

# Itaconic Acid Grafting on LDPE Blended in Molten State

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Received 7 September 1996; accepted 13 January 1997

**ABSTRACT:** Grafting of itaconic acid on low density polyethylene in the molten state has been investigated. Static and dynamic mixers assembled on the Brabender plastograph have been used as a blender of reagents and as a chemical reactor. Shear rates were 50 and 100 s<sup>-1</sup>. Dicumyl peroxide; 2,5-dimethyl-2,5-di-(*tert*-butylperoxy)hexane; 2,2-di-(*tert*-butylperoxy)-5,5,6-trimethylbicyclo-[2,2,1]-heptane; 2,2-di(3-methyl-1-butyne-3-peroxy)-5,5,6-trimethylbicyclo[2,2,1]heptane; 2,5-dimethyl-2-hydroxy-5-*tert*-butylperoxy-3-hexyne were used as peroxide initiators of grafting. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1493–1502, 1997

**Key words:** reactive processing; itaconic acid; grafting; LDPE; mechanochemical modification reactive extrusion; dynamic mixer; static mixer

## INTRODUCTION

Research in functionalization of olefin polymers by grafting of unsaturated low molecular compounds containing polar functional groups has been conducted actively. This is related to a potential scope of functionalized polymers application in polymer blends with improved compatibility of components.<sup>1,2</sup>

Grafting reactions can be run in a moving molten polymer in reactive extrusion in the presence of peroxide initiators. In such a case, extruding equipment acts as a reactor, in which chemical processes take place.<sup>3</sup> Despite the fact that much experience has been found in reactive extrusion, only few detailed works can be found in the literature on chemical transformations within moving reactive blends based on molten polymers. Most investigations were done to understand how polyethylene and polypropylene interact with a maleic

anhydride and its derivatives,<sup>4–8</sup> glycidyl methacrylate,<sup>9,10</sup> and acrylic compounds.<sup>11,12</sup> Several patents<sup>13–15</sup> give information on prospects of polyolefin functionalization by grafting itaconic acid (IA). Because of IA grafting, the miscibility of polyolefin with polar engineering thermoplastics (e.g., polyamides, polyalkyleneterephthalate, etc.)<sup>16</sup> improves. Also, adhesional interaction with metals becomes much more active.<sup>17</sup>

This work considers some study of interaction of itaconic acid and low-density polyethylene (LDPE), depending on the blending conditions of molten components, the nature, and concentration of a peroxide initiator.

## EXPERIMENTAL

### Materials

Low-density polyethylene (LDPE) with a density of 0.92 g/cm<sup>3</sup> and a melting temperature 105°C from Polimir company (Polotsk, Belarus) and ita-

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**Table I Characteristics of Peroxide Initiators**

Chemical Name	Trade Name/Producer	Active Oxygen (Approx.) %	Half-Life Time (min)
Dicumyl peroxide	DCP/AO Kazanorgsintez Russia	5.92	30 <sup>a</sup>
2,5-dimethyl-2,5-di-( <i>tert</i> -butylperoxy) hexane	L-101/Elf-Atokem France	11.03	24 <sup>b</sup>
2,2-di-( <i>tert</i> -butylperoxy)-5,5,6-trimethylbiscyclo-[2,2,1]-heptane	D-1/Chemico-Technological Center of Belarus Academy of Sciences	10.17	30 <sup>c</sup>
2,2-di(3-methyl-1-butyne-3-peroxy)-5,5,6-trimethylbiscyclo[2,2,1] heptane	D-2/as above	9.57	75 <sup>d</sup>
2,5-dimethyl-2-hydroxy-5- <i>tert</i> -butylperoxy-3-hexyne	OP-2/as above	7.50	78 <sup>b</sup>

<sup>a</sup> Measured at 140°C.<sup>b</sup> Measured at 145°C.<sup>c</sup> Measured at 120°C.<sup>d</sup> Measured at 102°C.

conic acid (IA)  $\text{CH}_2=\text{C}(\text{COOH})-\text{CH}_2-\text{COOH}$  from Chemical Division Pfizer Inc., NY, were used. Table I lists the properties of peroxide initiators used.

### Apparatus

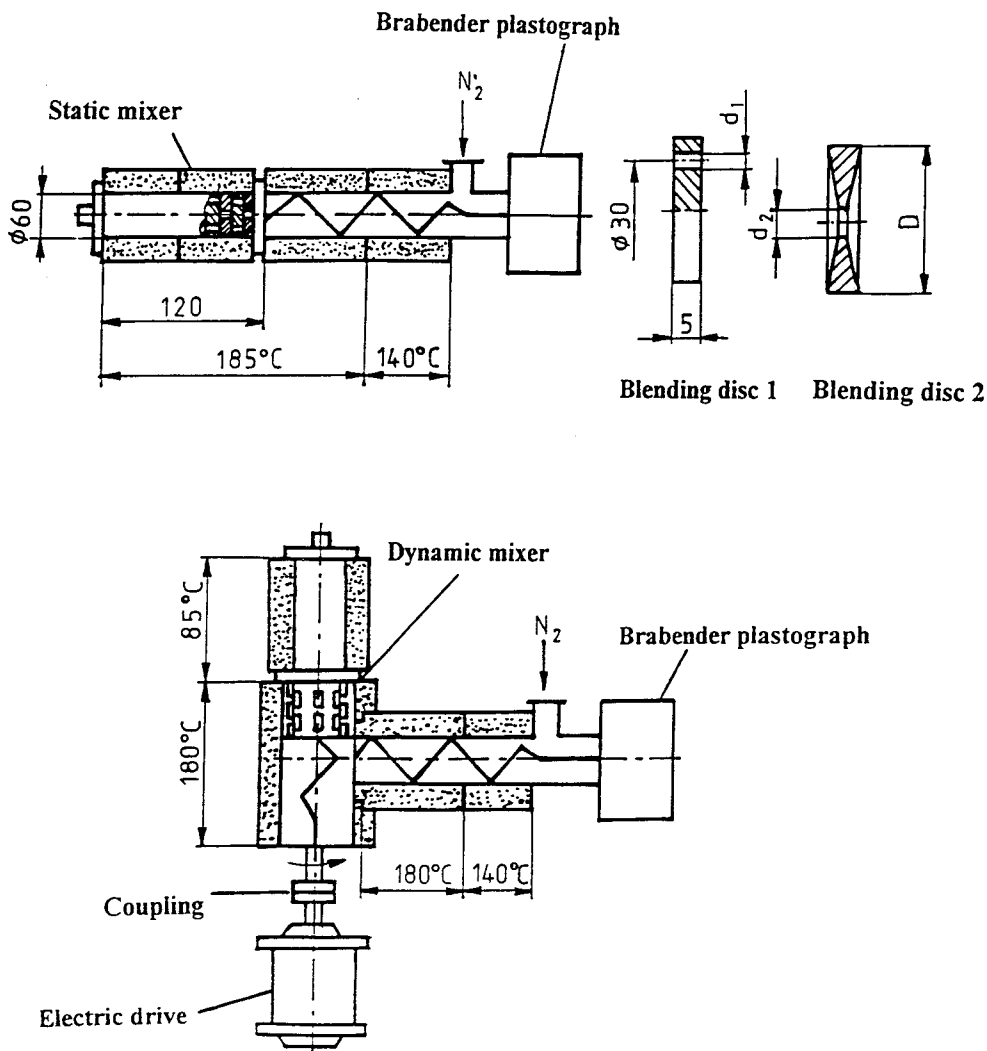
Itaconic acid was grafted using the laboratory mixing equipment based on modified Brabender plastograph.<sup>18-24</sup> Mixers of two types—dynamic and static—were attached to the typical plastograph's extruder with the conveying screw of 16 mm in diameter to allow mixing and reacting of components under controlled conditions. This plastograph is used as melting and conveying extruder fed with granules of LDPE covered with a thin layer of the initiator. The dynamic mixer (Cavity Transfer Mixer type) provides shear rates of the moving melt of about  $100 \text{ s}^{-1}$ . This shear rate was found as a difference of linear speed between an outer surface of the rotated rotor and the immovable barrel of the mixer.

The design of the static mixer was such that it allows performance of grafting at shear rates of  $50 \text{ s}^{-1}$  or  $100 \text{ s}^{-1}$ . Based on Player's theory, resistance of flow through the channel in the inserts was found. Next, based on Rabinowitsch-Mooney equations, a shear rate in the static mixer was calculated. For the shear rate of  $50 \text{ s}^{-1}$ , mixing discs (2 in Fig. 1) were used, having 12 holes with diameter  $d_1 = 1.2 \text{ mm}$ , whereas to apply a shear rate of  $100 \text{ s}^{-1}$ , discs (2) having 24 holes of  $d_1$

= 0.9 mm were made. In the discs (1) the central hole of  $d_2 = 5 \text{ mm}$  was drilled. Discs (1) and (2) have the outer diameter  $d = 39 \text{ mm}$ . Their thicknesses are 4 and 5 mm, respectively. The length of the static mixer, in which discs (1) and (2) alternated, is 120 mm.

The rates at which the molten batch was moving through the static and dynamic mixers were so selected that the reaction periods (i.e., time during which the reactive mixture is in the regions heated up to 185°C) were similar, and last about 4 min. These conditions were chosen to ensure sufficiently deep diffusion of reacting components.

Grafting process were run as follows. First, 1.0 wt % of powdered IA was added to the LDPE granules, the mixture thoroughly stirred, and then processed using a typical single-screw shaping extruder, having  $L/D = 20 : 1$ , at a temperature between 125 and 135°C. The extrudate was cooled down, pelletized, and dried. No grafting of IA on LDPE was detected at these conditions. Then, a peroxide initiator was added to the prepared granulate by treating the granules being dissolved in acetone. A uniform distribution of peroxide was provided by continuous stirring of the granules until the acetone was evaporated. Next, the granules were charged into the Brabender plastograph and grafting was carried out while gaseous nitrogen was continuously fed into a load hopper to reduce thermooxidative degradation. The melt was cooled in water upon leaving the mixer, and product of grafting was pelletized.



**Figure 1** Diagrams of static (a) and dynamic (b) mixers along with their temperature profiles in these.

### Characterization

The grafting efficiency (the ratio of the grafted IA to its total quantity added to the polymer) was used as the parameter to characterize the course of grafting reactions.<sup>25</sup> To determine experimentally the grafting efficiency, films of 30–40  $\mu\text{m}$  thickness were molded from granules of modified LDPE. The films were immersed in ethanol at 70°C when ungrafted IA was extracted. IA concentration in the samples was estimated from variations in optical density of the carbonyl groups, an absorption band at 1720  $\text{cm}^{-1}$ . The extraction kinetics of IA from LDPE with the help of ethanol is shown in Figure 2. The ungrafted IA is seen to have been completely removed in 5 h. The grafting

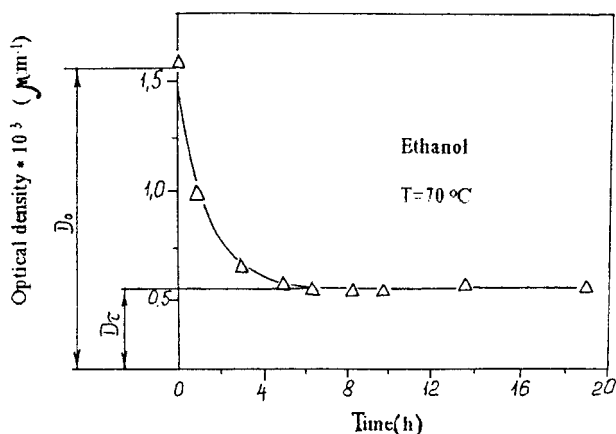
efficiency was found from the following expression:

$$\text{Grafting efficiency} = \frac{D_r}{D_o} 100[\text{wt } \%],$$

where  $D_r$  and  $D_o$  are optical density values, related to the unity of the film thickness. IR-spectra were recorded using a spectrophotometer M-80 (Karl Zeiss, Jena, Germany).

Viscosity of a melt was characterized by the melt flow index found at 190°C under 10 kg loading.

Electron paramagnetic resonance technique (EPR) was used to characterize the segmental mobility of functionalized LDPE macromolecules.



**Figure 2** Effect of extraction time in ethanol on relative optical density of carbonyl groups absorptions band.

The value of the spin correlation period of the stable nitroxyl probe-radical, for which 2,2,6,6-tetra-methyl-4-oxopiperidine-1-oxyl was employed to estimate the segmental mobility. The probe-radical was incorporated in the film sample of 200  $\mu\text{m}$  thick. It was performed by diffusion from the gaseous phase at 70°C for 2 h. EPR spectra were recorded by a spectrometer type RE-1306 at a room temperature. The spin correlation time for the probe-radical was calculated following the procedure described by L. I. Antsiferova et al.<sup>26</sup> Material's crystallinity was found from the data obtained by the DSC technique. The differential spectra were recorded at the scanning rate of 16°C/min and a load of 5 mg. The crystallinity degree variations in the samples caused by the modification were determined from the ratio of the melting heat of the functionalized LDPE to the original polymer containing 1.0 wt % of ungrafted IA.

Transparency of the functionalized LDPE film samples was estimated from the light transmission coefficient. The measurements were performed in the visible light using a photoelectric calorimeter KFK-2 (Optical Engineering Factory, Zagorsk, Russia). The film thickness was 500  $\mu\text{m}$ .

## RESULTS AND DISCUSSION

### Effect of Blending Conditions

Figure 3(a), (b), and (c) shows that type of mixer configuration influence essentially output of the grafted product (LDPE-*g*-IA) and its rheological and optical properties. The grafting efficiency of the material prepared using the dynamic mixer appeared higher than that for the static mixer

over the whole range of studied concentrations. For both mixer types, the increased grafting efficiency was accompanied by a higher viscosity of the molten compound [Fig. 3(a) and (b)].

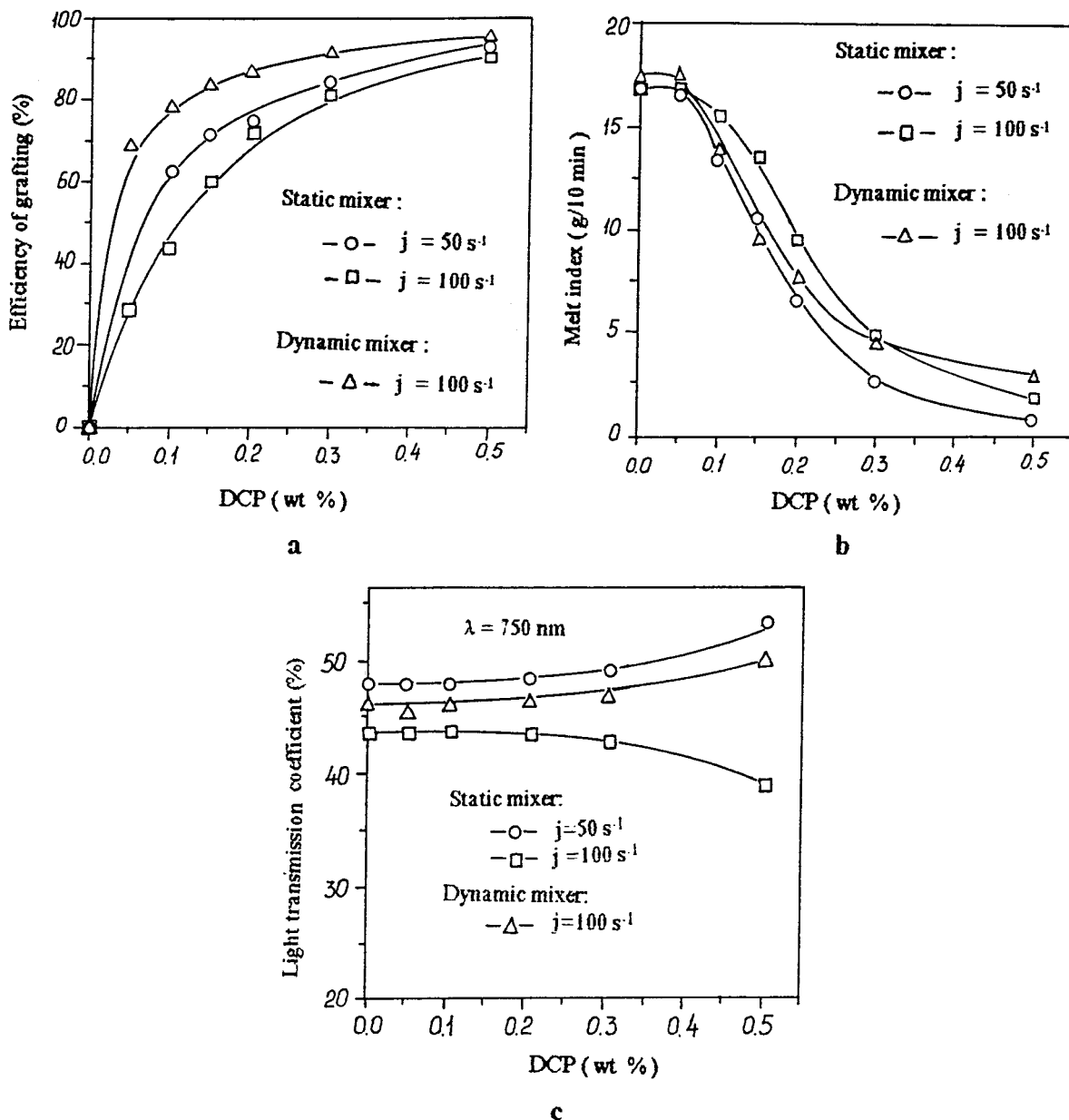
This displays two basic competing free radical mechanism<sup>4,5</sup> processes in the reactive mixture—IA grafting and crosslinking of PE macromolecules. With identical values of grafting efficiency, the melt flow index of LDPE-*g*-IA, prepared in a dynamic mixer is much higher than that in the static one. Because the dynamic mixer ensures more homogeneous reactive blends, the output of the grafted product can be controlled by varying only mixing conditions, while the values of heat parameters and reagents' ratios remain unchanged.

An increased shear rate in the static mixer might seem to improve the components' dispersion and to increase the grafting efficiency. However, according to our experimental findings with LDPE-*g*-IA, using a static mixer at the shear rate of 100  $\text{s}^{-1}$  gives the lowest value of grafting efficiency, which is shown in Figure 3(a). LDPE-*g*-IA prepared in the static mixer at the shear rate of 100  $\text{s}^{-1}$ , unlike the material prepared in other mixers, was gray. The color intensity increases as DCP concentration grows [Fig. 3(c)]. No change in color is observed in pure LDPE when it passed through the mixer. Due to this, probably, the color change of the tested product was caused by thermomechanical transformations in IA initiated by the field of shear forces generated in the molten reactive blend.

The intensity of shear on the melt in the static mixer, at the rate of 100  $\text{s}^{-1}$  is probably so high that it can cause thermomechanical cracking of the macromolecules. As a result, macroradicals are formed and recombined with the free radicals generated when the peroxide has decomposed. Due to this, if the peroxide concentration is low (e.g., 0.1–0.25 wt %), the number of free radicals generated during peroxide decomposition is insufficient to start grafting and crosslinking reactions. Therefore, LDPE-*g*-IA prepared in the static mixer at the shear rate of 100  $\text{s}^{-1}$ , with [DCP] = 0.1–0.3 wt %, showed a higher melt flow index value, but the lowest grafting efficiency [Fig. 3(a) and (b)].

### Effect of Peroxide Initiator Concentration

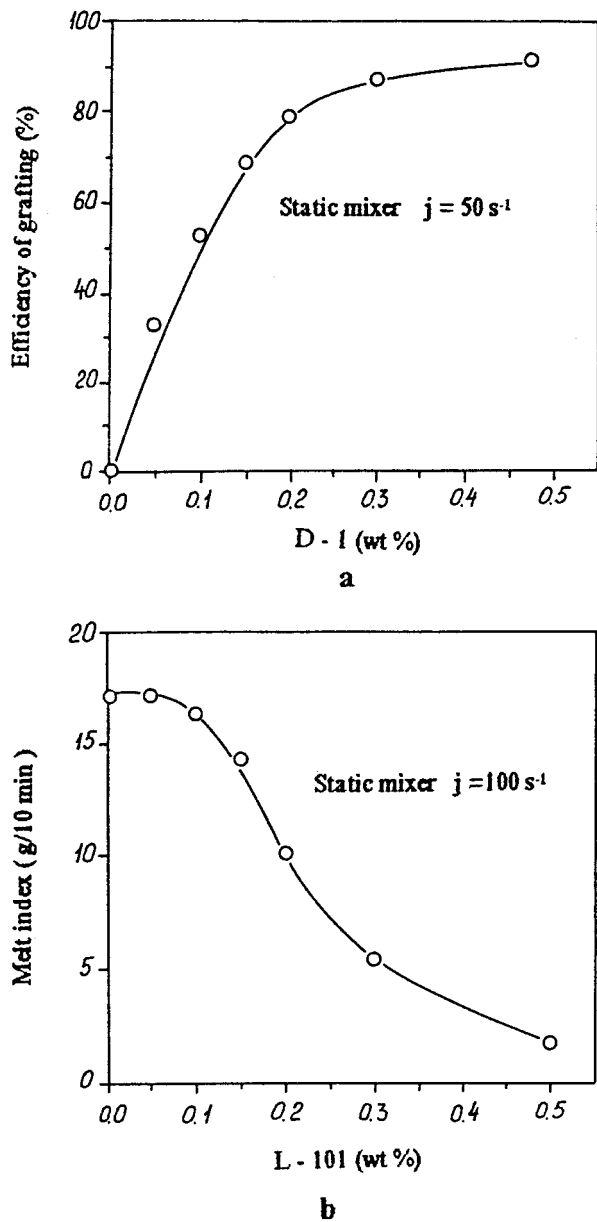
Figures 3, 4, and 5 show the effect of different peroxide initiator concentration on the IA grafting capacity and on the melt flow index values. The inverse nature of the concentration dependence of



**Figure 3** Effect of mixer and DCP concentration on efficiency of grafting (a), melt flow indexes of LDPE (b), and light transmission coefficient of film samples (c).

the grafting capacity and the melt flow index values is shown to be typical for different peroxides and blending conditions. However, the extent to which the values vary depends on both the nature of peroxide and the mixer design. Three characteristic regions can be distinguished on the concentration curves of the parameters investigated; namely, first, peroxide concentration up to 0.1 wt %; second, between 0.1 and 0.3 wt %; and third, more than 0.3 wt %. Region first is characterized

by negligible variations in the melt flow index values, while the grafting capacity essentially varied with the peroxide concentration. Therefore, free radicals, formed during peroxide decomposition, are spent mostly to start grafting IA on LDPE macromolecules. In the second region peroxide concentration is quite sufficient to form so many free radicals that they readily start two simultaneous reactions: IA grafting on macromolecules and intermolecular crosslinking reaction of the



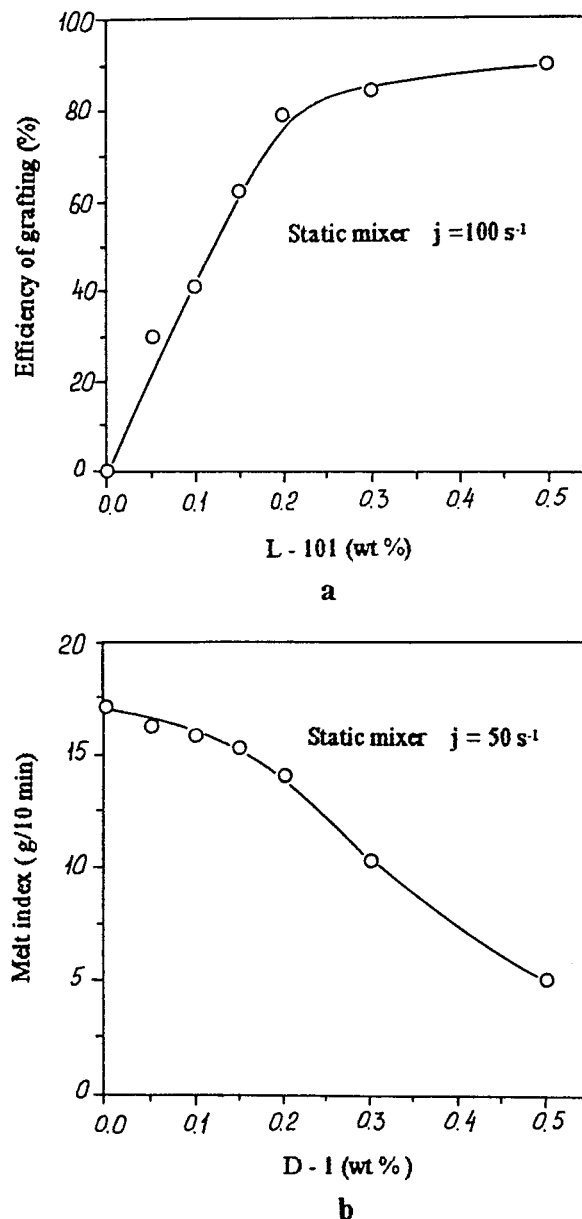
**Figure 4** Effect of peroxide (L-101) concentration on IA efficiency of grafting (a) and melt flow indexes (b).

latter. The third region is characterized by high concentrations of the peroxide initiator, so high concentrations of free radicals are present in the reaction blend, which are quite sufficient to provide limiting grafting values (88–93%) of the system. Impossibility to reach 100% grafting could probably be explained by the steric factor: if the grafting extent is high, the macromolecular segmental mobility is restricted. Here, free radicals are hampered to leave the “cage,” and there is no molecular LDPE contact with IA that is important

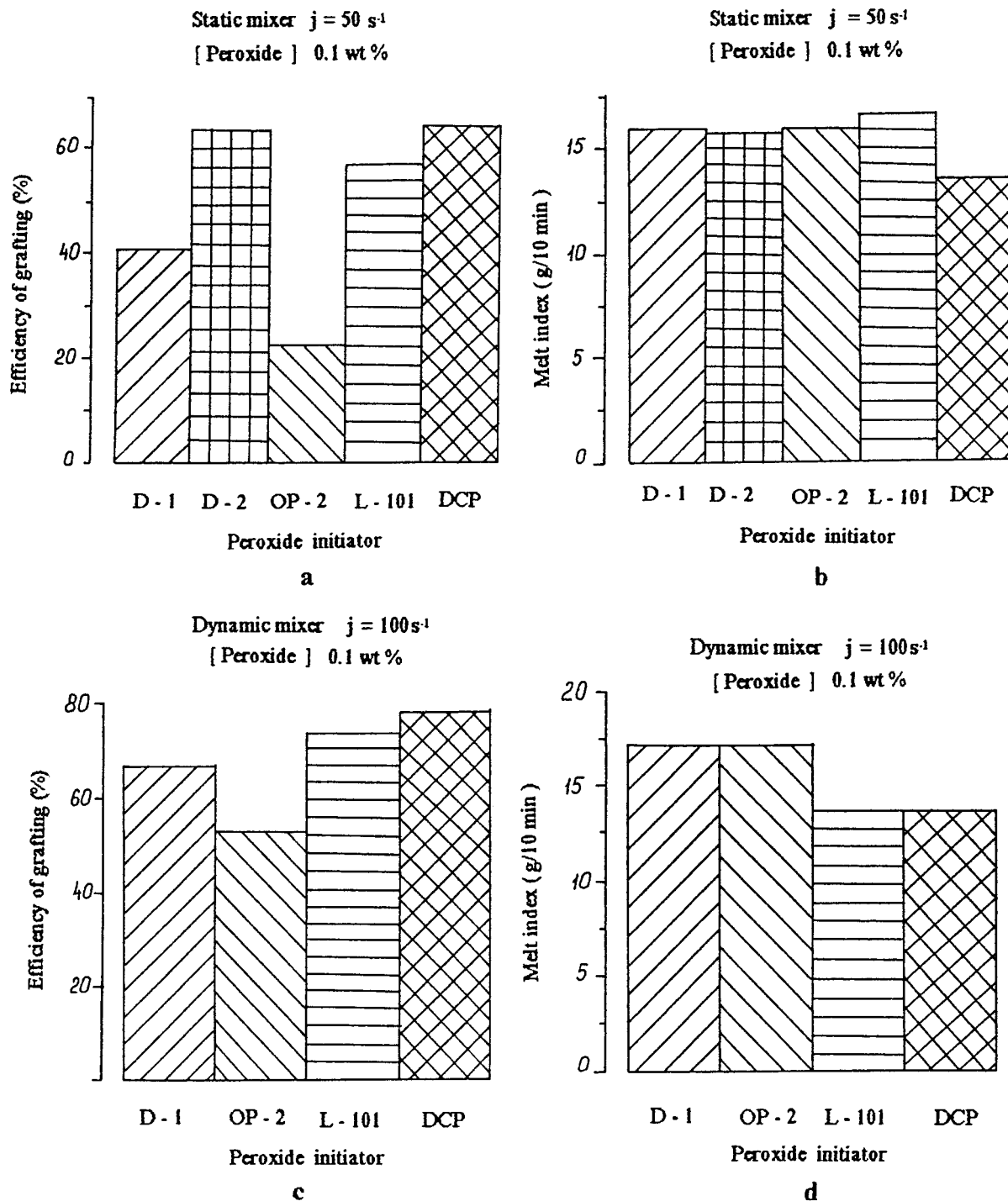
to start the grafting reaction. Therefore, in the third region, peroxide is mostly spent to start reactions of LDPE intermolecular crosslinking.

#### Effect of Peroxide Initiators

The role of peroxide chemical structure can be seen in Figure 6. As with high peroxide concentrations (more than 0.3%) the peroxide gets leveled (Figs. 3, 4, and 5) so we give data of the peroxide



**Figure 5** Effect of peroxide (D-1) concentration on efficiency of grafting (a) and melt flow indexes (b).



**Figure 6** Effect of peroxide nature on IA efficiency of grafting (a) and (c), and melt flow indexes (b) and (d).

concentration of 0.1 wt %. When analyzing data in Figures 3, 4, 5, and 6, we have noticed that the tested peroxides fall as follows:  $\text{DCP} \cong \text{L-101} \cong \text{D-2} > \text{D-1} > \text{OP-2}$  regarding their weakening

effect on the grafting efficiency. The peroxides, regarding their effect on decreasing the melt flow index, behave in the same manner. Peroxides L-101 and D-2 could provide grafting values close

**Table II** Variation of Crystallinity of LDPE-*g*-IA Samples in Response to the Mixing Conditions and DCP Concentrations

Mixing	$\Delta I$ , Depending on $N_{DCP}$ (wt %)			
	0	0.1	0.2	0.5
Static 50 s <sup>-1</sup>	1.00	1.03	0.98	0.88
Static 100 s <sup>-1</sup>	1.00	1.00	0.96	0.91
Dynamic 100 s <sup>-1</sup>	1.00	0.99	1.03	0.92

to DCP and can crosslink LDPE-*g*-IA to a smaller degree than DCP. Therefore, these peroxides are preferable for practical applications.

The peroxide efficiency in IA grafting on LDPE is not a direct consequence of active oxygen concentration presents in it (Table I). An example of it is DCP being a very active initiator of grafting having the lowest concentration of active oxygen. The decisive role is probably played by solubility of peroxides in molten LDPE, the temperature range where peroxides ease decomposition, by their volatility and half-life time, and types and stability of radicals generated that all affects the true peroxide concentration in the system.

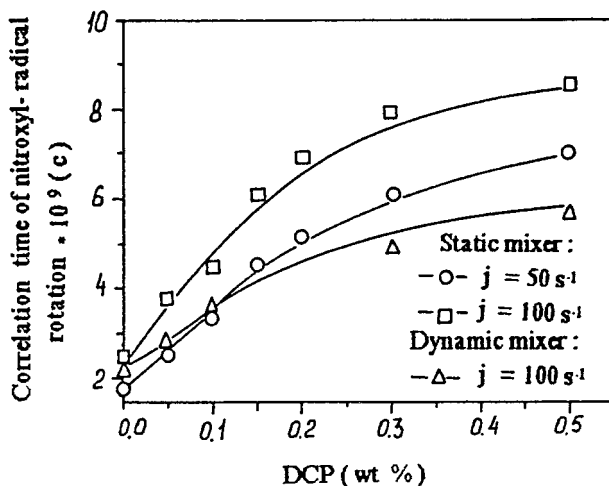
### Structural Features

Table II lists the results of DSC analysis of LDPE crystalline structure altered by IA grafting. Measuring absolute values of crystallinity to estimate variations in the crystallinity is not needed. Using the crystallinity index that illustrates the ratio of LDPE-*g*-IA weight crystallinity to that of the initial one (which did not pass a static or dynamic mixer) of LDPE containing 1 wt % of IA, evaluating changes of structure is possible. It can be seen that IA grafted at DCP concentrations of 0.1 and 0.2 wt % would not, in fact, alter either the LDPE crystallinity or its melting temperature. Only with DCP concentration of 0.5 wt %, at which decrease in the melt flow index was observed [Fig. 3(b)] the material crystallinity and melting temperature is largely decreased. This is a typical effect observed in LDPE crosslinking with the help of peroxides.

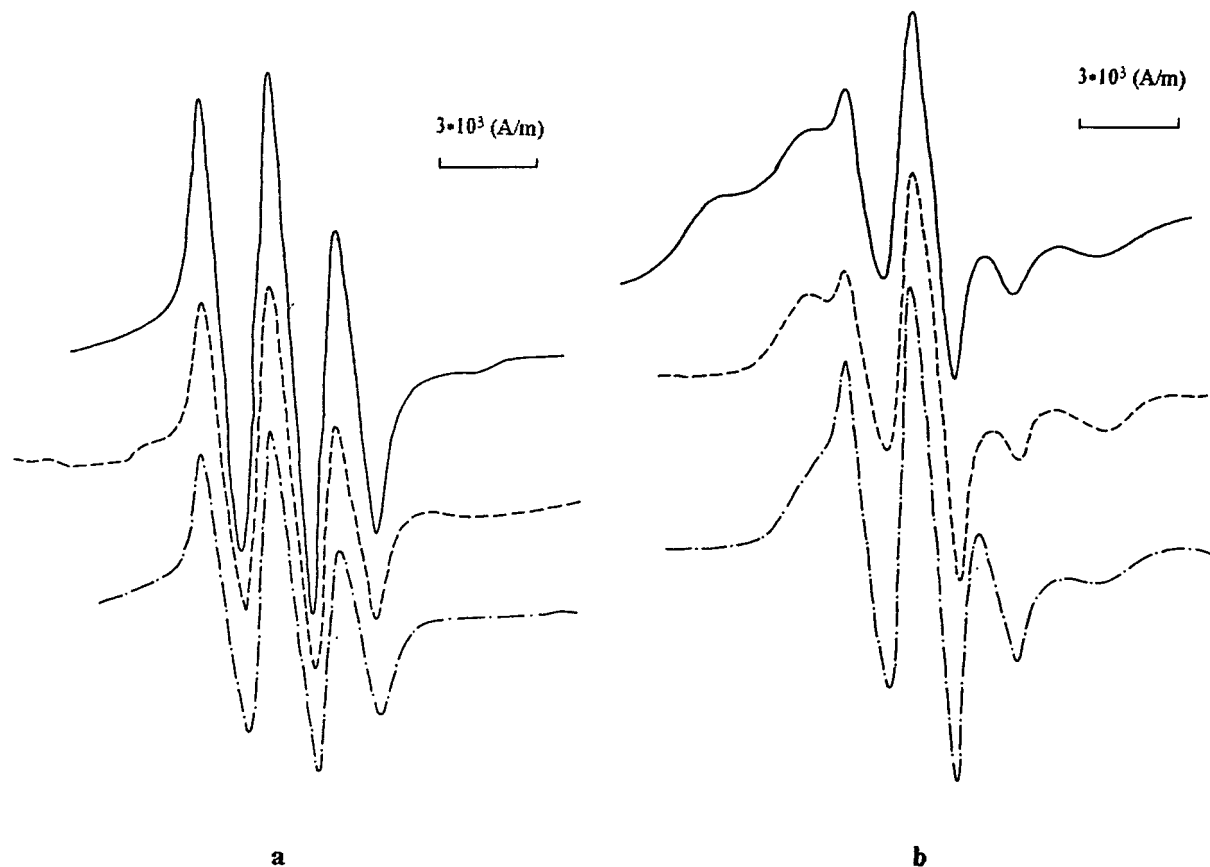
Figures 7 and 8 show the results on LDPE-*g*-IA obtained by the electron paramagnetic resonance technique (EPR). As the nitroxyl probe-radical can mostly diffuse only in the amorphous polymer,<sup>26</sup> the correlation time values for its spinning, along with EPR spectra, give an insight into this

phase structure in LDPE-*g*-IA (segmental macromolecular mobility in the amorphous phase). In Figure 7 is seen a small difference in correlation times of the probe-radical in the samples prepared in different mixers with DCP concentration of 0.05 wt %. On increasing the DCP concentration, however, the difference becomes more significant. With peroxide concentrations between 0.1 and 0.3 wt % most suitable for practical purposes, the correlation times of the probe-radical, and, therefore, segmental macromolecular mobility in LDPE-*g*-IA prepared in different mixers, differs substantially. The highest segmental mobility was observed in the samples prepared in the dynamic mixer. The EPR spectra of the probe-radical recorded in the samples prepared in the static and dynamic mixers have different features [Fig. 8(b)]. This refers to the regions of fast and slow spinning.

The difference in segmental mobilities in the amorphous part of LDPE-*g*-IA in comparison to pure LDPE can influence application of functionalized polyethylene as a component of the polymer blends compatibilizer. Obviously, dissimilar components should have a sufficiently high molecular mobility to most fully ensure interaction of functional groups. Data in Figure 7 shows that segmental mobilities in amorphous LDPE-*g*-IA can differ, depending on the mixer used with approximately identical values of grafting efficiency and a melt flow index. In view of the above, we believe the dynamic mixer to be more suitable for preparing LDPE-*g*-IA with most higher capacity and

**Figure 7** Correlation times for probe-radical spinning in LDPE and LDPE-*g*-IA and concentration.





**Figure 8** EPR spectra of probe-radical in LDPE containing 1 wt % of IA (a) and LDPE-*g*-IA prepared in presence of DCP (0.3 wt %): (—) static mixer, 50 s<sup>-1</sup>; (--) static mixer, 100 s<sup>-1</sup>; (- · -) dynamic mixer.

segmental mobility of macromolecules then those without grafting.

## CONCLUSIONS

Grafting efficiency IA on LDPE when a molten reactive batch is flowing, output of a product, and its structure depends on a kind of mixer, nature, and concentration of an initiator.

Dynamic mixer allowing one to obtain LDPE-*g*-IA with the highest efficiency of grafting and segmental mobility of macromolecules is the most applicable for practical purposes.

Peroxide initiators regarding their effect on grafting and crosslinking effectiveness and rheological properties could be ordered as follows: L-101  $\cong$  D-2 > DCP > D-1 > OP-2.

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