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Free-radical grafting of itaconic acid onto LDPE by reactive extrusion: I. Effect of initiator solubility

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Abstract

The effect of the peroxide initiator nature on the grafting of itaconic acid (IA) onto low-density polyethylene (LDPE) was investigated in the course of the reactive extrusion. It was shown that at other equal conditions, the solubility of the peroxide initiator in the molten polymer is most important in the IA grafting onto LDPE. The thermal stability of peroxide initiators is also important. At the synthesis conditions of preparing the grafted products by the reactive extrusion, peroxides, which decompose at temperatures far below the IA melting point (also in the feed zone of the extruder), can be used to initiate grafting reactions. It is very probable that radicals formed from peroxide decomposition interact first with LDPE macromolecules, while the formed macroradicals initiate IA grafting reactions. Peroxides, which are easily dissolved in LDPE, are recommended for initiating the efficient grafting reactions. The closer the thermodynamic affinity between the peroxide and the monomer, the less the efficiency of grafting. Higher transportation velocities of the reactive blend in the extruder-reactor intensify LDPE crosslinking, thus lowering the IA grafting efficiency. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Itaconic acid; Grafting; Organic peroxide

1. Introduction

Functionalisation of olefin polymers and copolymers by grafting onto their macromolecules of unsaturated monomers, which contain polar functional groups, is highly important for processing polymer blends, preparation of polyolefin with improved adhesion towards solid surfaces, and for polymer waste processing. In most cases, the grafting is carried out in molten polyolefin during the reactive extrusion [1]. Usually, this process is run in the presence of substances being a source of free radicals, viz. organic peroxides [1–3]. During the reactive extrusion, the reactions take place in continuously moving polymer melt, within the mechanical stress field, at variable temperatures, from the feed zone to the discharge zone, during a relatively short span of time. Under such conditions, the course of grafting reactions and concomitant chemical conversions can be affected by chemical activity and by solubility of the initiators and other additives in the initial components of the polymer/monomer reactive blend [4,5]. The solubility of the components may be especially important for relatively poor mixing that can be observed, e.g. in the single-screw extruders [6].

In previous articles [7–9], grafting of itaconic acid (IA) to LDPE by reactive extrusion was described. In the melt, IA and LDPE form a heterogeneous system owing to their obvious thermodynamic immiscibility (the solubility parameters of IA and LDPE are 24.6 and 16.1 $(\mathrm{J\,cm^{-3}})^{0.5}$, respectively). Therefore, the LDPE–IA system is convenient for analysing the distribution effects of peroxides between components of the reactive blend on the course of the grafting reaction and associate processes. This work analyses the role of organic peroxide initiators in IA–LDPE grafting reactions; also, the grafting effect of stabilisers that follow the principle of free-radical acceptance is examined.

2. Experimental

2.1. Materials

The following materials were used in this work: low-density polyethylene (LDPE) (supplied by “Polimer”, Novopolotsk Belarus: Grade 15803-020; GOST 16337-77; density 0.92 $\mathrm{g\,cm^{-3}}$; melting point 105°C); IA (Chemical Division of Pfizer Co., USA); organic peroxides of different

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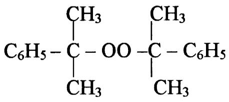
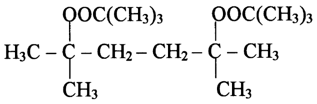
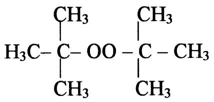
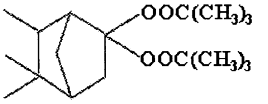
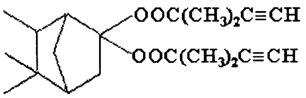
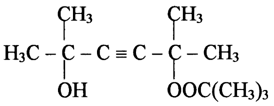
Table 1
Characteristics of peroxide initiators

Peroxide	Abbreviated marking	Structural formula	δ (J cm^{-3})$^{0.5}$	Concentration of active oxygen (%)
Dicumyl peroxide	DCP	 $C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-OO-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5$	17.4	5.92
2,5-dimethyl-2,5-di(*tert*-butyl peroxy)-hexane	L-101	 $H_3C-\underset{CH_3}{\overset{OOC(CH_3)_3}{C}}-CH_2-CH_2-\underset{CH_3}{\overset{OOC(CH_3)_3}{C}}-CH_3$	15.5	11.03
Tert-butyl peroxide	TBP	 $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OO-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$	15.3	10.95
2,2-di(*tert*-butyl peroxy)-5,5,6-trimethyl bicyclo [2.2.1] heptane	D-1		16.1	10.17
2,2-di(3-methyl-1-butine-3-yllperoxy)-5,5,6-trimethyl bicyclo [2.2.1] heptane	D-2		16.3	9.57
2,5-dimethyl-2-hydroxy-5-*tert*-butyl peroxy-3-hexine	OP-2	 $H_3C-\underset{OH}{\overset{CH_3}{C}}-C\equiv C-\underset{OOC(CH_3)_3}{\overset{CH_3}{C}}-CH_3$	19.1	7.5

structures, viz. monoperoxides—*tert*-butyl peroxide (TBP), dicumyl peroxide (DCP) (supplied by "Orgsintez", Russia); 2,5-dimethyl-2-hydroxy-5-*tert*-butyl peroxy-3-hexine (OP-2) [10]; diperoxides: 2,5-dimethyl-2,5-di(*tert*-butyl peroxy)-hexane (L-101) (ELF Atochem, France), 2,2-di(*tert*-butyl peroxy)-5,5,6-trimethyl bicyclo [2.2.1] heptane (D-1) and 2,2-di(3-methyl-1-butine-3-yllperoxy)-5,5,6-trimethyl bicyclo [2.2.1] heptane (D-2) [11]; and organic stabilisers of phenolic type—ester of 3,5-di-*tert*-butyl-4-hydroxyphenyl-propanoic acid and pentaerythritol (Irganox 1010, I-1010, Ciba Geigy, Switzerland).

Details about the peroxides used in this work are listed in Table 1. Values of the solubility parameters (δ) were calculated following the group contribution principle [12–14]

$$\delta = \sqrt{\frac{\sum_i \Delta E_i}{N_a \sum_i \Delta V_i}} \tag{1}$$

where ΔE_i is the contribution of every atom and type of the intermolecular interaction in the molar cohesion energy of the substance; N_a is the Avogadro number; $\sum_i \Delta V_i$ is the van der Waals volume of an elementary unit of a molecule being the sum of van der Waals volumes of the atoms ΔV_i; and ΔE_i and ΔV_i are the tabular values taken from Ref. [14].

The values of δ were calculated for 25°C (298 K). It is quite understandable that variations in the temperature will change δ-values for the peroxides.

The mode of δ-temperature changes, however, was found to be similar for both the polymers and the low molecular weight substances, and could be expressed by the following relationship:

$$\log \delta_T = \log \delta_{298} - \alpha k(T - 298) \tag{2}$$

were δ_T and δ_{298} are the δ-values at a temperatures T and 298 K; k is the coefficient ($k \approx 1$ for the polyolefin and $k \approx 1.25$ for the peroxides and the monomer (IA) [15,16]; and α is the thermal (linear) expansion coefficient. Therefore, the solubility of the peroxides and IA in LDPE, characterised by the solubility parameters at 25°C, are objective enough. The calculated values for the LDPE and IA solubility parameters

Table 2
Derivatograph data on thermal stability of peroxides and their half-life time in hydrocarbon environment

Peroxide	DTG			TG Weight loss (%)	DTA			Decomposition parameters for peroxide in hydrocarbon environment	
	Beginning of decomposition peak (°C)	Completion (°C)	Maximum (°C)		Melting point (°C)	Exopeak (°C)			
						Beginning	Maximum	T (°C)	$\tau_{0.5}$, min
DCP	131	202	162	74.5	43	131	162	160	4–7
L-101	118	176	155	94.0	–	123	162	180	0.9
TBP	15[a]	125[a]	103[a]	96.0[a]	–	30[a]	98[a]	160	6–8
D-1	95	125	117	84.0	52	96	118	180	0.6
D-2	85	110	104	86.0	40	86	104	160	22–25
OP-2	130	200	170	88.0	–	133	172	180	2.3

[a] Parameters characterising processes of evaporation and partial decomposition of TBP.

are 16.1 and 26.4 (J cm^{-3})$^{0.5}$, respectively, and for I-1010—19.34 (J cm^{-3})$^{0.5}$.

It should be noted that the δ-value calculated from expression (1) correlates quite well (error does not exceed 10%) with the experimental values obtained by measuring the vaporisation heat of the substances. It is reported in Ref. [17], that the calculated δ-values, for which the absolute error is ± 0.1 (J cm^{-3})$^{0.5}$, are, in many cases, more accurate than the experimental ones.

2.2. Preparation of test specimens

In most cases, the grafting reactions were run in a single-screw extruder (screw diameter 36 mm, $L/D = 20$) at the following regime: 27 rev/min (the shearing rate was about 30 s^{-1}); temperatures—zone I = 160°C; zones II, III and IV = 185°C. In addition, static and dynamic mixers described elsewhere [7] were used as extruder-reactors if the grafting experiments were run in the presence of a stabiliser. The shearing rate in the static mixer was 50 s^{-1}. It is stated in our previous paper [9] that the main relationships that describe the courses of the grafting reactions as well as secondary processes, and also the quantitative yield of LDPE-*g*-IA, when the single-screw extruder-reactor and the reactor-based Brabender plastograph with a static mixer were used, are similar. Because of this, products obtained by use of these extruders at equal thermal conditions are comparable and this procedure is applicable.

In order to prepare a reactive blend, the LDPE granules were first covered by 1 wt% IA powder and run through the single-screw extruder at 125–135°C. The extrudate was then cooled, ground and dried. No grafting of IA to LDPE took place at these conditions. The resultant granulate was treated subsequently with a peroxide solution or with a solution of a mixture of the peroxide with a stabiliser in acetone, then the granules were stirred to completely evaporate the solvent. Then the granules were fed into the extruder-reactor and grafting was performed, while nitrogen was continuously supplied to the feed hopper. After leaving the extruder, the melt was cooled in water and ground, forming new granules.

2.3. Characterisation

The grafting efficiency, i.e. the ratio of grafted acid to its total amount, added to the polymer, was used as the parameter describing the course of the grafting reaction. The efficiency of grafting was determined by the absorptive IR-spectroscopy technique based on the analysis of IA added to the initial LDPE, and that in LDPE extracted in ethanol at 70°C [7,18].

The polymer melt viscosity was evaluated from the melt flow index (MFI), which was determined at 190°C and a 10 kg load, using the IIRT-AM instrument (Ekodatchik Co., Tula, Russia). Thermal decomposition of the peroxides was examined using derivatograph Q-1500 (MOM, Budapest, Hungary) at the heating rate of 5°C/min for 100 mg weight of the sample.

3. Results and discussion

3.1. Effect of peroxide initiators

Peroxides D-1 and D-2, having the solubility parameter (δ) similar to that of the polymer (Table 1), possess the highest solubility in LDPE. The δ value of L-101 approaches that of LDPE, which fact implies a high solubility of this peroxide in the molten polymer. As it is reported in a paper [17], substances are thermodynamically miscible in the absence of strong specific interactions between them, if their δ-values differ by less than 2 (J cm^{-3})$^{0.5}$. The peroxide OP-2 solubility parameter is much higher than that of LDPE. Besides, it contains a hydroxyl group, and this fact should provide for a better thermodynamic affinity between OP-2 and the monomer [17].

The analysis of derivatograph findings (Table 2) shows significant differences in the thermal stability of the peroxides used here. It should be noted that more accurate data were obtained for solid peroxides, e.g. DCP, D-1 and D-2, for which there was a good coincidence in the temperatures of the beginning of decomposition and the maximum decomposition rate, as indicated by DTG and DTA curves. For liquid peroxides OP-2 and L-101, there was observed

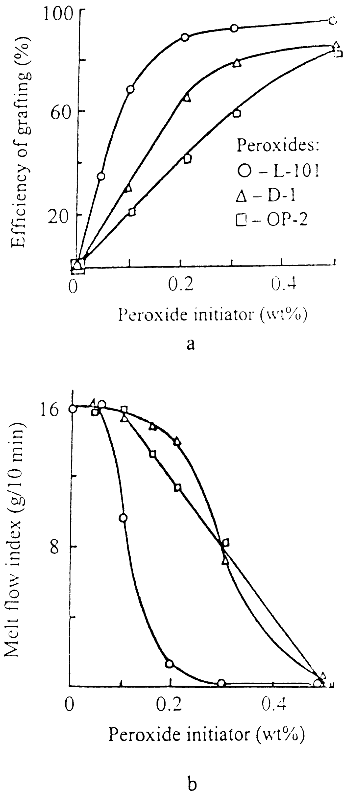


Fig. 1. Effect of peroxide concentration on: (a) grafting efficiency; and (b) melt flow index. The single-screw extruder was operated at 27 rev/min.

some shifting in maxima on DTG and DTA curves towards the high-temperature region, associated, probably, with their volatility. It was rather difficult to obtain reliable data on thermal decomposition of *tert*-butyl peroxide, because it was highly volatile during heating. Dicumyl peroxide and acetylene hydroxy-peroxide OP-2 exhibited the highest thermal stability. They started to decompose with noticeable rates and distinct exothermal effects at 130–133°C. The least stable were anticipated to be gem-diperoxides D-1 and D-2; comparing them, D-1 appeared more thermally stable. The rapid decomposition temperature range for it is between 95 and 125°C; the maximum appeared at 117°C, as found by the DTG procedure. D-2 decomposed between 85 and 110°C with the maximum at 104°C. Thermal decomposition of D-1 in decane was examined by other workers [10] who found that in thermal resistance to a hydrocarbon environment it resembles gem-diperoxides based on cycloaliphatic ketones [19]. The half-life time $(\tau_{0.5})$ for DCP and L-101 in a hydrocarbon environment at 180°C, listed in Table 2, correlate with the derivatograph findings.

We could not determine the half-life time for the peroxides in the moving LDPE melt under shearing conditions. However, as our experiments were run on the extruder with the main reaction zone at 185°C, it is obvious that peroxides DCP, L-101, OP-2, D-1 and D-2 could completely decompose.

Fig. 1 shows concentration dependencies of the grafting efficiencies and the MFI for LDPE-*g*-IA prepared in the presence of peroxides L-101, D-1 and OP-2. Data in Table 1 imply that peroxides L-101 and D-1 must easily dissolve in LDPE. However, their thermal stability differs considerably (Table 2), viz. D-1 quickly decomposes at a relatively low temperature (exopeak begins at 96°C for D-1, while it begins at 123°C for L-101). Thermal stability differs insignificantly for L-101 and OP-2; their solubility parameters, however, differ markedly (Table 1). Fig. 1 shows an identical mode of the concentration dependencies of the grafting efficiency and the MFI for L-101 and D-1, whereas it markedly differs for OP-2. Diperoxide L-101 easily initiates grafting of IA onto LDPE over the whole concentration range (efficiency of grafting changes from 50 to 90% for L-101 concentrations varied between 0.05 and 0.3 wt%). At concentrations over 0.1 wt%, however, it was observed that LDPE was crosslinked, which was accompanied by a significant decrease in the MFI: from 16 g/10 min at 0.05 wt% concentration up to 9.5 g/10 min at 0.1 wt% concentration. When D-1 was used, grafting became more intensive at higher peroxide concentrations, and reached 50–80% at 0.15–0.3 wt% concentrations.

The differences in the effectiveness to initiate the free-radical grafting reactions with IA and in LDPE crosslinking by peroxides L-101 and D-1, which are easily dissolved in LDPE, can, probably, be explained by a lower thermal stability of D-1. The experimental conditions provide a temperature of 160°C in the feed zone of the extruder-reactor. Within this zone, D-1 dissolves in the molten LDPE and fully decomposes to radicals. As the IA melting point is 172°C, D-1 cannot dissolve in acid, being in a solid state; any interactions of radical decay products are hardly possible with it. Therefore, radicals attack polyethylene macromolecules. The macroradicals thus formed begin to react with IA to give grafted products; they also recombine between themselves to result in crosslinking of macromolecules. As diperoxide D-1 ensures relatively high grafted efficiency, one can guess that the formed macroradicals have rather long life times (at the experimental conditions in Fig. 1, the total residence time for the reactive blend in the extruder-reactor (Fig. 2(b)), was 1.5 min). The result obtained offers an essential opportunity to use peroxides with lower thermal stability for initiating the grafting reaction, in the case of unsaturated monomers and polyolefin macromolecules, by means of reactive extrusion.

Peroxide OP-2 exhibited much weaker initiating activity as compared with L-101; this was especially typical of low peroxide concentrations, between 0.05 and 0.25 wt% (Fig. 1(a)); this can be explained by differences in solubility of peroxides in the components of the monomer–polymer reactive blend. Unlike L-101, peroxide OP-2 is insoluble in LDPE. Therefore, with poor dispersion, which is the case with a single-screw extruder [6], the forming and grafting reactions of macroradicals are only feasible in places where OP-2 aggregates have local contacts with the LDPE phase. Since specific interactions can take place between

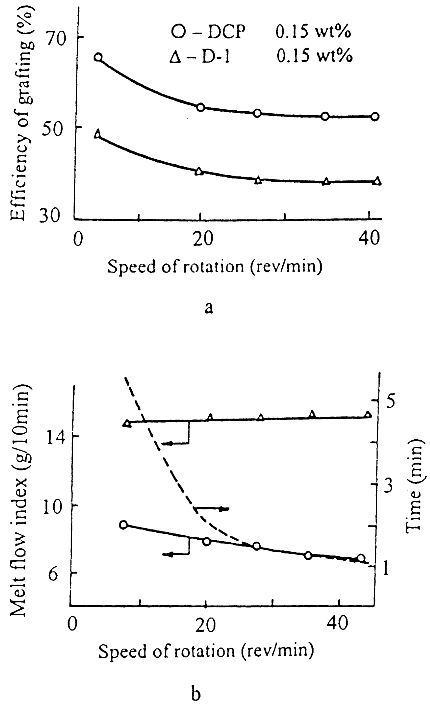


Fig. 2. (a) Grafting efficiency; and (b) melt flow index and residence time for a molten batch in the extruder-reactor versus speed of screw rotation.

OP-2 and IA molecules, IA oligomerisation in molten LDPE can obviously be initiated by radical products of the peroxide decomposition.

Hence, the course of grafting reactions and yield of the grafted product during reactive extrusion depend, mainly, not on the reactivity of the peroxide initiator but on its solubility in the initial components of the reactive system. It is also evident that oligomerisation of the grafted monomer is hardly possible, if the solubility parameters of the monomer and the peroxide differs much.

Effects of other peroxides on the grafting efficiency of IA onto LDPE and the MFI of LDPE-*g*-IA are shown in Table 3. When compared, the data in Table 3 and Fig. 1 indicate that *tert*-butyl had the lowest initiating activity—for 0.1–0.3 wt% concentration, the grafting efficiency was between 11 and 60%; with increasing concentration, the degree of LDPE crosslinking increased significantly.

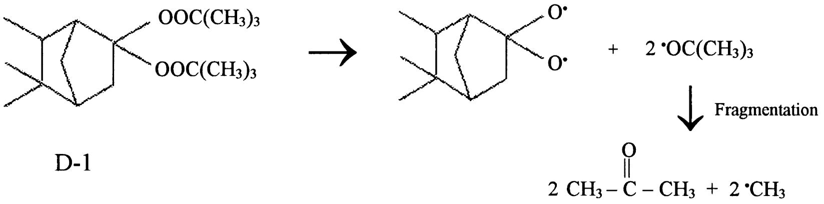
TBP differs from other peroxides by high volatility, low thermal stability (Table 2), and high concentration of active oxygen (Table 1). When it decomposes, the yield of active radicals $\cdot OC(CH_3)_3$ and $\cdot CH_3$ [19] is higher than with the remaining tested peroxides. Therefore, more LDPE macroradicals can, probably, be formed as early as in the extruder's feed zone; these radicals are preferably recombined with each other. Therefore, TBP ensures high yield of the crosslinked polymer at low grafting efficiency of IA.

Dicumyl peroxide resembles diperoxide L-101 in its efficiency in initiating the grafting reaction of IA to LDPE at 0.1–0.3 wt% concentration, as can be seen in Table 3. Somewhat lower grafting efficiency (about 20% at 0.1–0.2 wt% concentrations) with DCP can be explained by a greater affinity between dicumyl peroxide and the monomer (Table 1). It should be noted that within the concentration range between 0.1 and 0.3 wt%, the grafting degree of the polymer is much lower with dicumyl peroxide than with L-101 diperoxide (the MFI are listed in Table 3 and Fig. 1(b)). The decomposition temperature range for DCP is optimal from the IA grafting viewpoint (Table 3). A maximum amount of free radicals should be formed during DCP decomposition when IA is in the molten reactive state. Therefore, despite lower concentration of active oxygen in DCP, as compared with other peroxides (Table 1), DCP efficiently initiates IA grafting and polymer crosslinking (Table 3). Gem-diperoxide D-2, which can be considered as an unsaturated analogue of D-1, exhibits lower initiating activity (Table 3) as compared with D-1. However, if it is used at 0.3 wt% concentration, IA can be efficiently grafted onto LDPE (61%) without polymer crosslinking (the MFI is 13.4 g/10 min at 0.3 wt% concentration; 15.3 g/10 min at 0.1 wt% concentration).

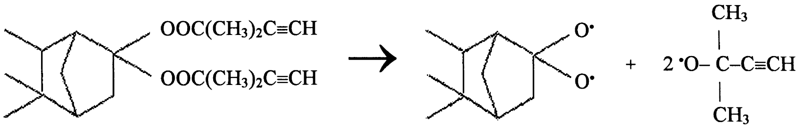
One of the causes leading to lower initiating activity of D-2, as compared with D-1, which are similar in structure and solubility in LDPE, is lower thermal stability of D-2 (Table 2). Another cause may be that D-2 decomposes with the formation of less active radicals. Probable decomposition routes for peroxides D-1 and D-2 at initial stages can be represented as follows [19]:

Table 3
Effect of peroxide on efficiency of grafting and melt flow index of LDPE-*g*-IA

Peroxide	Concentration of peroxide (wt%)	Efficiency of grafting (%)	Melt flow index (g/10 min)
DCP	0.1	49.6	13.2
	0.2	67.4	6.4
	0.3	83.2	2.4
TBP	0.1	11.0	14.0
	0.2	30.4	6.9
	0.3	59.9	2.0
D-2	0.1	24.1	15.3
	0.2	41.1	14.3
	0.3	60.8	13.4



D-1



D-2 A

It is probable that radicals $\cdot OC(CH_3)$ and $\cdot CH_3$, formed during diperoxide D-1 decomposition, possess higher initiating activity in comparison with radical $\cdot OC(CH_3)_2$-C≡CH that is formed during peroxide D-2 decomposition. Biradical A exhibits low activity owing to steric factors [19], and it cannot influence markedly the initiating activity of peroxides.

The differences in the reaction course of grafting and crosslinking, detected for certain peroxides (Fig. 1, Table 3), remained after the rotation speed of the extruder screw was varied within a wide range, the reactive blend transportation speed depends on this speed, and hence on the duration of chemical conversions (Fig. 2). Consequently, the peroxide nature is of prime importance for radical reactions at the present experimental conditions, and not the processing parameters, which influence the duration of interaction between the reactants.

It should be noted that with DCP, which easily initiates IA grafting reaction and macromolecular crosslinking, there was observed a substantial decrease in the MFI, implying an intensive crosslinking in LDPE-*g*-IA system, if the rotation speed of the screw was raised from 7 to 43 rpm (the residence time decreased from 5.3 to 1.05 min), Fig. 2(b). These observations can, probably, be explained as follows. As IA cannot be dissolved in LDPE easily enough, the grafting efficiency might be decreased by shorter reacting time and lack of molecular contact between IA and the formed macroradicals. Therefore, these macroradicals are predominantly consumed in the recombinative reactions with each other leading to crosslinking. For peroxide D-1, exhibiting low thermal stability, decomposition accelerates in the mechanical stress field—in the extruder feed zone—if shearing is intensified by quicker melt transportation. Despite higher free-radical amounts resulting from lower temperature reaction in the feed zone, the crosslinking degree of macromolecules remains in fact unchanged (Fig. 2(b)), while the grafting efficiency decreases, as is the case with DCP, Fig. 2(a).

3.2. Effect of Irganox 1010

In the presence of classical stabilisers, which follow the principle of accepting free radicals, the rate of free-radical reactions was observed to decrease [20]. Other findings were that grafting of maleic anhydride onto polyethylene would be fully inhibited by adding a phenolic stabiliser to the reactive blend [21]. It was reported, however [22], that at certain conditions (higher concentrations and temperatures) the stabilisers' efficiency would sharply decrease and they could sometimes initiate reactions that followed the free-radical mechanism. It was therefore interesting to estimate the effect of stabilisers on grafting of IA onto LDPE.

The experiments were performed on a Brabender plastograph, equipped with a static mixer [7]. Peroxide L-101, which quite easily dissolves in LDPE, was the initiator.

Fig. 3 shows that the effect of the stabiliser depends much on both its and L-101 concentrations, the latter used as the initiator. The grafting efficiency in the presence of I-1010 was somewhat lower as a whole (Fig. 3(a)). At higher concentrations of stabiliser (>0.3 wt%), however, there was observed some improvement in the grafting efficiency. While the stabiliser did not change the grafting rate significantly (Fig. 3(a)), the melt viscosity (higher MFI) of LDPE-*g*-IA prepared with L-101 0.3 wt% was much lower (Fig. 3(b)).

We saw that I-1010, being a classical stabiliser of the phenolic type, used in the reactive blend could not severely inhibit the grafting reaction of IA onto LDPE in the course of reactive extrusion. Stabilisation seems helpful in preparing LDPE-*g*-IA with higher MFI without decreasing the grafting rate much.

It is quite probable that the effect of stabilisers on grafting and the secondary process of LDPE crosslinking depends on their thermodynamic affinity to the reactive blend's components, as is the case with the initiators. Special investigations are required in order to understand this problem and discuss the cause of how stabilisers influence the course of grafting reactions as well as secondary processes. This problem is investigated in more detail in the second part of this paper.

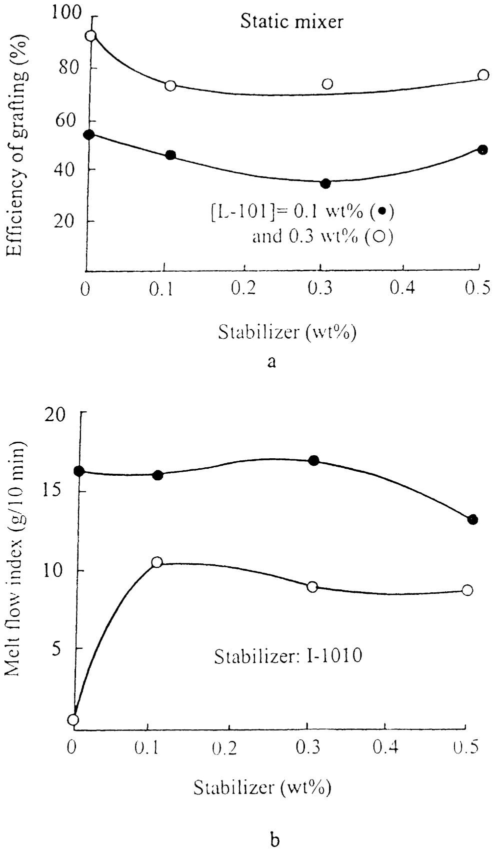


Fig. 3. Effect of Irganox 1010 (I-1010) stabiliser concentration on: (a) the grafting efficiency of IA onto LDPE; and (b) the melt flow index for LDPE-*g*-IA. L-101 peroxide concentrations were 0.1 (●) and 0.3 wt% (○).

4. Conclusions

At other equal conditions, the solubility of peroxide initiator in the molten polymer decisively affects grafting of IA onto LDPE. This conclusion was supported by research findings [23]. The thermal stability of the peroxide initiators is also important. When grafted products were synthesised by reactive extrusion, peroxides that decompose at temperatures much lower than the IA melting point can be used to initiate the grafting reactions also in the feeding zone of the reactor.

It is most probable that radicals formed during peroxide decomposition first interact with LDPE, then the formed macroradicals initiate IA grafting reactions. Peroxides, which can dissolve easily in LDPE, are preferable for effectively initiating the grafting reactions. Increased thermodynamic affinity between the peroxide and monomer would decrease the efficiency of grafting. Higher rates of transportation of the reactive blend in the extruder-reactor both intensifies crosslinking of LDPE and decreases the IA grafting efficiency.

Addition of stabilisers (Irganox 1010) to the reactive blends favours inhibition of the secondary reaction—LDPE crosslinking—and allows to produce LDPE-*g*-IA with high MFI with a relatively low decrease in the grafting efficiency.

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