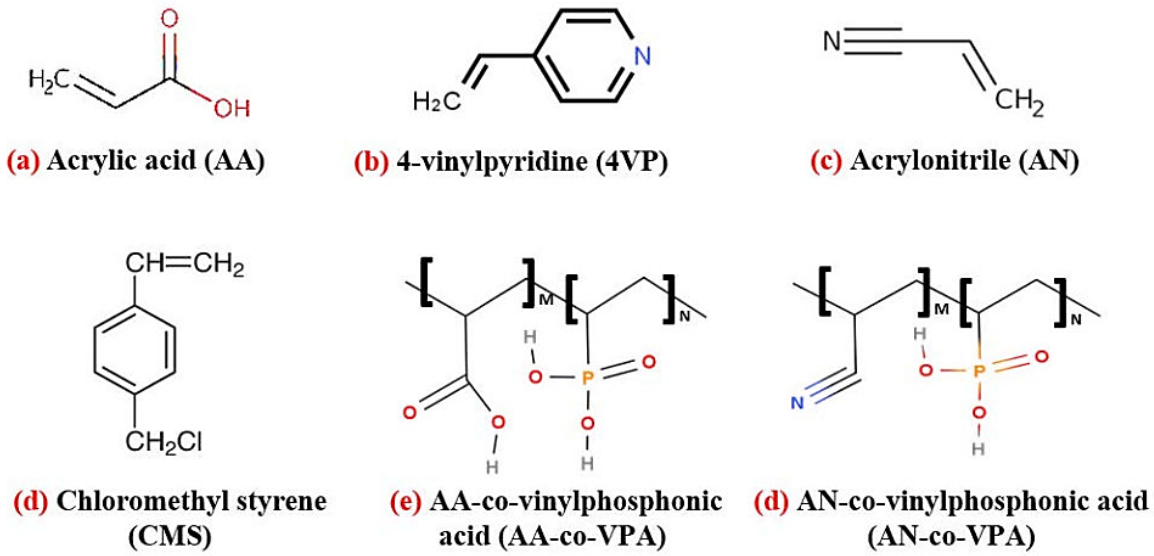

Figure 1. Structure of grafted monomers; acrylic acid (AA) (a), 4-vinylpyridine (4VP) (b), acrylonitrile (AN) (c), Chloromethylstyrene (CMS) (d), copolymers such as AA–vinylphosphonic acid (AA-co-VPA) (e) and AN–vinylphosphonic acid (AN-co-VPA) (d).

Table 1. Formulations of the grafting rates used.

Monomers	Formula
Acrylic acid (AA)	$\%\,(AA) = \frac{\%\,(O)\cdot M_{AA}}{32}$
Vinyl phosphonic acid (AVP)	$\%\,(AVP) = \frac{\%\,(O)\cdot M_{AVP}}{48}$
Acrylonitril (AN)	$\%\,(AN) = \frac{\%\,(N)\cdot M_{AN}}{14}$
Chloromethylstyrene (CMS)	$\%\,(CMS) = \frac{\%\,(Cl)\cdot M_{CMS}}{35.5}$

Table 2. Monomers Used and Corresponding Elements for Elemental Analysis.

Monomers	Corresponding element
Acrylic Acid (AA)	Oxygen (O)
Vinyl phosphonicAcid (AVP)	Oxygen (O)
Acrylonitril (AN)	Nitrogen (N)
Chloromethylstyrene (CMS)	Chlorine (Cl)

2.6 Fourier Transform Infrared spectroscopy (FT-IR)

The analyses were performed on both grafted and non-grafted polyethylene (PE) films. These samples were prepared by hot pressing at a pressure of 150 bar and 200°C, utilizing a Perkin-Elmer apparatus. The thickness of the prepared PE films was on the order of 1 mm. The samples were characterized by Fourier-Transform Infrared (FTIR) spectroscopy. The measurement mode employed was Attenuated Total Reflectance (ATR), which is particularly suitable for analyzing the surface modifications of thicker polymer films. This spectroscopic technique was used to determine the grafting rates of the synthesized copolymers.

$$G\,(\%) = \frac{\left(\frac{A_G}{A_R}\right)_G - \left(\frac{A_{NG}}{A_R}\right)_{NG}}{\left(\frac{A_{NG}}{A_R}\right)_{NG}} \times 100$$

A_G : The absorbance of the characteristic band of the grafted monomer.

A_{NG} : The absorbance of the characteristic band of the non-grafted monomer.

A_R : The absorbance of the reference band of polyethylene.

$\left(\frac{A_G}{A_R}\right)_G$: The ratio of the grafted sample.

$\left(\frac{A_{NG}}{A_R}\right)_{NG}$: The ratio of the non-grafted (blank) sample.

2.7 Elemental analysis procedure

Table 2, summarizes each monomer used, along with the corresponding elemental analysis, which ultimately allows for the determination of the grafting rate.

3. Results and discussion

3.1 Activation of peroxides and hydroxides

The optimization of the polyethylene ozonization operation was carried out in a subsequent study [16]. The ozonization reaction leads to the formation of peroxide and hydroperoxide groups according to the reaction scheme proposed by Kefeli [18].

Figure 2–3, present the FT-IR analysis of both ozonized and non-ozonized polyethylene (LDPE and HDPE). The spectra display a prominent band at 1712 cm^{-1}, which is characteristic of the carbonyl (C=O) functional group. This band is more intense in LDPE than in HDPE, indicating a higher level of ozonization in LDPE. The difference in the intensity of this band can be attributed to the crystallinity of the two polyethylene types [14]. HDPE, which has a higher crystallinity than LDPE, tends to be more resistant to ozonization. Crystallinity refers to the degree of structural order in the polymer; in crystalline regions, molecules are packed more tightly, reducing the polymer's accessibility to reactive species like ozone. As a result, HDPE is less susceptible to the oxidative attack of ozone, leading to fewer carbonyl groups being introduced into the polymer structure compared to LDPE, which has lower crystallinity and is more readily activated by ozone.

This difference in the susceptibility to ozonization can also influence the subsequent grafting process, with HDPE exhibiting greater resistance to grafting due to its more robust crystalline structure.

3.2 Quantification of peroxides and hydroperoxides

The quantification of peroxide and hydroperoxide groups in ozonized LDPE and HDPE are carried out using DPPH, followed by a selective determination of hydroperoxides using ferrous ion Fe^{2+}, according to a previously described method[16]. Table 3 presents the results of the quantification of peroxide and hydroperoxide functions in the case of ozonized LDPE and HDPE.

Table 3, compares the oxidative functionalization of ozonized LDPE and ozonized HDPE. LDPE shows a higher total concentration of oxygen-containing reactive species (NROOX: 3.20 × 102 meq·g^{-1}) than HDPE (2.44 × 102 meq·g^{-1}), indicating greater ozone uptake due to its amorphous and branched structure. LDPE also has a higher proportion of peroxides (65%) compared to HDPE (42%), while HDPE contains more hydroperoxides (58%) than LDPE (35%). Additionally, the carbonyl group content a key indicator of oxidation level is significantly greater in LDPE (50%) than in HDPE (17%). These results highlight the higher reactivity and functionalization potential of LDPE, making it more suitable for subsequent grafting processes.

According to the histogram (Figure 4), it is evident that the production yields of peroxides and carbonyl groups are significantly higher in LDPE compared to HDPE, with an increase of approximately 54% in LDPE relative to HDPE.

Conversely, an opposite trend is observed for hydroperoxide formation, where HDPE shows a hydroperoxide content approximately 65% higher than that of LDPE. This contrast can be explained by the inherent structural differences between the two types of polyethylene. HDPE contains a higher proportion of methyl and ethyl groups relative to tertiary carbon atoms, which contributes to its greater chemical resistance and higher degree of crystallinity. As a result, HDPE tends to favor the formation of hydroperoxides, while LDPE, being more amorphous and reactive, facilitates the generation of peroxides and carbonyl groups.

Consequently, the grafting reactions were carried out using LDPE only, as it exhibited the highest peroxide content. This finding is in full agreement with the FTIR analysis discussed earlier (Figure 2), where LDPE showed greater reactivity than HDPE, evidenced by the more intense carbonyl (C=O) absorption bands.

3.3 Synthesis of grafted copolymers

At this stage, the grafting reactions were conducted using two different approaches: mass grafting and solution grafting. In both cases, a defined amount of ozonized LDPE and the target monomer were introduced into the grafting cells. The reaction was then initiated by heating under controlled conditions.

The copolymerization was performed using acrylic acid and acrylonitrile, both of which exhibit higher reactivity compared to vinyl phosphonic acid, thereby favoring more efficient grafting onto the polyethylene backbone. The experimental protocol adopted, along with the corresponding results, is summarized in Table 4.

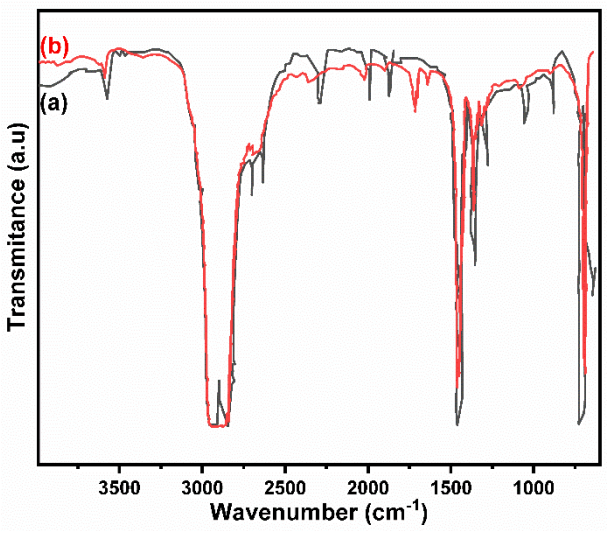

Figure 2. Infrared Spectrum of Non-Ozonized LDPE (a), and Ozonized LDPE (b).

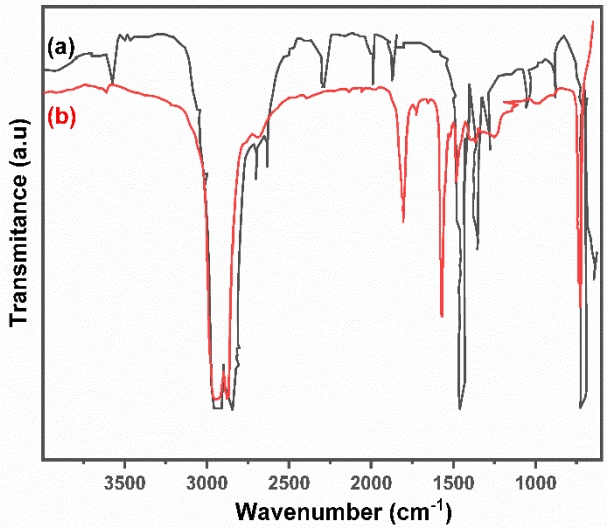

Figure 3. Infrared Spectrum of Non-Ozonized HDPE (a), and Ozonized HDPE (b).

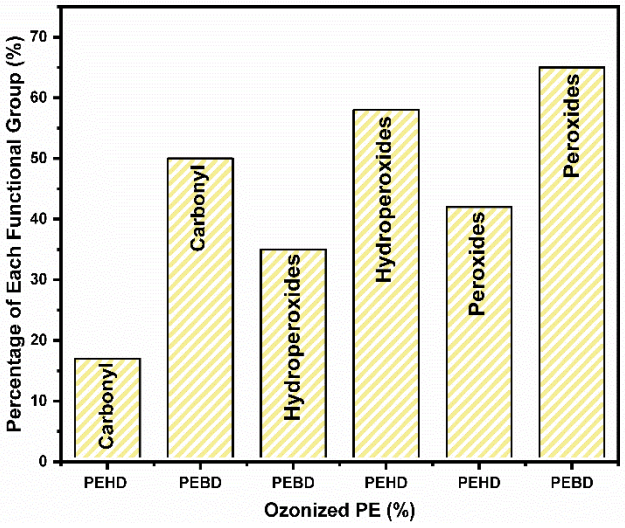

Figure 4. Histogram showing the percentage of each functional group in relation to the ozonized polyethylene (LDPE and HDPE).

Table 3. Degree of Ozonation of PEHD and PEBD.

	Ozonized LDPE	**Ozonized HDPE**
N_{ROOX} [10^2 meq·g^{-1}]	3.20	2.44
N_{ROOH} [10^2 meq·g^{-1}]	1.12	1.41
Peroxides [en %]	65	42
Hydroperoxides [en %]	35	58
Carbonyl Function [en %]	50	17

Table 4. Grafting rate of the prepared copolymers and the operating conditions.

	Type of reaction	**Reaction duration [h]**	**Temperature [°C]**	**Washing solvent**	**Grafting rate [%]**
LDPE-g-AA	Solution	14	80	Acetone	20
	Mass	14	80	Acetone	15
LDPE-g-AN	Solution	7	80	Acetone	10
	Mass	7	80	Acetone	8
LDPE-g-CMS	Solution	15	90	Toluene	12
	Mass	15	90	Toluene	20
LDPE-g-4VP	Solution	13	80	Acetone	20
	Mass	13	80	Acetone	30
LDPE-g-(AN-co-VPA)	Solution	14	80	Acetone, ether	15
	Mass	14	80	Acetone, ether	10
LDPE-g-(AA-co-VPA)	Solution	14	80	Acetone, ether	20
	Mass	14	80	Acetone, ether	15

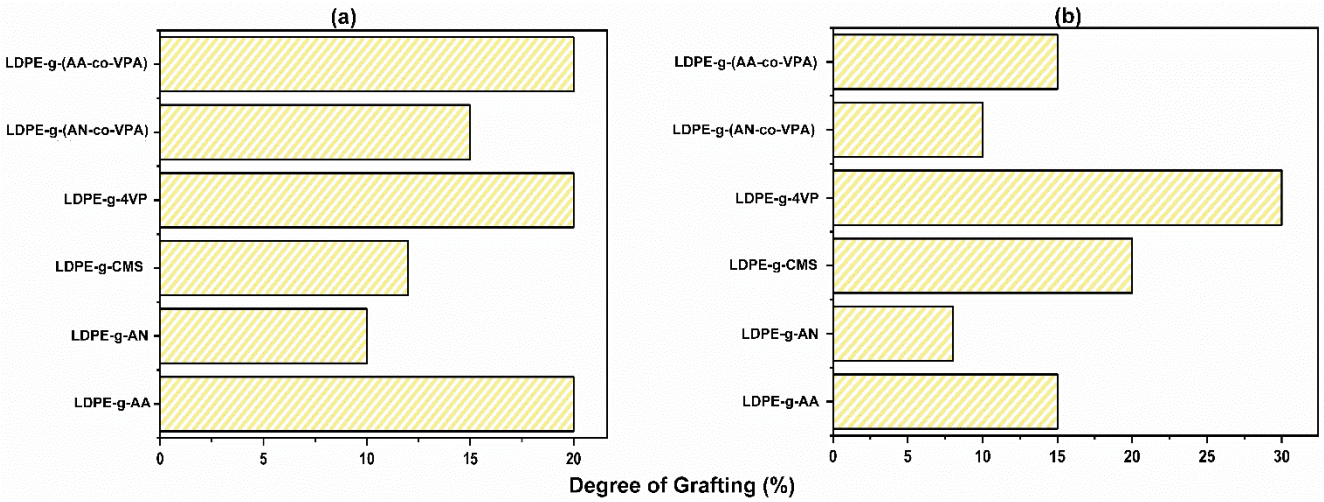

Figure 5. Grafting rate in Solution and in Mass.

The macroradicals generated by the thermal decomposition of peroxides and hydroperoxides initiate the formation of both grafted copolymers and free homopolymers, as illustrated by the mechanism previously described [17]. This process involves radical propagation along the polymer backbone or in the surrounding medium, leading either to grafting onto the LDPE chains or to the formation of homopolymer chains in parallel.

According to Figures 5, it can be observed that all the grafting rates obtained for the different monomers are greater than or equal to 10%. These values were determined from the infrared spectra using the ratio between the intensity of the characteristic absorption band of the grafted monomer and that of the C–C stretching band centered at 2843 cm^{-1}.

A notably high grafting rate of vinyl phosphonic acid (VPA) was achieved under solution grafting conditions. This enhanced efficiency can be attributed to the presence of the solvent, which reduces the viscosity of the reaction medium while promoting the swelling of the LDPE powder, thereby facilitating the diffusion of the monomer into the polymer matrix.

On one hand, acrylic acid (AA) and acrylonitrile (AN), which are more reactive than vinyl phosphonic acid, yielded satisfactory grafting rates as well. On the other hand, the grafting reactions were found to be effective at temperatures ranging from 80°C to 90°C, favoring monomer diffusion and activation of the reactive sites within the polymer structure.

3.4 Characterization of grafted copolymers

3.4.1 Elemental composition results

The grafting rates of various monomers onto the LDPE backbone were quantitatively determined through elemental analysis, focusing

on the content of oxygen (O), nitrogen (N), and chlorine (Cl) within the copolymer samples (Table 2). These elements serve as reliable markers since they are specific to the grafted monomer units and are absent or minimal in the pristine LDPE matrix. Notably, the oxygen content originating from the ozonized LDPE base material was excluded from the calculations to avoid overestimating the grafting degree.

The grafting efficiency of various monomers onto the LDPE backbone was quantitatively evaluated using elemental analysis, with the results summarized in Table 5. The grafting rates were deduced based on the unique elemental signatures of the grafted monomers namely oxygen (O), nitrogen (N), and chlorine (Cl)which are not inherently present in the pristine LDPE matrix.

Among the different monomers investigated, acrylic acid (AA) exhibited the highest grafting yield, with an oxygen content of 9.4% corresponding to a grafting rate of 21.15%. This suggests a strong affinity and reactivity of AA with the ozonized LDPE matrix, likely due to the high polarity and reactivity of the carboxylic acid functional group under the applied grafting conditions.

In the case of chloromethylstyrene (CMS), the chlorine content reached 4.5%, leading to a grafting rate of 19.4%. The relatively high grafting yield indicates successful incorporation of CMS units into the LDPE backbone, facilitated by the reactive chloromethyl group that may promote grafting through radical or ionic mechanisms.

For acrylonitrile (AN), nitrogen content analysis revealed a grafting yield of 10.03% based on a nitrogen percentage of 2.65%. The presence of the nitrile group is a strong indicator of AN incorporation, though its grafting efficiency was moderate compared to AA and CMS. This might be attributed to steric or electronic effects associated with the nitrile group, which could limit its reactivity under the same experimental conditions.

Finally, vinyl phosphonic acid (VPA) grafting was confirmed through oxygen content analysis, showing a 7% oxygen level that translates to a grafting rate of 15.75%. Although VPA does not contain nitrogen or chlorine, its phosphonic acid moiety contributes to the oxygen signal. The notable grafting rate implies effective interaction with the LDPE matrix, likely promoted by its dual-functional acidic structure.

Overall, these results highlight the varying grafting efficiencies of different monomers, influenced by their chemical functionalities, polarity, and steric factors. Acrylic acid demonstrated the highest reactivity, followed closely by CMS and VPA, while AN showed the lowest grafting rate among the studied monomers. These findings provide critical insights into the selection of monomers for targeted modification of polyethylene materials, enabling tailored functional properties in the resulting copolymers. Crucially, the high grafting rates obtained, particularly for AA and CMS, confirm that a dense layer of polar functional groups (such as carboxylic, nitrile, and phosphonic acids) was successfully introduced. This massive incorporation is the determining factor that allows for a significant change in the surface hydrophilicity of the polyethylene, thereby considerably improving the material's affinity for polar media and its relevance for applications requiring enhanced wettability. This improved hydrophilicity constitutes one of the main practical utilities of this research.

3.4.2 FT-IR analysis of the synthesized copolymer

The FT-IR spectrum of the LDPE-g-(AA-co-VPA) copolymer (Figure 6(a)) shows the appearance of a band at 937 cm^{-1}, which is attributed to the stretching vibration of the phosphonic –P–OH group from the 4-vinylphenylphosphonic acid (VPA) unit. This band is absent in the spectrum of the unmodified, ozonized LDPE (Figure 2(b)), confirming the successful grafting of VPA onto the polymer matrix (LDPE). In addition, the spectrum exhibits a carbonyl band around 1712 cm^{-1}, consistent with the presence of acrylic acid (AA).

These findings collectively confirm the copolymerization of AA and VPA onto the LDPE backbone. Similarly, the FT-IR spectrum of LDPE-g-(AN-co-VPA) (Figure 6(b)) also shows a distinct band at 937 cm^{-1}, corresponding to the phosphonic –P–OH vibration, indicating the grafting of VPA. Additionally, a band at 2242 cm^{-1} is observed, which is assigned to the nitrile (–C≡N) stretching vibration, characteristic of acrylonitrile (AN). The presence of both the phosphonic and nitrile bands confirms the co-grafting of AN and VPA onto the LDPE backbone, resulting in a copolymer with both polar and reactive functionalities.

Table 5. Results of the grafting rate (%) obtained by the percentage calculation.

PE	Grafted copolymers	O [%]	N [%]	Cl [%]	AA [%]	CMS [%]	AN [%]	AVP [%]
LDPE	P_{AA}	9.4	-	-	21.15	-	-	-
	P_{CMS}	-	-	4.5	-	19.4	-	-
	P_{AN}	-	2.65	-	-	-	10.03	-
	P_{AVP}	7	-	-	-	-	-	15.75

Table 6. Infrared Absorption Bands of Ozonized LDPE and Synthesized Copolymers.

Copolymers	υ [cm^{-1}]
LDPE ozonized	2843, 1712, 1463, 719
LDPE-g-AA	2843, 1712, 1463, 719
LDPE-g-AN	2843, 2242, 1712, 1463, 719
LDPE-g-CMS	2843, 1712, 1463, 837, 719, 678
LDPE-g-4VP	2845, 1716, 1597, 1556, 1463, 719
LDPE-g-(AN-co-AVP)	3603, 2843, 2242, 1712, 1463, 936, 719
LDPE-g-(AA-co-AVP)	3603, 2843, 1712, 1463, 1177, 930, 719

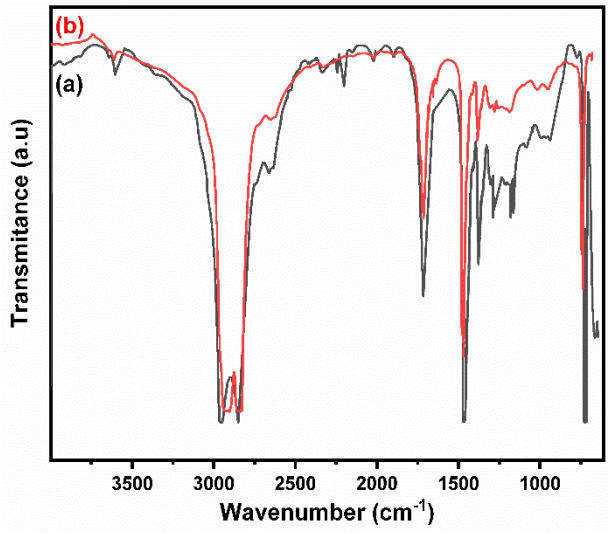

Figure 6. FT-IR spectrum of LDPE-g-(AN-co-VPA) (a), and LDPE-g-(AA-co-VPA) (b).

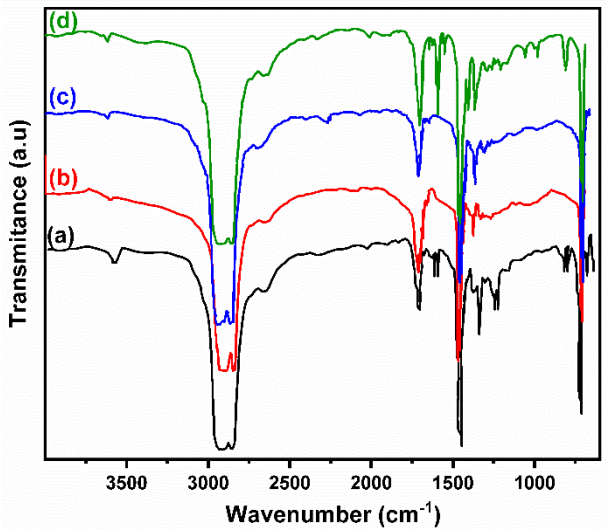

Figure 7. Infrared spectrum of LDPE-g-AA (a), LDPE-g-CMS (b), LDPE-g-AN (c), and LDPE-g-4VP (d).

The FT-IR spectrum of the LDPE-g-AA copolymer (Figure 7(a)) displays a distinct absorption band at 1712 cm^{-1}, which is assigned to the carbonyl (C=O) stretching vibration of the carboxylic acid group. This feature is not present in the spectrum of the unmodified LDPE and thus confirms the successful grafting of acrylic acid (AA) onto the polymer chain. The presence of this carbonyl peak indicates that the AA monomer was covalently bonded to the LDPE, contributing a polar functional group that could enhance hydrophilicity or facilitate further chemical interactions.

Table 6, summarizes the characteristic absorption bands of ozonized LDPE and LDPE grafted with monomers including acrylic acid (AA), acrylonitrile (AN), chloromethylstyrene (CMS), and 4-vinylpyridine (4VP), as well as copolymers such as AA–vinylphosphonic acid (AA-co-VPA) and AN–vinylphosphonic acid (AN-co-VPA). The interpretation of these bands has been discussed above the table. This summary provides a clear reference for the functional groups introduced by each grafting.

The spectrum of the LDPE-g-CMS copolymer (Figure 7(b)) reveals two additional absorption bands, not found in the base polymer. The first is observed at 676 cm^{-1}, corresponding to the stretching vibration of the chloromethyl group (–CH_2–Cl). The second appears at 837 cm^{-1}, which is characteristic of a 1,4-disubstituted benzene ring (i.e., para-substituted aromatic ring), attributed to the aromatic structure of chloromethylstyrene (CMS). These new features are indicative of the successful grafting of CMS onto the LDPE chains. The presence of both aliphatic chlorine and aromatic functionalities provides potential reactive sites for further chemical modifications or cross-linking.

In the case of the LDPE-g-AN copolymer (Figure 7(c)), a strong and distinct band appears at 2242 cm^{-1}, which is attributed to the stretching vibration of the nitrile group (–C≡N). This absorption is a definitive fingerprint of acrylonitrile (AN), confirming its successful grafting onto the LDPE matrix. The presence of the nitrile group introduces significant polarity and chemical reactivity, which could be beneficial in enhancing compatibility with other polar fillers or for subsequent chemical derivatization.

The FT-IR spectrum of the LDPE-g-4VP copolymer (Figure 7(d)) shows multiple new bands that are indicative of the pyridine ring structure from 4-vinylpyridine (4VP). Specifically, two absorption bands at 1597 cm^{-1} and 1556 cm^{-1} correspond to the C=N stretching vibrations of the pyridine ring, while an additional band at 822 cm^{-1} is attributed to a monosubstituted aromatic ring out-of-plane C–H bending. These spectral features confirm the grafting of 4VP onto the LDPE chain, introducing nitrogen-containing aromatic functionalities that may provide coordination sites for metal ions or offer basic character to the material surface.

4. Conclusions

In this study, we successfully demonstrated the effectiveness of ozonization in activating polyethylene chains, particularly LDPE, by introducing peroxide functional groups that facilitate grafting reactions. The comparison between LDPE and HDPE revealed the superior reactivity of LDPE, which was attributed to its more amorphous and branched structure. The subsequent grafting of various monomers onto ozonized LDPE showed higher grafting efficiencies in solution than in mass LDPE, emphasizing the critical role of the reaction medium in optimizing monomer incorporation. FTIR spectroscopy and elemental analysis confirmed the successful grafting and the presence of the expected functional groups. These findings pave the way for the development of functionalized polyethylene-based copolymers with potential applications in various industries requiring materials with tailored properties. Furthermore, the successful incorporation of highly polar groups, as confirmed by the high grafting yields, ensures a substantial enhancement in the surface hydrophilicity, thereby maximizing the potential utility of these new copolymers for applications requiring improved wettability.

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