Grafting of Itaconic Acid onto LDPE by the Reactive Extrusion: Effect of Neutralizing Agents

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ABSTRACT: Grafting of itaconic acid (IA) onto low-density polyethylene (LDPE) was performed by reactive extrusion where the initiator was dicumyl peroxide, and the neutralizing agents (NAs) were zinc oxides and hydroxides as well as magnesium oxides and hydroxides. The carboxyl groups were neutralized in molten LDPE directly in the course of acid grafting, and in prefabricated functionalized polyethylene (LDPE-*g*-IA). It was found that neutralizing agents introduced into the initial reaction mixture increase the yield of LDPE-*g*-IA while the carboxyl groups were neutralized partially or totally through chemical reactions. The physical structure of LDPE-*g*-IA did not in fact suffer any substantial changes. From the standpoint of neutralization activity, the NAs studied could be arranged as follows: $Zn(OH)_2 > ZnO > Mg(OH)_2 > MgO$. NA, added into the initial reaction mixture improved the grafting efficiency of IA onto LDPE. In case of the one-step process (neutralization simultaneously with grafting), the neutralizing effect appears stronger than that in the two-step process (neutralization of prepared LDPE-*g*-IA). This means that neutralization of carboxyl groups in IA was less effective when NA was introduced into LDPE-*g*-IA than for the case of the initial reactive mixture. Chemical neutralization of grafted IA results in products of improved resistance to thermal oxidation and thermal stability of melt. This result is of practical importance to the opportunities for widening the application range for PE modified by grafting IA, while preparing polymer blends to be compounded, processed, and used at elevated temperatures. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 828–836, 2003

Key words: itaconic acid; grafting; grafting efficiency; neutralizing agents; cation origin; neutralization; reactive processing; reactive extrusion

INTRODUCTION

The reactive extrusion (RE) process has been used to produce a wide variety of polymer products.[1] Polyolefins are the most preferable polymers used for this process. This is because they are inexpensive, find wide application in engineering, and grafting can control both their chemical and physical properties. In particular, RE has been used to modify chemically polymers and copolymers of olefins and their blends by grafting polar monomers onto macromolecules to improve the adhesion in polymer/polymer systems, as well as producing compatibilizers for them.[1,2] The list of monomers that can be grafted is, however, relatively short, owing to a set of requirements imposed on them which are associated with the peculiarities of the RE process.

In recent years, many aspects of the grafting mechanisms of IA with respect to polyolefin macromolecules have been investigated.[3–8] The most important formulation and technological factors have been determined and optimized so as to control the course of the grafting process, the grafting efficiency, the course of the by-process (i.e., crosslinking of polyethylene macromolecules), as well as the PE-*g*-IA physical structure. Blends of LDPE-*g*-IA with Polyamide 6 were chosen to show that IA grafted onto PE improves interphases adhesion in the blends, increases the impact strength of the materials, and improves their processability.[9–11]

However, grafted carboxyl-containing monomers are harmful for the resistance of functionalized PE against thermal oxidation; this fact can negatively affect both the technological and usage properties of the materials fabricated with PE.[10] Articles in the literature[12,13] state that LDPE-*g*-IA undergoes oxidation at a higher rate than LDPE both in air and in aqueous media. It is also known that the chemical neutralization of carboxyl groups grafted onto polyolefin macromolecules greatly influences their compatibilizing activity in blends of thermoplastics and increases thermal stability and, as a result, the properties of modified polyolefins.[14] Therefore, in certain instances it is advisable that the grafted carboxyl groups be chemically neutralized.[1,5–16]
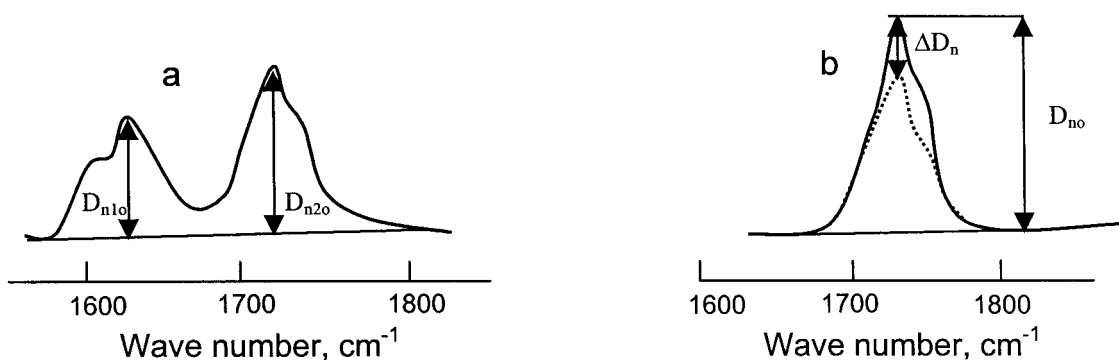
Figure 1 (a) Fragments of IR-spectra of initial LDPE-g-IA$^-$M$^+$ and (b) ones treated in 30% HCl aqueous solution.

In spite of the practical importance of neutralization of grafted acid groups, there are only a few works that explain the grafting mechanisms for monomers in the presence of NA. The two processes are to be performed in the extruder-reactor technology of such materials. They are based on utterly differing mechanisms, namely, grafting of unsaturated monomer that usually follows the free-radical mechanism and neutralization that follows the ionic mechanism. The two processes must take place within a moving molten polymer while thermal and force fields act simultaneously upon it during a relatively short time.

The present article is concerned with the above problem exemplified by grafting IA onto LDPE using the RE technology.

EXPERIMENTAL

Materials

The object of study was low-density polyethylene (LDPE): grade 15803-020; GOST 16337-77; density 0.92 g/cm^3; melting point 105°C; supplied by Polimir Co. (Novopolotsk, Belarus). The IA used was produced by the Chemical Division of Pfizer (New York, NY). Dicumyl peroxide (DCP) was the initiator. According works in the literature,[3,5] when IA was grafted, this peroxide possessed sufficient effectiveness. Its mechanism of action is typical of organic peroxides, which show a rather high thermal stability.[6] The IA concentration was 1.0 wt % in all the experiments. Chemically pure (reagent-grade) zinc oxide and hydroxide and also magnesium oxide and hydroxide served as the neutralizing agents. Average size of particles was as follows: ZnO, ~0.6 μm; MgO, ~2.0 μm; Zn(OH)$_2$, ~0.7 μm; Mg(OH)$_2$, ~1.6 μm.

Preparation of test specimens

The grafting reactions were performed in the single-screw extruder (screw diameter 25 mm; L/D = 25), equipped with a static mixer[3] at the following conditions: the screw rotation velocity was 27 rev/min (the

shear rate was approximately 30 s^{-1}); the temperatures were 165°C in Zone I; 190°C in Zones II, III, and IV.

To prepare a reaction mixture required for IA grafting without neutralization, LDPE granules were first treated with a solution of peroxide in acetone while thoroughly stirring the granules until the solvent completely evaporated. Then the granules were covered with IA powder. After that, the granules were loaded into the extruder reactor and the grafting process was performed. The discharged molten grafted LDPE was cooled in water and granulated.

The carboxyl groups of IA were neutralized in two ways. The first way was realized in a one-step grafting process with simultaneous neutralization. To do this, powdered NA and IA are first blended thoroughly with each other and are then added to LDPE; subsequently, the grafting process was run at the regimes similar to those of pure IA grafting. The average residence time for the material in the extruder barrel was ~4 min.

For the second, two-step process, LDPE-g-IA granules were treated with NA fine powders using the two-blade high-speed (1000 rev/min) mixer. After that, granules were passed again through the extruder reactor without changing any RE process parameters. Because NA was used in low amounts and the particle size was rather small, satisfactory uniform distribution of NA over polymer granules was ensured.

The NA concentration was calculated proceeding from the stoichiometry of neutralizing reactions between IA and the oxides and hydroxides used. NA was added either in somewhat deficient quantities in order to obtain partially neutralized IA (up to 70%) or in excessive quantities to obtain completely neutralized NA. In the latter instance, NA amounted to 150% of the calculated value required to totally neutralize the carboxyl groups.

Characterization

The grafting efficiency, i.e., the ratio of the grafted monomer to its total quantity added to the polymer,
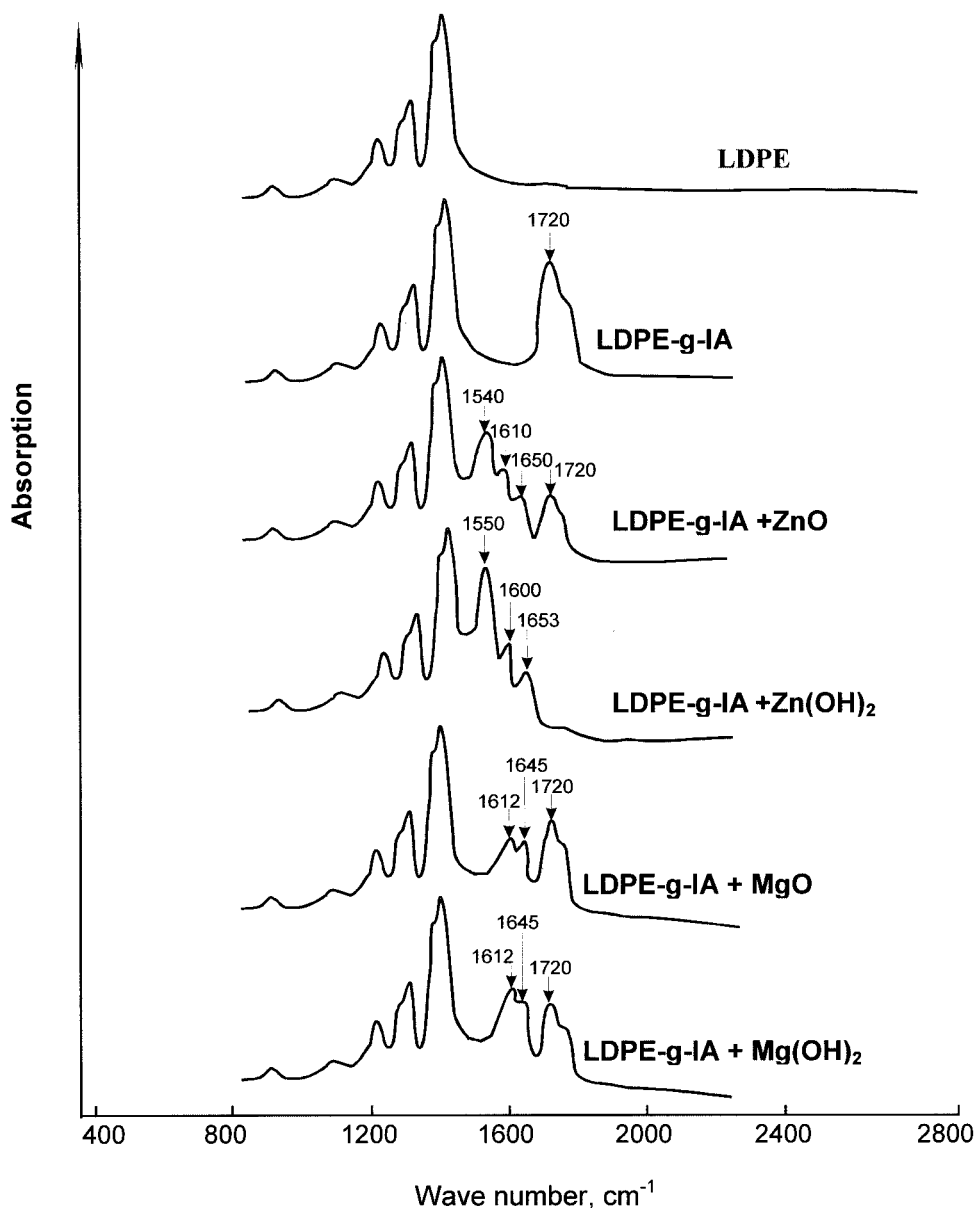
Figure 2 IR-spectra of initial LDPE, LDPE-*g*-IA, and LDPE-*g*-IA$^-$M$^+$ prepared with different neutralizing agents used in quantities exceeding by 50% the calculated quantity required to totally neutralize the carboxyl groups; the samples of LDPE-*g*-IA and LDPE-*g*-IA$^-$M$^+$ were extracted in ethanol before recording IR-spectra.

served as the parameter to characterize the course of grafting reactions. The values of grafting efficiency (α), same as in another work,[3] were determined using film specimens of 40 μm in thickness by absorption IR-spectroscopy (spectrophotometer M-80, Karl Zeiss, Jena, Germany), based on the content analysis of monomer in the initial LDPE-g-IA and that (LDPE-*g*-IA) extracted in ethanol at 70°C

$$\alpha = (D_\tau/D_o) \cdot 100\% \qquad (1)$$

where D_0 and D_τ are, respectively, the relative optical densities of carbonyl absorption (determined with respect to the optical density of the absorption band at

4325 cm^{-1} by internal standard) before and after the films were extracted in ethanol. In view of another research[17] it was believed that the extinction coefficient of absorption for C=O groups belonging to the carboxyl groups of grafted and nongrafted IA does not alter. When determining the grafting efficiency, the arithmetic average was calculated using the data obtained for 6–9 specimens.

The melt viscosity was determined using the melt flow index value which was estimated at temperature 190°C and load 10 kg with the help of the instrument IIPT-AM (AOZT Ekodatchik, Tula, Russia).

The thermal stability of polymer materials was investigated using a derivatograph Q-1500 (MOM, Budapest,

Hungary) at the heating rate 5°C/min and using 200-mg samples. The thermogravimetric curves were mostly used to do the analysis.

The differential scanning calorimetry (DSC) was used to investigate structure of the grafted PE on 4-mg samples heated at the rate of 16°C/min. For this purpose, devise DSM-3A (Institute of Biological Instruments, Russian Academy of Sciences) was used. Variations in the crystallinity degree were determined as ratios of the peak area of crystallization of the grafted PE to that of the initial polymer. In order to eliminate the influence of thermal prehistory on polymer crystallinity, the measurements were done on samples heated up to 190°C in the cells of the calorimeter unit, exposed at this temperature for 1 min, cooled to 40°C at the cooling rate 16°C/min, and then used for repeated analysis. The results of the five parallel measurements were averaged to obtain quantitative information on the temperatures of phase transitions as well as relative degree of crystallinity. The accuracy of temperature measurements was ±0.3°C.

The relaxation characteristics were studied using the reversible torsion pendulum of operating frequency 1 Hz that had been used in another work.[18] The test samples were in the form of plates measuring $50 \times 5 \times 0.5$ mm; the test temperature varied between $-150°C$ up to $+110°C$. The accuracy of measurements and maintaining of a given temperature was ±0.1°C. The maximum shear strain developed in the specimen during testing was below 10^{-2}. The measurement error of the mechanical loss tangent values was 5%. The mean values of test parameters were found by averaging the values of parallel tests conducted on three identical specimens. The deviation of one measurement from the arithmetic average did not exceed 5%.

RESULTS AND DISCUSSION

Effect of neutralization on IA grafting

First, we consider in detail the method of determining α in grafted product LDPE-g-IA$^-$M$^+$, in which acid groups were neutralized by metal ions M$^+$. Figure 1 shows an IR-spectrum of LDPE-g-IA$^-$M$^+$, which unlike that of LDPE-g-IA has both a band of carbonyl absorption for the carboxy-group at 1720 cm^{-1} and an absorption band in the region 1550–1650 cm^{-1}. The latter band is typical of salt compounds[19] and directly evidences a neutralization reaction that runs at the conditions of our experiment. When carboxyl groups undergo neutralization, the optical density of 1720 cm^{-1} carbonyl absorption band weakens by a certain value ΔD_n, in addition to the presence of an absorption band of salt groups. To consider these changes, while determining the grafting efficiency for LDPE-g-IA$^-$M$^+$, the film samples of this material were treated by 30% HCl aqueous solution at 70°C during 20 h, to

convert the salt groups to COOH-groups. Then, the absorption band of salt groups in the IR-spectrum of LDPE-g-IA$^-$M$^+$ disappeared, whereas the optical density of the carbonyl absorption band increased by ΔD_n. The increment in the optical density of carbonyl absorption band was constant irrespective of the neutralization level for similar NA,

$$\Delta D_n / \Delta D_{n1} = k \qquad (2)$$

If the k value is known for every type of NA, it is possible, based on IR-spectra of film samples of the initial LDPE-g-IA$^-$M$^+$ and that extracted in ethanol to find the α value. The optical density recalculated for carbonyl absorption in the initial LDPE-g-IA$^-$M$^+$ is found using the following equation:

$$D_{no} = D_{n2o} + \Delta D = D_{n2o} + k \cdot D_{n1o} \qquad (3)$$

After the nongrafted monomer has been extracted, the optical density will be:

$$D_{n\tau} = D_{n2\tau} + k \cdot D_{n1\tau} \qquad (4)$$

where D_{n1o}, D_{n2o} are the relative optical densities of absorption for proper carboxylate and carboxyl groups before extraction; $D_{n1\tau}$, $D_{n2\tau}$ are the relative optical densities of carboxylate and carboxyl groups after extraction in ethanol (Fig. 1).

The grafting efficiency for LDPE-g-IA$^-$M$^+$ was found to be as follows:

$$\alpha = (D_{n\tau} / D_{no}) \cdot 100\% \qquad (5)$$

The comparison of IR-spectra of LDPE, LDPE-g-IA, and LDPE-g-IA$^-$M$^+$ (Fig. 2) shows that qualitative differences in them are only found in the regions of carboxylate and carbonyl absorption at 1500–1800 cm^{-1}.

It should be noted that the frequency pattern and absorption band intensity of salt groups are sensitive to the cation origin. For instance, the IR-spectrum of LDPE-g-IA$^-$Zn$^+$ at frequencies 1500–1700 cm^{-1} has a complex absorption band consisting of three components with absorption maxima at 1540 cm^{-1} (neutralization of ZnO) or 1550 cm^{-1} (neutralization of Zn(OH)$_2$), 1610 cm^{-1} (neutralization of ZnO) or 1600 cm^{-1} (neutralization of Zn(OH)$_2$), and 1650 cm^{-1} (neutralization of ZnO) or 1653 cm^{-1} (neutralization of Zn(OH)$_2$). In the IR-spectrum of LDPE-g-IA$^-$Mg$^+$, within the frequency range of carboxylate absorption, the band is split in two components with maxima at 1612 cm^{-1} and 1645 cm^{-1} for the two types of NA containing magnesium. The carbonyl absorption band with the maximum at 1720 cm^{-1}, found along with the carboxylate absorption band, evidences a partial neutralization in spite of excess NA. It is only with

TABLE I
Effect of Neutralization of Carboxyl Groups on Characteristics of Modified LDPE for
Two-Step Process of Neutralization

Test materials (concentration of NA and DCP, wt %)	α, %	D', rel. unit	MFI, $g/10$ min
1. LDPE-g-IA (0.15% DCP)	65.0		15.5
2. LDPE-g-IA (0.3% DCP)	87.1		4.7
3. LDPE-g-IA$^-$Mg$^+$ (70% MgO, 0.15% DCP)	77.6	0.12	18.5
4. LDPE-g-IA$^-$Mg$^+$ (150% MgO, 0.15% DCP)	79.8	0.15	17.6
5. LDPE-g-IA$^-$Zn$^+$ (70% ZnO, 0.15% DCP)	80.7	0.36	18.3
6. LDPE-g-IA$^-$Zn$^+$ (150% ZnO, 0.15% DCP)	83.0	0.42	19.0
7. LDPE-g-IA$^-$Mg$^+$ (70% Mg(OH)$_2$, 0.15% DCP)	78.8	0.10	18.4
8. LDPE-g-IA$^-$Mg$^+$ (150% Mg(OH)$_2$, 0.15% DCP)	80.8	0.19	16.4
9. LDPE-g-IA$^-$Zn$^+$ (70% Zn(OH)$_2$, 0.15% DCP)	76.3	0.38	19.0
10. LDPE-g-IA$^-$Zn$^+$ (150% Zn(OH)$_2$, 0.15% DCP)	77.9	0.79	16.4
11. LDPE-g-IA$^-$Mg$^+$ (70% MgO, 0.3% DCP)	90.3		10.1
12. LDPE-g-IA$^-$Mg$^+$ (150% MgO, 0.3% DCP)	93.6		9.0
13. LDPE-g-IA$^-$Zn$^+$ (70% ZnO, 0.3% DCP)	90.1		6.1
14. LDPE-g-IA$^-$Zn$^+$ (150% ZnO, 0.3% DCP)	90.5		9.3
15. LDPE-g-IA$^-$Mg$^+$ (70% Mg(OH)$_2$, 0.3% DCP)	88.2		8.2
16. LDPE-g-IA$^-$Mg$^+$ (150% Mg(OH)$_2$, 0.3% DCP	90.7		7.5
9. LDPE-g-IA$^-$Zn$^+$ (70% Zn(OH)$_2$, 0.3% DCP)	90.4	0.36	7.0
10. LDPE-g-IA$^-$Zn$^+$ (150% Zn(OH)$_2$, 0.3% DCP)	92.8	0.70	5.8

D' is the relative optical density of absorption maximum in the carboxylate region. MFI is the melt flow index.

Zn(OH)$_2$ that neutralization can be assumed as complete since there is no absorption band at 1720 cm^{-1} in IR-spectrum of LDPE-g-IA$^-$M$^+$ (Fig. 2).

The absorption intensity at 1500–1670 cm^{-1} and at 1700–1800 cm^{-1} for specimens subjected to extraction in ethanol were found to mainly depend on NA quantity added to the reaction system. If NA quantity was increased, the absorption intensity also increased at 1500–1670 cm^{-1} (Tables I and II), but decreased at 1700–1800 cm^{-1}. This is evidently caused by variations in the degree of neutralization of acid groups. The results obtained unambiguously point out to neutralization reactions that occur between NA and IA,

grafted onto LDPE macromolecules, at the conditions of our experiment.

The complex behavior of the carboxylate absorption suggests that IA and NA salts contain both ionized and unionized metal–carboxyl groups. According to works in the literature,[20,21] the higher frequency absorption at 1645–1655 cm^{-1} should be related to valence vibrations C=O in metal–carboxyl groups. The bands at 1612, 1600, and 1550 cm^{-1} belong to nonsymmetrical and symmetrical vibrations of $\left(-C\diagdown_O^{O}\right)^-$ groups.

It is also evident that absorption intensity in the discussed regions of carboxyl and carboxylate absorp-

TABLE II
Effect of Neutralization of Carboxyl Groups on Characteristics of Modified LDPE for
One-Step Process of Neutralization

Test materials (concentration of NA and DCP, wt %)	α, %	D', rel. unit	MFI, $g/10$ min
1. LDPE-g-IA$^-$Mg$^+$ (70% MgO, 0.15% DCP)	76.3	0.13	14.5
2. LDPE-g-IA$^-$Mg$^+$ (150% MgO, 0.15% DCP)	79.0	0.19	13.7
3. LDPE-g-IA$^-$Zn$^+$ (70% ZnO, 0.15% DCP)	79.4	0.39	11.5
4. LDPE-g-IA$^-$Zn$^+$ (150% ZnO, 0.15% DCP)	83.5	0.51	9.6
5. LDPE-g-IA$^-$Mg$^+$ (70% Mg(OH)$_2$, 0.15% DCP)	78.2	0.12	13.1
6. LDPE-g-IA$^-$Mg$^+$ (150% Mg(OH)$_2$, 0.15% DCP)	82.0	0.34	11.3
7. LDPE-g-IA$^-$Zn$^+$ (70% Zn(OH)$_2$, 0.15% DCP)	78.9	0.40	13.0
8. LDPE-g-IA$^-$Zn$^+$ (150% Zn(OH)$_2$, 0.15% DCP)	81.7	0.96	9.1
9. LDPE-g-IA$^-$Mg$^+$ (70% MgO, 0.3% DCP)	90.6	0.08	3.2
10. LDPE-g-IA$^-$Mg$^+$ (150% MgO, 0.3% DCP)	94.8	0.10	4.4
11. LDPE-g-IA$^-$Zn$^+$ (70% ZnO, 0.3% DCP)	95.6	0.28	4.6
12. LDPE-g-IA$^-$Zn$^+$ (150% ZnO, 0.3% DCP)	96.1	0.38	3.0
13. LDPE-g-IA$^-$Mg$^+$ (70% Mg(OH)$_2$, 0.3% DCP)	94.4	0.08	3.2
14. LDPE-g-IA$^-$Mg$^+$ (150% Mg(OH)$_2$, 0.3% DCP	95.9	0.20	2.5
15. LDPE-g-IA$^-$Zn$^+$ (70% Zn(OH)$_2$, 0.3% DCP)	93.2	0.36	4.1
16. LDPE-g-IA$^-$Zn$^+$ (150% Zn(OH)$_2$, 0.3% DCP)	95.2	0.84	3.8

D' is the relative optical density of absorption maximum in the carboxylate region. MFI is the melt flow index.
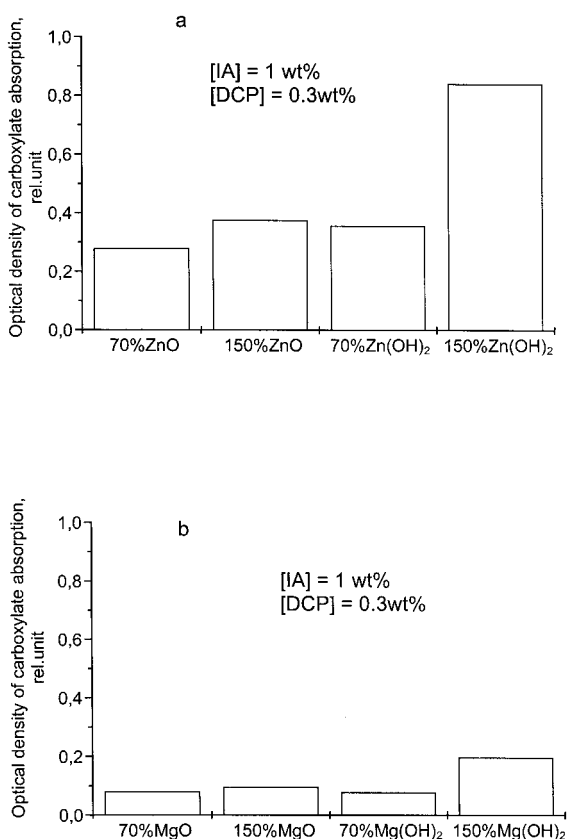
Figure 3 Effect of carboxyl groups neutralized by (a) zinc compounds and (b) magnesium compounds on optical density of carboxylate absorption

tion can serve as a criterion of neutralizing activity of NA. Thus, the comparison of optical densities of absorption bands in carboxylate region for LDPE-g-IA$^-$M$^+$ specimens prepared with equal stoichiometric quantities of NA, could be arranged as follows: Zn(OH)$_2$ > ZnO > Mg(OH)$_2$ > MgO (Tables I and II). In spite of the fact that NA containing magnesium must be more chemically active from the viewpoint of kinetics of typical acid-base interactions than NA containing zinc, our results show that NA leads to a lower degree of neutralization (Tables I and II). One of probable reasons of this can be larger average particle size of Mg(OH)$_2$ and MgO in comparison with zinc oxide and hydroxide. As a result, the area of contact between reagents must decrease. This fact is important for heterogeneous reactions. Besides, Zn^{+2} ions, unlike those of Mg^{+2}, are capable of active coordination interaction with carboxylate ions of IA, which is most likely important for reaction occurring rather in molten polymer than in aqueous media.

The depth at which neutralization takes place largely depends on the processing conditions. For instance, in case of one-step process (neutralization simultaneously with grafting) the neutralizing effect appears stronger than for two-step process (neutraliza-

tion of previously prepared LDPE-g-IA). This most likely could be explained by better contacting NA and IA molecules when grafted by the one-step process. In the latter case, LDPE granules coated with DCP and powdered with IA were treated with NA fine powder. In case of the two-step process, powdered NA is first dispersed in molten LDPE-g-IA where crosslinks are formed between molecules thus increasing its viscosity in comparison with molten initial LDPE. The dispersion efficiency of NA particles in such a melt, hence the development of molecular contact with IA, will be worse than in case of the one-step process. It should be noted that during the two-step neutralization of LDPE-g-IA that was prepared with increased concentration of peroxide (0.3 wt %) added to the initial reaction mixture, which leads to a high degree of crosslinking in the grafted PE,[3,6] an absorption band at 1500–1670 cm^{-1} in IR-spectra of these specimens was only observed if zinc hydroxide served as the NA. With other NA, no salt compounds were detected by the IR-spectroscopy technique (Table I). Therefore, we used only samples prepared by the one-step procedure in our further investigations (when the thermal and structural analyses were performed). Information
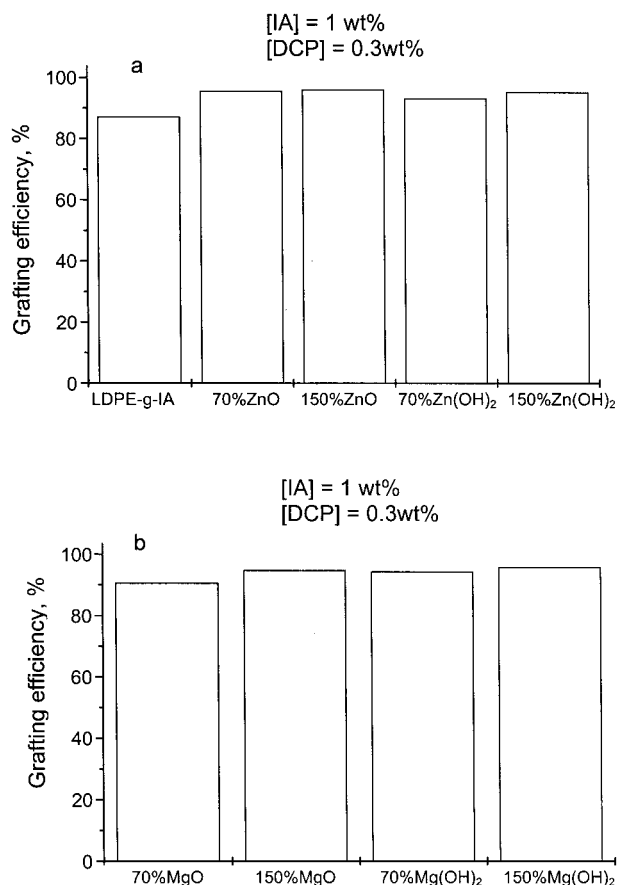

Figure 4 Effect of carboxyl groups neutralized by (a) zinc compounds and (b) magnesium compounds on grafting efficiency of IA onto LDPE.
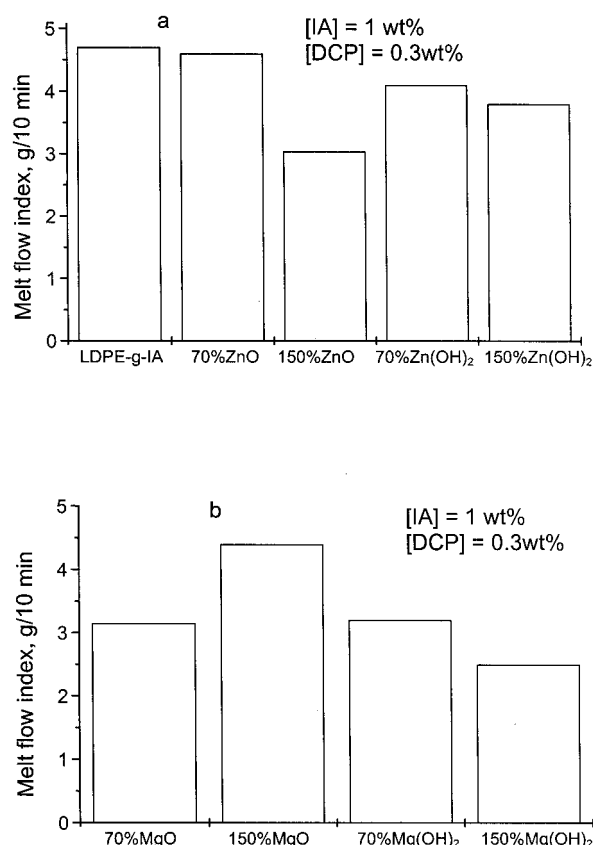
Figure 5 Effect of carboxyl groups neutralized by (a) zinc compounds and (b) magnesium compounds on the melt flow index for modified LDPE.

on the optical density of the band in the region of carboxylate absorption, efficiency of grafting, and MFI of the polymer is given in Table II and Figures 3–5.

The one-step process of grafting and neutralization of IA ensures higher grafting efficiency (Tables I and II, Fig. 4). This result is typical of all NAs tested. The

explanation may be as follows: increased reactivity of IA salts in grafting reactions that follow the free-radical mechanism along with activated break-down of peroxide initiator (DCP) caused by NA lead to this. A similar result was obtained by other researchers[22] when they grafted Na-salt of maleic acid onto PE. The grafting efficiencies little varies when different NA were added, though ZnO gave somewhat higher α values (Table II, Fig. 4).

It should be noted that the two-step grafting-and-neutralization process also resulted in higher α values for LDPE-g-IA$^-$M$^+$ against LDPE-g-IA (Table I). If the peroxide initiator underwent total breakdown in the course of LDPE-g-IA preparation, we believe that additionally grafted IA at the neutralization stage results from mechanical activation of formation of PE macroradicals and their reaction with the monomer.[3,5]

The analysis of variations in MFI caused by NA (Fig. 5, Tables I and II) shows that these variations are, as a rule, small and depend on the preparation method of polymer specimens, as well as on NA and DCP concentrations. The two-step neutralization leads to LDPE-g-IA$^-$M$^+$ with higher MFI, whereas the one-step process, on the contrary, leads to lower MFI in comparison with LDPE-g-IA. We believe that the two-step process of neutralization leads to higher MFI owing to mechanical breakdown of macromolecules. The formed macroradicals initiate additional grafting of IA onto the macromolecules thus increasing the grafting efficiency. Most likely, variations in MFI for molten LDPE-g-IA$^-$M$^+$ can be caused by the effect of NA on the crosslinking degree of macromolecules during grafting. The effect of neutralized carboxyl groups on the intensity of intermolecular interactions in molten polymer should also be taken into account, along with the effect of excessive unreacted metal oxides and hydroxides upon the rheological behavior of the melt.

TABLE III
DSM Data for One-Step Process of Neutralization

Test materials (concentration of NA and DCP, wt %)	T_m, °C	T_{cr}, °C	ΔI, rel. unit
1. LDPE	105	88	1.0
2. LDPE-g-IA (0.15% DCP)	106	89	0.82
3. LDPE-g-IA (0.3% DCP)	106	89	0.78
4. LDPE-g-IA$^-$Zn$^+$ (70% ZnO, 0.15% DCP)	103	88	0.65
5. LDPE-g-IA$^-$Zn$^+$ (150% ZnO, 0.15% DCP)	105	89	0.72
6. LDPE-g-IA$^-$Mg$^+$ (70% Mg(OH)$_2$, 0.15% DCP)	105	91	1.20
7. LDPE-g-IA$^-$Mg$^+$ (150% Mg(OH)$_2$, 0.15% DCP)	107	88	0.81
8. LDPE-g-IA$^-$Zn$^+$ (70% Zn(OH)$_2$, 0.15% DCP)	106	89	0.83
10. LDPE-g-IA$^-$Zn$^+$ (150% Zn(OH)$_2$, 0.15% DCP)	106	89	0.87
11. LDPE-g-IA$^-$Zn$^+$ (70% ZnO, 0.3% DCP)	105	89	0.78
12. LDPE-g-IA$^-$Zn$^+$ (150% ZnO, 0.3% DCP)	107	89	0.77
13. LDPE-g-IA$^-$Mg$^+$ (70% Mg(OH)$_2$, 0.3% DCP)	104	87	0.66
14. LDPE-g-IA$^-$Mg$^+$ (150% Mg(OH)$_2$, 0.3% DCP)	105	89	0.66
15. LDPE-g-IA$^-$Zn$^+$ (70% Zn(OH)$_2$, 0.3% DCP)	105	89	0.75
16. LDPE-g-IA$^-$Zn$^+$ (150% Zn(OH)$_2$, 0.3% DCP)	105	88	0.76

T_m, T_{cr} are the melting and crystallization temperatures, respectively; ΔI_{cr} is the relative degree of crystallization.

TABLE IV
Derivatography Data for One-Step Process of Neutralization

Test materials (concentration of NA and DCP, wt%)	T_{bd}, °C	T_{10}, °C	T_{50}, °C	T_0, °C
1. LDPE	385	430	472	195
2. LDPE-g-IA (0.15% DCP)	382	408	468	182
3. LDPE-g-IA$^-$Mg$^+$ (70% MgO, 0.15% DCP)	385	410	470	198
4. LDPE-g-IA$^-$Mg$^+$ (150% MgO, 0.15% DCP)	380	420	470	192
5. LDPE-g-IA$^-$Zn$^+$ (70% ZnO, 0.15% DCP)	390	428	472	200
6. LDPE-g-IA$^-$Zn$^+$ (150% ZnO, 0.15% DCP)	390	420	470	200
7. LDPE-g-IA$^-$Mg$^+$ (70% Mg(OH)$_2$, 0.15% DCP)	386	422	470	195
8. LDPE-g-IA$^-$Mg$^+$ (150% Mg(OH)$_2$, 0.15% DCP)	380	424	475	198
9. LDPE-g-IA$^-$Zn$^+$ (70% Zn(OH)$_2$, 0.15% DCP)	397	423	470	190
10. LDPE-g-IA$^-$Zn$^+$ (150% Zn(OH)$_2$, 0.15% DCP)	362	403	468	187

T_{bd}, T_{10}, T_{50}, T_0 are the temperature of beginning of degradation, weight losses of 10% and 50%, and beginning of oxidation, respectively.

Thermal and relaxation characteristics of LDPE-g-IA$^-$M$^+$

The DSC data show that IA grafted on LDPE macromolecules shifts the melting and crystallization peaks by 1°C to the higher-temperature region. The crystallinity of LDPE-g-IA decreases as determined from variations in the area under the crystallization peak of the polymer (Table III). These changes result from the fact that grafted IA followed by crosslinking disturb the polymer chain's regularity thus forming steric and kinetic barriers against macromolecular packing.

When carboxyl groups were neutralized with grafted IA, the temperature locations of melting and crystallization peaks shift but negligibly in comparison with LDPE-g-IA (Table III). The crystallinity of the specimens remained on the same level as in LDPE-g-IA. It is only with LDPE-g-IA$^-$M$^+$ in which the acid had been partially neutralized (70% of Mg(OH)$_2$ was neutralized), the relative degree of crystallinity appeared higher than that in the initial LDPE (Table III). It is most likely, that at the conditions of our experi-

ment, Mg(OH)$_2$ could act as a nucleus-forming agent and accelerate crystallization; the highest crystallization temperature was observed with this substance.

The derivatography findings show that neutralization of grafted carboxyl groups improves the thermal stability of the functionalized PE (Table IV). Especially substantial effect was achieved at temperature T_0, i.e., the beginning of oxidation; its maximal values could be reached with ZnO and Mg(OH)$_2$. Thus, chemical neutralization of grafted IA results in products of improved resistance to thermal oxidation and thermal stability of the melt. This conclusion is of practical importance to the opportunities for widening the application range for PE modified by grafting IA, while preparing polymer blends to be compounded, processed and used at elevated temperatures.

The relaxation spectra of LDPE-g-IA$^-$M$^+$ showing the temperature dependence of the mechanical loss tangent are qualitatively similar to that for the initial LDPE (Fig. 6). These spectra clearly show two maxima, one at −125°C, the other at −27°C. The −125°C
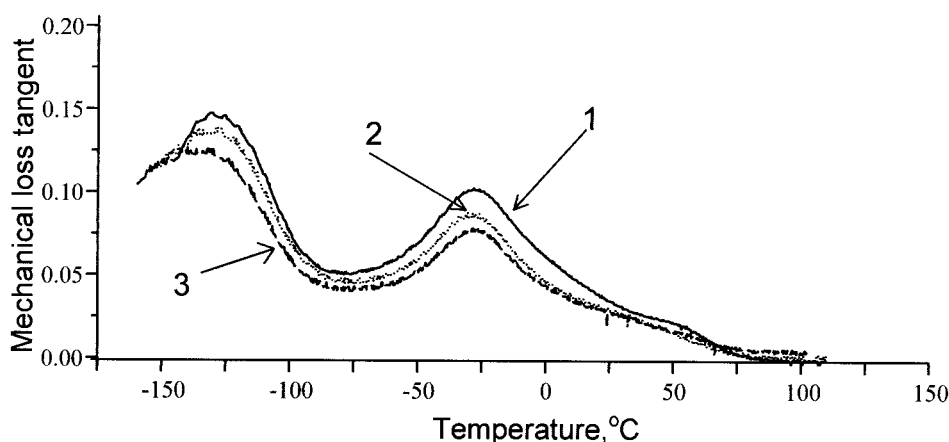

Figure 6 Temperature dependence of mechanical loss tangent for LDPE (1), LDPE-g-IA with 0.3 wt % DCP (2), and LDPE-g-IA$^-$M$^+$ with 150% Mg(OH)$_2$, 0.3 wt % DCP (3).

TABLE V
The Relaxation Spectrometry Data (One-Step Process of Neutralization)

Test materials (concentration of NA and DCP, wt %)	β = relaxation, °C	α = relaxation, °C
1. LDPE	−125	−27
2. LDPE-g-IA (0.15% DCP)	−130	−28.3
3. LDPE-g-IA (0.3% DCP)	−130	−28.3
LDPE-g-IA$^-$Zn$^+$ (70% ZnO, 0.15% DCP)	−130	−28
LDPE-g-IA$^-$Zn$^+$ (70% ZnO, 0.3% DCP)	−130	−28.3
LDPE-g-IA$^-$Zn$^+$ (150% ZnO, 0.15% DCP)	−130	−30
LDPE-g-IA$^-$Zn$^+$ (150% ZnO, 0.3% DCP)	−130	−30
LDPE-g-IA$^-$Zn$^+$ (150% Zn(OH)$_2$, 0.15% DCP)	−130	−30
LDPE-g-IA$^-$Zn$^+$ (150% Zn(OH)$_2$, 0.3% DCP)	−130	−29
LDPE-g-IA$^-$Mg$^+$ (150% Mg(OH)$_2$, 0.15% DCP)	−130	−30
LDPE-g-IA$^-$Mg$^+$ (150% Mg(OH)$_2$, 0.3% DCP)	−132	−28

maximum can be explained by unfreezed mobility of side branches in the main chain (β-relaxation).[23] The −27°C maximum can be explained by devitrification of segments of the main chain within the amorphous regions of PE (α-relaxation).[23] It is shown in Table V that chemical modification of LDPE shifts the two peaks towards lower temperature region (for β-transition by 5–7°C; for (α-transition by 1–3°C).

The shift of β-transition towards the lower temperature region could result, most likely, from greater branching of PE owing to secondary reactions when IA is grafted onto LDPE.[3,6] The shift of α transition towards the lower temperature region could result from weakened energy of interaction between chain segments in PE owing to lower regularity of macro chains in the modified polymer (Table V).

CONCLUSIONS

It was found that the addition of neutralizing agents (oxides and hydroxides of zinc and magnesium) to the initial reaction mixture (LDPE + IA + DCP) results in LDPE-g-IA with partially or totally neutralized carboxyl groups. The physical structure of LDPE-g-IA does not suffer marked changes. In the order of decreasing neutralizing activity the tested NAs can be arranged as follows: Zn(OH)$_2$ > ZnO > Mg(OH)$_2$ > MgO. The addition of NA to the initial reaction mixture improves the grafting efficiency of IA towards LDPE. If NA is added to LDPE-g-IA, the IA-carboxyl groups are more difficult to neutralize than in the case where NA is added to the initial reaction mixture.

The modified PE with neutralized carboxyl groups of grafted IA improved thermal stability and higher resistance to thermal oxidation, as compared with LDPE-g-IA.

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