

# Solubility of Additives: Grafting of Itaconic Acid onto LDPE by Reactive Extrusion. II. Effect of Stabilizers

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**ABSTRACT:** Static and dynamic mixers set on the Brabender plastograph were used to investigate the grafting of itaconic acid (IA) onto low-density polyethylene (LDPE) by the reactive extrusion. The initiators of free-radical reactions were monoperoxide 2,5-dimethyl-2-hydroxy-5-*tert*-butylperoxy-3-hexyne and diperoxide 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-hexane. The reaction mix contained stabilizers of phenolic type as follows: 2,6-ditert-butyl-4-methyl phenol; ester of 3,5-ditert-butyl-4-hydroxyphenyl-propanoic acid and pentaerythritol; 4-alkoxy-2-hydroxy-benzophenone; and 1,4-dihydroxybenzene. The effect of stabilizers, which follow the radical mechanism on the grafting of IA and on the crosslinking, depends on their solubility in the polymer and the monomer. The stabilizers (e.g., 1,4-dihydroxybenzene) with increased affinity toward the monomer reduce the grafting yield and inhibit crosslinking. At 0.3–0.5 wt % of the stabilizer insoluble in the monomer, the grafting yield can be increased, while inhibiting the LDPE-*g*-IA crosslinking, irrespective of the peroxide used. Hence, classical stabilizers can initiate grafting reactions at raised concentrations, temperatures, and application of the shearing stresses. They also help to obtain a high-grafting yield and a reduced crosslinking degree. A stabilizer, having a close affinity toward LDPE, influences the LDPE-*g*-IA structure. The stabilizer content of 0.5 wt % transforms the topological structure of LDPE-*g*-IA into uniblock. Its molecular weight distribution (MWD) may be narrow ( $\overline{M}_w/\overline{M}_n < 2$ ) or broad ( $\overline{M}_w/\overline{M}_n > 2$ ), depending on the concentration of the initiator used. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3439–3448, 2001

**Key words:** itaconic acid; grafting; grafting efficiency; stabilizer; solubility; solubility parameter; thermomechanical analysis

## INTRODUCTION

The functionalization of olefin polymers and copolymers by grafting polar monomers in the course of

reactive extrusion is based on free-radical chemical reactions.<sup>1,2</sup> Usually, numerous secondary processes, such as crosslinking (for polyethylene and ethylene/propylene copolymers),<sup>1,3–9</sup> degradation (for polypropylene),<sup>1,10–15</sup> oligomerization of the monomer,<sup>1,16–22</sup> and some others,<sup>1,23</sup> take place along with the grafting reaction.

To control the yield of the grafted products in the course of functionalization and to suppress

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the secondary reactions, it is advisable to add specialty additives to the reaction mix.<sup>16,21,24–26</sup> Of these additives, the role of polar organic compounds is evident.

It is anticipated that classical stabilizers that follow the mechanism of accepting free radicals, when added to the reaction mix, will substantially affect the free-radical reactions that take place during polyolefin functionalization. This is reported in some works. For instance, Pawda<sup>27</sup> stated a complete inhibition of maleic anhydride grafting onto polyethylene when a phenolic stabilizer had been added. We had earlier reported<sup>28</sup> that stabilizer, which easily dissolved in the molten low-density polyethylene (LDPE), inhibits the secondary reaction (*viz.*, crosslinking), while grafting the itaconic acid (IA) took place and led to high-grafting efficiency. Taking into consideration the great influence of the selective dissolution of the additives in the components of the polymer/monomer system,<sup>22,29,30</sup> it is believed that the stabilizers' behavior will depend both on their reactivity and on the distribution within the reaction mix.

This work was undertaken to continue learning the role of stabilizers in the grafting of IA onto LDPE in the presence of peroxide initiators.

## EXPERIMENTAL

### Materials

The polymer used for this work was LDPE, grade 15803-020; GOST 16337-77; density, 0.92 g/cm<sup>3</sup>; melting point, 105°C; supplied by Polimir Co., Novopolotsk, Belarus. IA was produced by the chemical division of Pfizer (USA). The organic peroxides characterized by thermodynamic affinity with respect to the polymer (LDPE) and the monomer (IA) were used: monoperoxide 2,5-dimethyl-2-hydroxy-5-*tert*-butylperoxy-3-hexyne (OP-2), having the solubility parameter  $\delta = 19.1$  (J cm<sup>-3</sup>)<sup>0.5</sup> and containing 7.5% of reactive oxygen, and diperoxide 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-hexane (L-101), ELF Atochem Co, France,  $\delta = 15.5$  (J cm<sup>-3</sup>)<sup>0.5</sup>; the reactive oxygen content was 11.03%.

Organic stabilizers included ester of 3,5-di-*tert*-butyl-4-hydroxyphenyl-propanoic acid and pentaerythritol, Irganox 1010 (I-1010), Ciba Geigy, Switzerland; 2,6-di-*tert*-butyl-4-methylphenol, Agidol 1 (A-1), and also 4-alkoxy-2-hydroxybenzophenone, Benzone OA (BOA), Research Institute of Additives to Polymeric Ma-

terials, Tambov, Russia; and 1,4-dihydroxybenzene, hydroquinone (HQ), Chemicals Factory, Shostka, Ukraine. Table I lists the characteristics of the stabilizers used. The  $\delta$  values were calculated after the group contribution method in accordance with the approaches described elsewhere.<sup>28</sup> Their values for the LDPE and IA, similarly calculated for 25°C, were 16.1 and 26.4 (J cm<sup>-3</sup>)<sup>0.5</sup>, respectively.

### Preparation of Test Specimens

The testing materials were prepared by grafting of IA onto LDPE. The process was run by using a Brabender plastograph equipped with static and dynamic mixers.<sup>3</sup> This device acted as a single-screw reactor extruder. The shearing rate was 50 s<sup>-1</sup> in the static mixer and 100 s<sup>-1</sup> in the dynamic mixer. The temperature in the blending zones of the reactor was constant, at 185°C.

To prepare a reaction mix as in work,<sup>3</sup> the LDPE granules were first covered with 1 wt % of IA powder, and then passed through the single-screw extruder at 125–135°C and granulated. Then the peroxide and stabilizer dissolved in acetone were mixed with the granules and, next, this product was dried. The grafting was conducted in flowing nitrogen atmosphere.

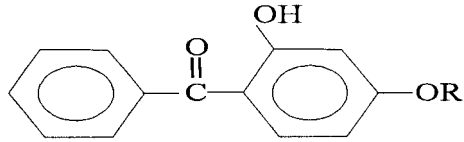
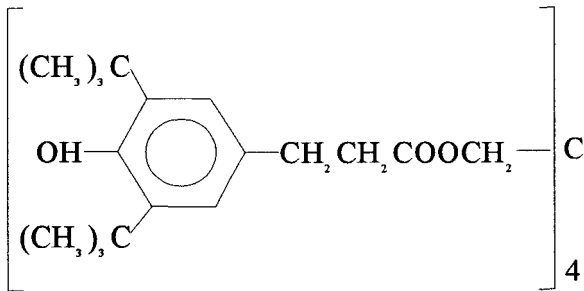
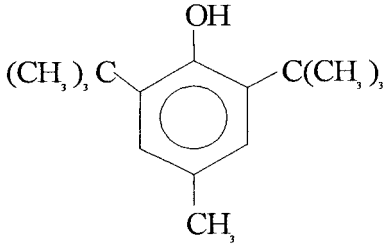

### Characterization

The following parameters were analyzed: the grafting efficiency ( $\alpha$ ) (parameter describing the yield of the basic product, LDPE-*g*-IA) and the MFI (parameter sensitive to the course of the secondary process, LDPE crosslinking).

The procedures for determining these parameters and the equipment used for this purpose are described in other works.<sup>3,28</sup>

The physical structures of the tested materials were judged from the results of thermomechanical analysis (TMA). We have learned earlier<sup>4</sup> the advantages of the TMA in analyzing the structures of LDPE-*g*-IA. It was of interest to learn changes in the LDPE-*g*-IA prepared in the presence of stabilizers. For such analysis, cylindrical specimens having two plane-parallel surfaces were used; their height was between 2 and 3 mm and their diameter was 4 mm. The measurements were made by using the UIP-70M device, which had been made by the Russian Academy of Sciences. The specimen of polymer under investigation was put into the thermostatic chamber of the instrument and cooled at the rate of 10°C/min up to about -120°C. The

**Table I Characteristics of Stabilizers**

Trade Name	Chemical Formula	Melting Point (°C)	$\delta$ (J cm <sup>-3</sup> ) <sup>0.5</sup>
Benzone OA	 <p>R = C<sub>7</sub>H<sub>15</sub> till C<sub>9</sub>H<sub>19</sub></p>	160 <sup>a</sup>	20.3
Irganox 1010		122	19.3
Agidol 1		70	19.9
Hydroquinone		174	29.1

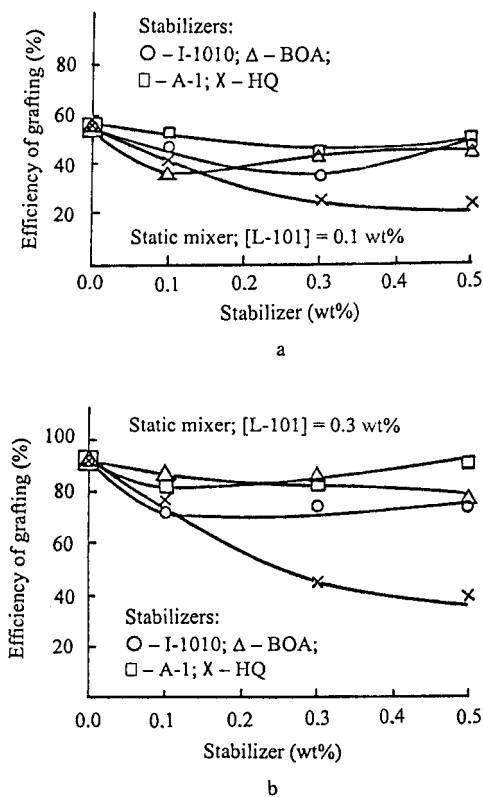
<sup>a</sup> Boiling temperature at a pressure of 5 GPa.

cold specimen was loaded with a quartz hemispherical probe having a tip radius of 1.5 mm. The load on the probe was 300 mg. Then the thermostatic chamber was heated at a rate of 5°C/min. The variations in the temperature and in the linear deformation of the specimen were simultaneously recorded. The principles of the TMA method and the procedure for generation of the thermomechanical curve (TMC) are described elsewhere.<sup>30-35</sup> The accuracy of the temperature measurements conducted in the thermostatic chamber was  $\pm 0.05^\circ\text{C}$  and that of deformation was  $\pm 0.005$  mm.

## RESULTS AND DISCUSSION

### Effect of Stabilizers

Now we analyze the data obtained with the static mixer. Figures 1 and 2 show that the stabilizer's nature and concentration substantially influence the course of grafting and crosslinking of LDPE initiated by peroxide L-101, which dissolves, quite easily, in LDPE. It is because the solubility parameters of the LDPE and L-101 are 16.1 and 15.5 (J cm<sup>-3</sup>)<sup>0.5</sup>, respectively. It is well known that miscibility between the solvent and the sub-

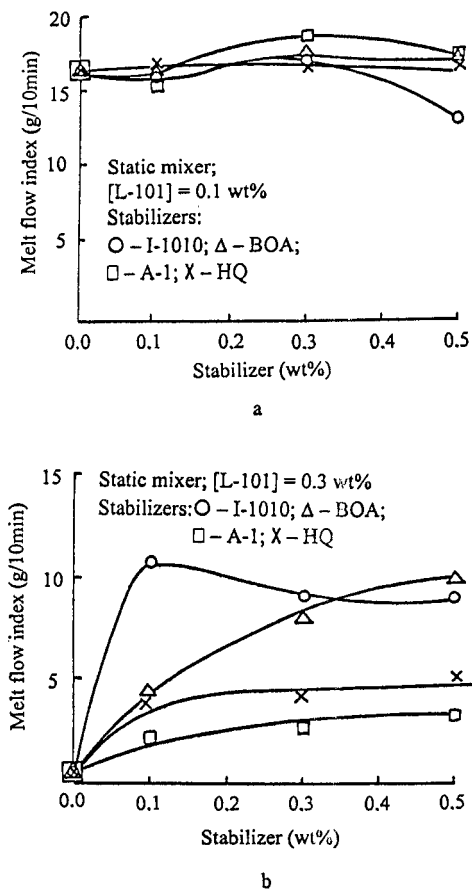


**Figure 1** Effect of concentration and nature of stabilizer on grafting efficiency; the L-101 peroxide concentrations: (a) 0.1 wt % and (b) 0.3 wt %.

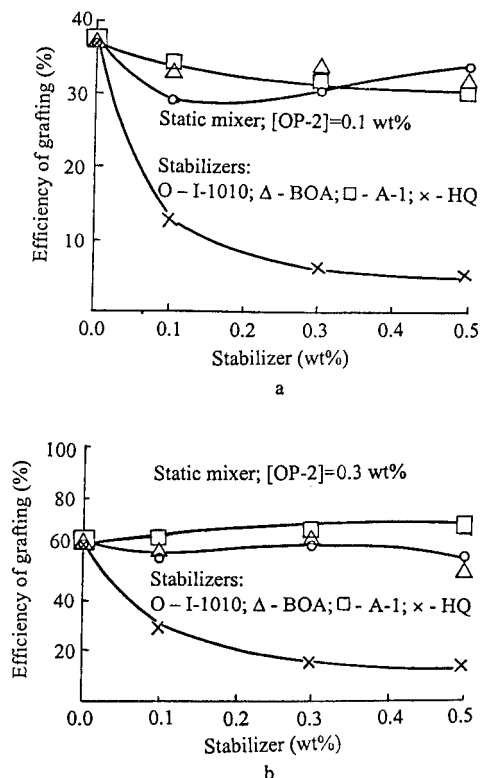
stance dissolved is observed if strong specific interactions between their molecules are not present and if the difference in solubility parameters does not exceed  $2 (\text{J cm}^{-3})^{0.5}$ . According to the data of Coleman et al.,<sup>36</sup> the stabilizer's nature and concentration substantially influence its solubility. There are some important points that we should emphasize. First, the grafting efficiency, in general, decreases in the presence of stabilizers. This influence, however, depends on its solubility in the basic components of the reaction mix. Minding the data in Table I, one can think that HQ is insoluble in LDPE, but possesses stronger affinity toward IA. The solubility parameters of other stabilizers are closer to that of LDPE than to IA. It is the better solubility of HQ in IA that explains the strong inhibiting effect of this stabilizer toward the grafting reaction, irrespective of the peroxide concentration [Fig. 1(a,b)]. The melt viscosity of LDPE-*g*-IA remains, in fact, the same in the presence of HQ at low concentrations of L-101 [Fig. 2(a)]. The viscosity undergoes less significant changes than with the materials prepared by using other types of stabilizer (except A-1) at higher L-101 concentrations

[Fig. 2(b)]. Hence, a stabilizer, which is insoluble in LDPE, cannot substantially influence the course of the main of secondary processes (viz., crosslinking of macromolecules); it efficiently inhibits the grafting of the monomer.

The effect of insoluble stabilizers in the monomer incompatible with IA depends on their concentrations. Characteristically, that low quantity (0.1 wt %) of the stabilizer added to the reaction system would reduce the grafting efficiency. Some improvement was observed after the stabilizer concentration had been raised up to 0.3–0.5 wt % [Fig. 1(a,b)]. There was observed some drop in the melt viscosity (or some rise in the MFI) [Fig. 2(a,b)]. Thus, by increasing the concentrations of stabilizers, which have higher affinity toward the polymer than toward the monomer, it seems possible to prepare polymers with higher MFI without substantially decreasing the grafting efficiency. This is an unexpected result, because Pawda<sup>27</sup> reported that the grafting of maleic anhydride onto polyethylene was completely inhib-



**Figure 2** Effect of concentration and nature of stabilizer on melt flow index of LDPE-*g*-IA; the L-101 peroxide concentrations: (a) 0.1 wt % and (b) 0.3 wt %.



**Figure 3** Effect of concentration and nature of stabilizer on grafting efficiency of IA into LDPE; the OP-2 peroxide concentrations: (a) 0.1 wt % and (b) 0.3 wt %.

ited by the addition of the reactive blend of the phenolic stabilizer capable of accepting free radicals.

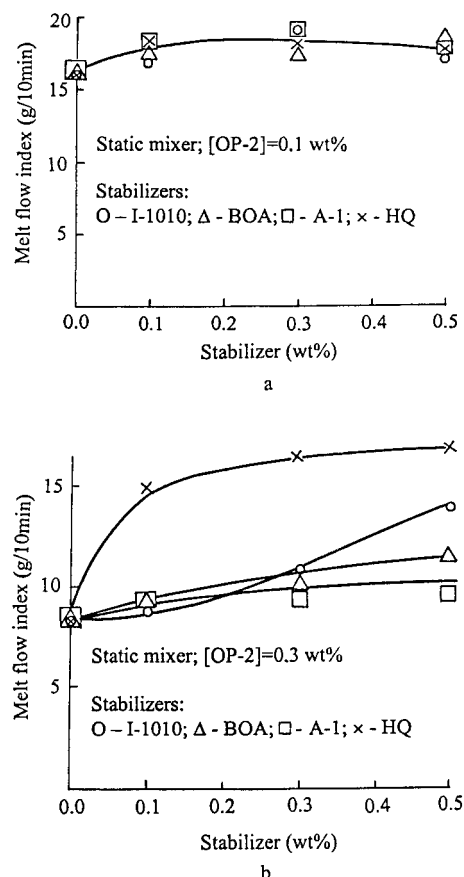
It is believed that, at a higher stabilizer concentration, the relatively stable radicals that resulted from labile hydrogen extracted from the stabilizers molecules can, themselves, initiate the formation of macroradicals, which can interact with the monomer and lead to grafting.<sup>37,38</sup>

The use of OP-2 peroxide (which is insoluble in LDPE and has an increased affinity toward the monomer owing to the hydroxyl group present in its composition) as the initiator does not change, mainly, the effect of stabilizers I-1010, BOA, and A-1 on the grafting efficiency and the MFI (Figs. 3 and 4). At OP-2 concentrations over 0.3 wt %, these stabilizers do not, in fact, change the grafting efficiency, but they markedly increase the MFI.

Hydroquinone, unlike the stabilizers mentioned above, more strongly suppresses the grafting reaction initiated by OP-2 than with L-101 initiator [Fig. 3(a,b)]. It should be mentioned that at a low OP-2 concentration (0.1 wt %), all tested stabilizers similarly influenced, in fact, the sec-

ondary reaction of crosslinking of macromolecules [Fig. 4(a)]. Probably at 0.1% concentration of OP-2, small quantities (up to 0.3%) of I-1010, A-1, and BOA stabilizers, which are insoluble in the monomer and in peroxide, can inhibit the macroradicals formed in the LDPE, thus reducing the grafting efficiency and increasing the MFI [Fig. 3(a,b)]. Upon raising the concentration of these stabilizers, the grafting efficiency tended to improve, while the MFI tended to decrease. This can only be explained by some extra amounts of free radicals generated by the stabilizer. This result supports the ability of stabilizers to initiate free-radical reactions, which take place at the conditions of reactive extrusion.

It is obvious that HQ efficiently suppresses the grafting of IA and crosslinking of macromolecules in the presence of OP-2, owing to closer, as compared with other stabilizers, thermodynamic affinity toward this peroxide, which in fact becomes evident when the solubility parameters of these



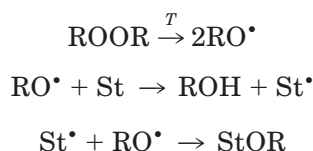
**Figure 4** Effect of concentration and nature of stabilizer on melt flow index of LDPE-g-IA; the OP-2 peroxide concentrations were: (a) 0.1 wt % and (b) 0.3 wt %.

ingredients are compared. The radicals formed from the OP-2 breakdown are, evidently, accepted immediately by HQ, thus retarding sharply both reactions, the grafting and the crosslinking of macromolecules.

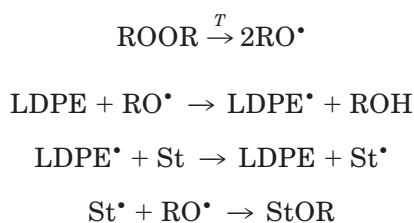
From the discussion above it is clear that in the case of OP-2, the peroxide which is insoluble in the polymer, and in the stabilizers, the latter, are mostly consumed to inhibit the secondary reactions. A stabilizer characterized by higher miscibility with the initiating peroxide can efficiently inhibit the grafting of the monomer and crosslinking of macromolecules.

The processes can be schematically represented as follows<sup>1,21,22,37,38</sup>:

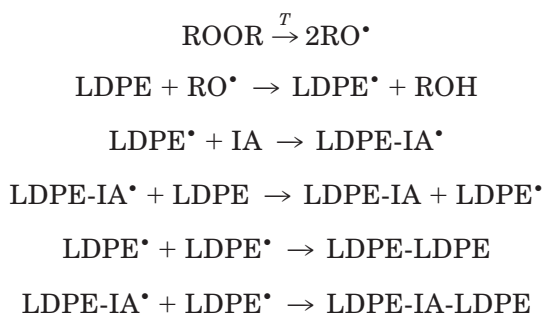
1. Inhibition, by a stabilizer (St) HQ, of primary radicals formed when the peroxide (ROOR) breaks down:



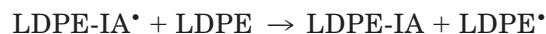
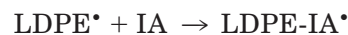
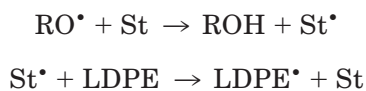
2. Inhibition, by a stabilizer, of the macroradicals' generation:



3. Inhibition of grafting and crosslinking of macromolecules by primary radicals resulted from peroxide breakdown:



4. Initiation of IA grafting by a St:

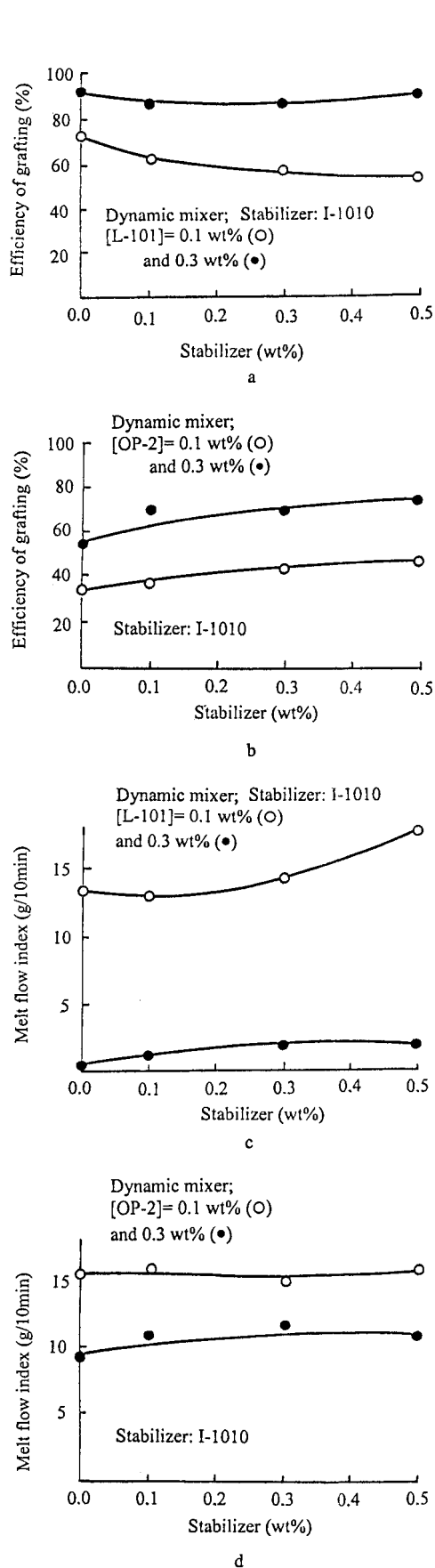


At the conditions where the ingredients can be thoroughly dispersed (e.g., where a dynamic mixer is used as a reactor<sup>3</sup>), the described mechanisms by which stabilizers influence the IA grafting and crosslinking of macromolecules are in action (Fig. 5). It should be noted that OP-2 peroxide affords higher amounts of grafting over the whole range of concentrations of Irganox 1010 than for unstabilized systems [Fig. 5(b)]. It can be anticipated that at higher shearing rates that can be reached in the dynamic mixer, the generation of free radicals by molecules of the stabilizer becomes more vigorous. As a result, the grafting somewhat improves; this improvement is most vivid for the systems containing OP-2 peroxide, the initiator, which is insoluble in LDPE [Fig. 5(a,b)].

As we have learned, the effect of the stabilizers depends, to a great extent, on solubility in the polymer and the monomer. An improvement in the stabilizer's solubility in a monomer and in a peroxide initiator reduces the grafting efficiency. The stabilizers with improved solubility in LDPE, but which are insoluble in IA, can inhibit the secondary process, crosslinking of macromolecules, without significantly decreasing the grafting efficiency. The latter conclusion is important for practical applications because LDPE-g-IA can be directly stabilized when it is synthesized during the reactive extrusion. A lower resistance of LDPE-g-IA to oxidation in air or in numerous aqueous media as compared with the initial LDPE explains the need of such stabilization.<sup>39</sup>

### Structure Features

The advantages of the TMA technique in studying changes in the molecular-topological structure of LDPE caused by the grafting reaction are described in Jurkowski et al.<sup>4</sup> It was of interest to use this technique to learn the changes in LDPE-g-IA synthesized in the presence of stabilizers. The test samples of the materials were prepared by using the dynamic mixer. Figure 6 shows the TMC for LDPE-g-IA prepared with different quantities of Irganox 1010. The addition of the stabilizer markedly influences the topological structure of the polymer. The coefficients of linear thermal expansion in the glassy and highly elastic states at the I-1010 concentrations of 0.1, 0.3, and 0.5 wt % are, respectively:  $\alpha_1 = 11.8 \times 10^{-5}$

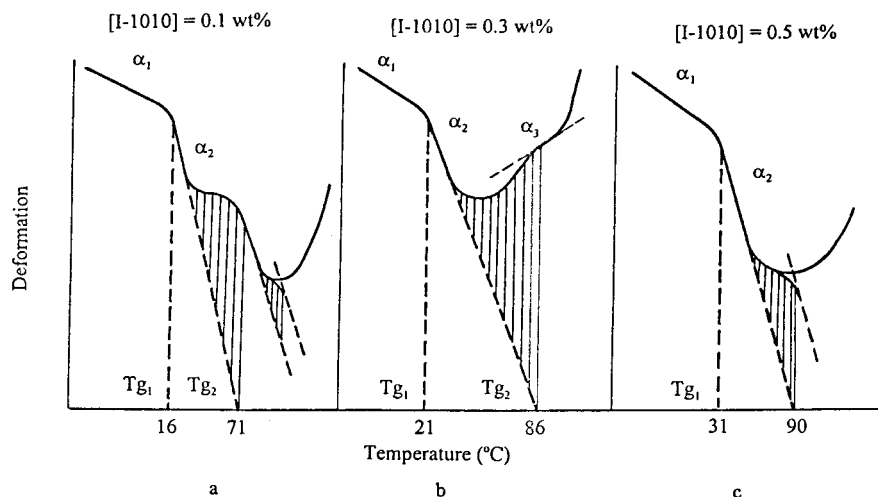


$\text{deg}^{-1}$ ,  $\alpha_2 = 23.21 \times 10^{-5} \text{ deg}^{-1}$ ;  $\alpha_1 = 8.25 \times 10^{-5} \text{ deg}^{-1}$ ,  $\alpha_2 = 13.31 \times 10^{-5} \text{ deg}^{-1}$ ;  $\alpha_1 = 8.25 \times 10^{-5} \text{ deg}^{-1}$ ,  $\alpha_2 = 13.31 \times 10^{-5} \text{ deg}^{-1}$ ,  $\alpha_3 = 13.0 \times 10^{-5} \text{ deg}^{-1}$ ;  $\alpha_1 = 12.35 \times 10^{-5} \text{ deg}^{-1}$ ,  $\alpha_2 = 33.6 \times 10^{-5} \text{ deg}^{-1}$ . The shape of the TMC in Figure 6 shows that the architecture of LDPE-g-IA changes from a diblock topological structure with a pseudo-network in the low temperature that had been prepared with 0.1 wt % of I-1010 to a uniblock one with 0.5 wt % of I-1010 added to the polymer. The increase in  $T_{g1}$  from 16 up to 31°C for the low-temperature block, after the I-1010 concentration had been raised from 0.1 up to 0.5 wt %, indicates a reduction in the mobility of the fragments of the chains between the junctions in the block. That is, formally, I-1010 behaves similar to an antiplasticizer. The mechanism of such action can probably be attributed to its influence on the degree of regularity in the grafted and crosslinked products. This is supported by complete homogenization of the LDPE-g-IA structure, when LDPE-g-IA was prepared with 0.5 wt % of I-1010 [Fig. 6(c)].

The  $T_g$  of the high-temperature block rises from 71°C at 0.1 wt % of I-1010 up to 86°C at 0.3 wt % of I-1010 [Fig. 6(a,b)]. The temperature of the beginning of a flow  $T_f$  varies between 86 and 93°C.

The molecular weight characteristics of LDPE-g-IA were observed to have varied with the Irganox concentration in the following manner (Fig. 7). At a minimum content of the stabilizer, the constituents of the diblock topological structure of the polymer have the following molecular weight characteristics: the low-temperature block  $\bar{M}_{n(n)} = 3450$ ,  $\bar{M}_{w(n)} = 4650$ , and  $K = 1.35$ ; the high-temperature block consists of high-molecular-weight fragments having a molecular weight of about 20,000 with a narrow MWD. On increasing the I-1010 concentration up to 0.3 wt %, the averaged molecular weights in the network of the low-temperature block increase up to the following values:  $\bar{M}_{n(n)} = 8270$ ,  $\bar{M}_{w(n)} = 10,900$ , and  $K = 1.32$ , whereas in the high-temperature block, they reduce to values of about 1000. At 0.5 wt % of I-1010, the LDPE-g-IA transforms its topological structure to a uniblock. The molecular weight characteristics of the polymer are as follows:  $\bar{M}_{n(n)} = 441.8 \times 10^3$ ,  $\bar{M}_{w(n)} = 1000 \times 10^3$ , and  $K = 2.27$ .

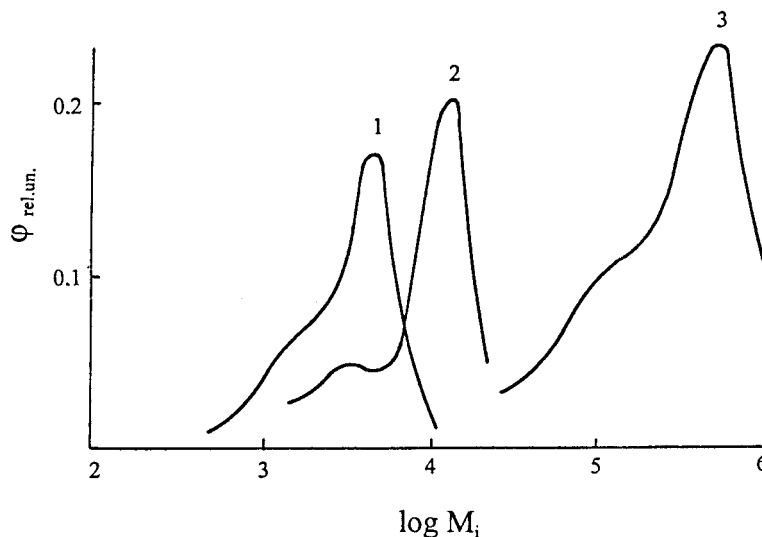
**Figure 5** Effect of concentration and nature of stabilizer on grafting efficiency of IA into LDPE (a) and (b) and the MFI of LDPE-g-IA (c) and (d).



**Figure 6** Thermomechanical curves for LDPE-*g*-IA prepared with 0.1 wt % of L-101; the I-1010 stabilizer concentrations: (a) 0.1 wt %; (b) 0.3 wt %; and (c) 0.5 wt %.

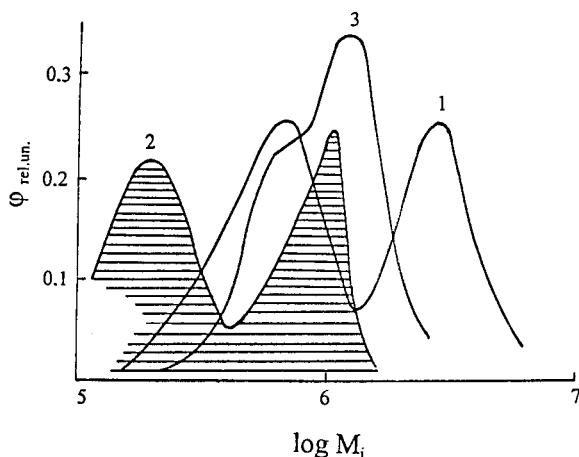
For the LDPE-*g*-IA systems prepared with 0.3 wt % of L-101 peroxide, the polymer's structure remains uniblock at the tested concentrations of I-1010. That is, higher concentrations of the peroxide initiator ensure complete homogenization of all structural irregularities in polyethylene bulk. The  $T_g$  is actually independent of the I-1010 concentration, reaching 26–31°C. The TMC for all the tested polymers have the same shape as that for the LDPE-*g*-IA prepared with 0.1 wt % of L-101 and 0.5 wt % of I-1010 [Fig. 6(c)]. It was learned that the increase in L-101 concentration

up to 0.3 wt % is followed by an improvement in the grafting efficiency along with the degree of crosslinking of the macromolecules; in the presence of the stabilizer, it leads to a homogeneous uniblock structure. The effect of I-1010 is expressed as changes in the molecular-weight characteristics of LDPE-*g*-IA and the shape of the MWD [Fig. 8]. For instance, at the I-1010 concentrations of 0.1 and 0.3 wt %, the average molecular weights remain, in fact, unchanged, being  $\bar{M}_{n(n)} = 638 \times 10^3$ ,  $\bar{M}_{w(n)} = 1402 \times 10^3$ , and  $\mathcal{H} = 2.2$  for 0.1 wt % of I-1010;  $\bar{M}_{n(n)} = 678 \times 10^3$ ,



**Figure 7** The MWD for the chains between the junctions in a low-temperature topological block of LDPE-*g*-IA prepared with L-101 0.1 wt % and I-1010 0.1 wt % (1); 0.3 wt % (2); also for the uniblock polymer containing L-101 0.1 wt % and I-1010 0.5 wt %.





**Figure 8** The MWD for LDPE-*g*-IA prepared with L-101 0.3 wt % and I-1010 0.1 wt % (1), also with I-1010 0.3 wt % (2) and 0.5 wt % (3).

$\bar{M}_{w(n)} = 1228 \times 10^3$ , and  $\mathcal{H} = 1.82$  for 0.3 wt % of I-1010. Similar in shape (bimodal) are the MWD.

On increasing the I-1010 concentration up to 0.5 wt %, the polymer's polydispersity reduces to  $K = 1.18$  at average values of  $\bar{M}_{n(n)} = 856.5 \times 10^3$  and  $\bar{M}_{w(n)} = 1007.6 \times 10^3$ .

## CONCLUSION

The effect of stabilizers, which follow the radical mechanism, on the grafting of IA onto LDPE and on the crosslinking depends on their solubility in the polymer and the monomer. The stabilizer (HQ), characterized by closer affinity toward the monomer, can reduce the grafting efficiency as well as inhibit the crosslinking of macromolecules. By increasing the concentration (up to 0.3–0.5 wt %) of the stabilizers, which are insoluble in the monomer, it is possible to somewhat improve the grafting efficiency while inhibiting the crosslinking of LDPE-*g*-IA, irrespective of the peroxide used. Hence, classical stabilizers can initiate grafting reactions during the reactive extrusion run at certain conditions (e.g., increased concentrations, temperature, and application of shearing stresses). The addition of stabilizers is an efficient means of preparing LDPE-*g*-IA with a high grafting efficiency and a reduced crosslinking.

A stabilizer, characterized by a thermodynamic affinity toward LDPE, can substantially affect the molecular and topological structure of LDPE-*g*-IA, as it was learned by the TMA technique. Their higher content (up to 0.5 wt %) transforms the

topological structure to a uniblock. The MWD may be either narrow ( $\bar{M}_{w(n)}/\bar{M}_{n(n)} < 2$ ) or broad ( $\bar{M}_{w(n)}/\bar{M}_{n(n)} > 2$ ), depending on the concentration of the peroxide initiator used to synthesize LDPE-*g*-IA.

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