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Grafting of Methylenebutanedioic Acid to Low-Density Polyethylene in the Course of Reactive Extrusion, Initiated with Carborane-Containing Peroxides

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Abstract—The influence of carborane-containing peroxides on the efficiency of grafting of methylenebutanedioic acid to low-density polyethylene in a single-screw extrusion reactor equipped with a static mixer was studied.

Grafting of monomers containing chemically active functional groups to polyolefin macromolecules is a subject of active study in many research centers [1–6], which is due to growing use of grafted products in preparation of polymeric composites, mostly of polymer blends and alloys. As a rule, grafting is performed in a polyolefin melt; as continuous reactors are used special extruders acting simultaneously as high-performance mixers of the components and providing controllable feeding of the components, removal of by-products, accurate temperature control, control of the velocity of the reaction mixture transport, etc. [1, 6]. The yield of the grafted product and the course of side processes are determined both by the extruder design features and by the reaction mixture composition [1, 5, 6]. In particular, we showed in [5, 6] that the course of grafting of methylenebutanedioic acid (MA) to low-density polyethylene (LDPE), at identical apparatus design and process (thermal) parameters, is largely influenced by the nature and concentration of the peroxide initiator. Use for these purposes of commercial peroxides [dicumyl peroxide (DCP), 2,5-dimethyl-2,5-di-*tert*-butylperoxyhexane, etc.] results in active chemical cross-linking of the macromolecules, occurring simultaneously with grafting of MA. As a result, strongly cross-linked products are formed, which limits their use for fabrication of composites. Furthermore, the product obtained by grafting of MA to LDPE (LDPE-*graft*-MA) with traditional peroxides exhibits a poor resistance to thermal oxidative degradation in air and in aqueous solution [7].

In [8–10] we described the synthesis of unsaturated carborane-containing peroxides. These peroxides can be used for cross-linking of polyethylene [11], initiating high-temperature radical cross-linking reactions. In contrast to cross-linked polyethylene prepared with traditional peroxides, the product obtained with carborane peroxides exhibits enhanced resistance to thermal oxidative degradation [11]. Presumably, the thermostabilizing effect of carborane peroxides is due to grafting of carborane-containing fragments formed by thermolysis of the peroxide to macromolecules and intermolecular cross-linking through boron atoms. The possibility of grafting to polyolefin molecules of functional groups of unsaturated peroxides is indicated, e.g., by Assoun *et al.* [12] who studied grafting of carboxy groups to polypropylene macromolecules in the melt under the action of peroxy acids.

It is interesting to evaluate the effect of carborane-containing peroxides as initiators of grafting of functional monomers to polyethylene macromolecules. Here this problem is studied with grafting of MA to LDPE as example.

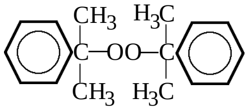
EXPERIMENTAL

We used LDPE of 15803–020 brand [GOST (State Standard) 16337–77, Polimir Production Association, Novopolotsk; density 0.92 g cm^{-3}, mp 105°C] and MA purchased from Chemical Division Pfizer, the United States. The following carborane-containing peroxides were chosen (Table 1): peroxy esters **I** and

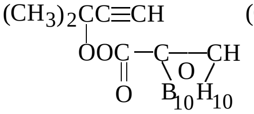
Table 1. Characteristics of peroxide initiators*

Peroxide	Name	Available oxygen content, %	
		found	calculated
DCP	Dicumyl peroxide	–	5.92
I	3-Methyl-3-(*o*-carboranoylperoxy)-1-butyne	5.66	5.92
II	3-Methyl-3-(*m*-carboranoylperoxy)-1-butyne	5.62	5.92
III	1,7-Bis(*tert*-butylperoxymethylvinylsilyl)-*m*-carborane	6.32	6.95
IV	Bis(3-methyl-3-*tert*-butylperoxy-1-butynyl)-1-*m*-carboranylmethanol	–	6.63
V	Bis(3-methyl-3-*tert*-butylperoxy-1-butynyl)-1-(7-isopropyl)-*m*-carboranylmethanol	–	6.1
VI	Bis(3-methyl-3-*tert*-pentylperoxy-1-butynyl)-1-*o*-carboranylmethanol	–	6.44
VII	Bis(3-methyl-3-*tert*-pentylperoxy-1-butynyl)-1-(2-isopropyl)-*o*-carboranylmethanol	–	5.94

*Structural formulas of peroxides:

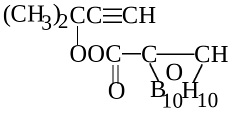


DCP



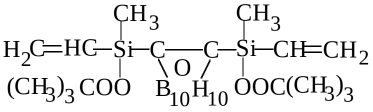
$$\begin{array}{l}(CH_3)_2CC\equiv CH\\ \quad\ \,|\\ \ \ OOC-C\text{——}CH\\ \quad\ \ \| \quad \backslash O /\\ \quad\ O \quad B_{10}H_{10}\end{array}$$

I



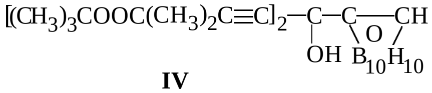
$$\begin{array}{l}(CH_3)_2CC\equiv CH\\ \quad\ \,|\\ \ \ OOC-C\text{——}CH\\ \quad\ \ \| \quad \backslash O /\\ \quad\ O \quad B_{10}H_{10}\end{array}$$

II



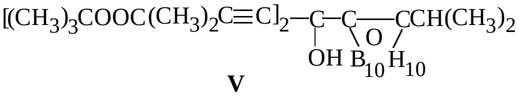
$$\begin{array}{l}\qquad\qquad\qquad CH_3 \qquad\qquad CH_3\\ H_2C{=}HC-\overset{|}{\underset{|}{Si}}-C\text{——}C-\overset{|}{\underset{|}{Si}}-CH{=}CH_2\\ (CH_3)_3COO \quad \backslash O / \quad OOC(CH_3)_3\\ \qquad\qquad\qquad B_{10}H_{10}\end{array}$$

III



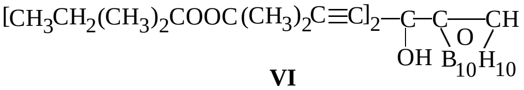
$$[(CH_3)_3COOC(CH_3)_2C\equiv C]_2-\underset{OH}{\underset{|}{C}}-\underset{B_{10}H_{10}}{C\overset{\backslash O /}{\text{——}}CH}$$

IV



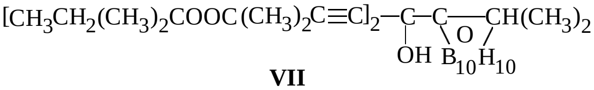
$$[(CH_3)_3COOC(CH_3)_2C\equiv C]_2-\underset{OH}{\underset{|}{C}}-\underset{B_{10}H_{10}}{C\overset{\backslash O /}{\text{——}}CCH(CH_3)_2}$$

V



$$[CH_3CH_2(CH_3)_2COOC(CH_3)_2C\equiv C]_2-\underset{OH}{\underset{|}{C}}-\underset{B_{10}H_{10}}{C\overset{\backslash O /}{\text{——}}CH}$$

VI



$$[CH_3CH_2(CH_3)_2COOC(CH_3)_2C\equiv C]_2-\underset{OH}{\underset{|}{C}}-\underset{B_{10}H_{10}}{C\overset{\backslash O /}{\text{——}}CH(CH_3)_2}$$

VII

II [8], silylcarborane **III** [9], and mixtures of peroxy alcohols with alkylperoxy groups **IV**–**VII** [10]. For comparison, we also used DCP whose effect on grafting of MA to LDPE, as well as the properties of the resulting products, are relatively well studied [5, 6, 13]. Also we tested mixtures of carborane-containing peroxides with DCP.

Grafting was performed in a single-screw extruder additionally equipped with a static mixing head, under the following conditions: nitrogen atmosphere; screw rotation rate 35 rpm; temperatures, °C: zone I 160 and zones II–IV and mixing head 185. The scheme of the extrusion reactor is similar to that shown in [6] for the Brabender plastograph equipped with a static mixer. The process for preparing the reaction mixture is also described in [6].

As parameter characterizing the progress of grafting, we used the grafting efficiency α: the weight ratio of the grafted acid to its total amount introduced into the polymer [6]. The quantity α was calculated from the content of MA in LDPE before and after extraction with ethanol at 70°C, determined by IR absorption spectroscopy [6, 14].

The viscosity of the polymer melt was evaluated by the melt flow index (MFI), which was determined at 190°C and a load of 10 kg with an IIRT-AM device (Ekodatchik Private Company, Tula, Russia).

The thermal stability of peroxides was evaluated with an MOM derivatograph (Hungary) under argon; the sample weight was 100 mg, and the linear heating rate, 7 $\deg\,min^{-1}$. The reaction order n of thermal decomposition of peroxides was calculated by the Kissinger method [15]. The apparent activation energy E_a was determined from the exothermic peak in the DTA curve in the temperature range where the linear dependence was preserved (up to 130°C for **I** and **II**, 160°C for **III**, and 155–160°C for **IV**–**VII**) [15]. The thermal analysis of the polymeric samples was performed with a derivatograph in air; the sample weight was 500 mg, and the heating rate, 2.5 $\deg\,min^{-1}$.

Tables 1 and 2 show that in peroxy esters **I** and **II** the available oxygen content is similar to that in DCP, but the thermal stability of **I** and **II** (T_{od} denotes the temperature of the onset of degradation) is lower: T_{od} = 116–118°C; for *ortho* isomer **I** n = 1.89 and E_a = 153 kJ mol^{-1}; for *meta* isomer **II** n = 1.63 and

Table 2. Characteristics of thermal stability of carborane-containing peroxides

Peroxide	Process stages	DTG, °C			TG, Δm, %	DTA				
		T_{onset}	T_{end}	T_{maximum}		mp, °C	exothermic peak, °C		n	E_a, kJ mol^{-1}
							T_{onset}	T_{maximum}		
DCP	1	127	177	162	43.0	43	127	163	1.16	154
	2	177	202	–	32.0					
I	1	118	150	134	55.0	95	118	136	1.89	153
	2	179	230	192	13.0					
II	1	116	158	140	20.0	85	115	142	1.63	112
	2	180	287	248	40.0					
	3	342	470	–	4.0					
III	1	135	192	164	25.0	–	136	167	1.68	179
IV	1	125	186	171	47.0	80	123	173	1.45	132
	2	186	485	–	7.0					
V	1	127	192	166	30.5	99	126	168	1.60	153
	2	192	257	–	5.0					
	3	257	463	–	32.0					
VI	1	125	185	170	50.0	–	124	172	1.43	130
	2	185	480	–	14.0					
VII	1	123	194	157	31.0	51	122	163	1.61	153
	2	194	272	–	8.0					
	3	272	470	–	41.0					

E_a = 112 kJ mol^{-1}; at the same time, for DCP T_{od} = 127°C, n = 1.16, and E_a = 154 kJ mol^{-1}. Peroxides **I** and **II** initiate grafting of MA to LDPE under experimental conditions (concentration 0.15 wt %) with an efficiency of 23–25% (with DCP α = 66.7%, Table 3). In diperoxy alcohols **IV**–**VII**, the available oxygen content is somewhat higher than in DCP (Table 1), and their thermal stability is similar to that of DCP (T_{od} = 123–127°C); however, the character of decomposition of **IV**–**VII** is different (n = 1.43–1.61, E_a = 130–153 kJ mol^{-1}). The performance of diperoxy alcohols in grafting MA to LDPE approaches that of DCP. At concentrations of the mixtures **IV** + **V** and **VI** + **VII** of 0.15 wt %, α = 37.5–40.9% (Table 3, entries 6 and 7). At a concentration of the mixture **VI** + **VII** of 0.3 wt %, the grafting efficiency is 83.1%, being similar to the grafting efficiency attained with DCP (84.4%) (Table 3, entries 6 and 7).

An important advantage of carborane-containing peroxides **I**, **II**, and **IV**–**VII** over DCP is suppression, to a large extent, of the concurrent cross-linking of polyethylene macromolecules. The parameter sensitive to cross-linking accompanying MA grafting is MFI

Table 3. Influence of peroxides on the MA grafting efficiency and MFI of the polymer

Entry	Initial composition	MFI, g/10 min	α, %
1	LDPE	16.9	–
2	LDPE/MA + 0.15DCP	10.2	66.7
3	LDPE/MA + 0.3DCP	2.8	84.4
4	LDPE/MA + 0.15(**I**)	16.5	23.1
5	LDPE/MA + 0.15(**II**)	16.9	24.9
6	LDPE/MA + 0.15(**IV** + **V**)	12.0	37.5
7	LDPE/MA + 0.15(**VI** + **VII**)	15.9	40.9
8	LDPE/MA + 0.15(**III**)	18.5	18.4
9	LDPE/MA + 0.3(**VI** + **VII**)	6.5	83.1
10	LDPE/MA + 0.3(**III**)	20.3	29.1
11	LDPE/MA + 0.15(DCP + **I**)	15.1	44.5
12	LDPE/MA + 0.3(DCP + **I**)	5.5	64.3
13	LDPE/MA + 0.15(DCP + **II**)	13.4	46.5
14	LDPE/MA + 0.3(DCP + **II**)	6.0	56.0
15	LDPE/MA + 0.15(DCP + **IV** + **V**)	14.2	46.7
16	LDPE/MA + 0.3(DCP + **IV** + **V**)	3.7	74.2

Note: Weight ratio of components in peroxide mixtures 1 : 1.

[6]. A significant decrease in MFI on grafting of MA to LDPE is one of the main drawbacks of the process based on using DCP. For example, Table 3 shows that MFI of the initial LDPE is 16.9 g/10 min. Grafting of MA in the presence of 0.15 and 0.3 wt % DCP yields a functionalized product with MFI of 10.2 and 2.8 g/10 min, respectively. Thus, with DCP it is impossible to graft MA to LDPE with a high (>80%) yield and therewith avoid strong cross-linking.

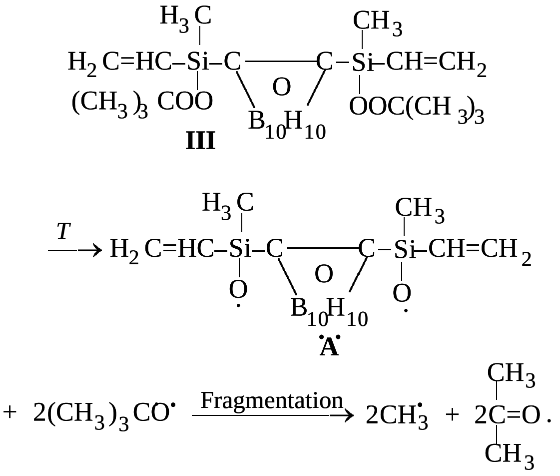
In contrast to the product obtained with DCP, MFI of polyethylene grafted with MA in the presence of peroxy esters **I** and **II** (0.15 wt %) is similar to that of the initial LDPE, which suggests practically no cross-linking. The occurrence of concurrent cross-linking of LDPE macromolecules with diperoxy alcohols **IV** + **V** and **VI** + **VII** depends on the structure of the *tert*-alkyl group at the O–O bond. For example, in the case of diperoxy alcohols **VI** + **VII** with *tert*-pentylperoxy groups (0.15 wt %) the cross-linking of macromolecules is insignificant (MFI 15.9 g/10 min), and with compounds **IV** + **V** containing *tert*-butylperoxy groups MFI of LDPE-*graft*-MA is 12.0 g/10 min (Table 3). It should be noted also that in the case of grafting initiation with peroxides containing *tert*-pentylperoxy groups grafting of MA to LDPE is more efficient (α = 40.9%) as compared to peroxy alcohols with *tert*-butylperoxy groups (α = 37.5%).

As seen from Table 3, addition of carborane-containing peroxide **I** or **II** or of a mixture of diperoxides **IV** + **V** to DCP allows significant reduction of the yield of the cross-linked product with a sufficiently high grafting efficiency. For example, the materials obtained with a mixture of DCP with **I**, **II**, or **IV** + **V** are characterized by MFI = 13.4–15.1 g/10 min and α = 44.5–46.7% (Table 3, entries 11, 13, 15).

With a concentration of the peroxide mixtures of 0.3 wt %, MFI is lower, 3.7–5.5 g/10 min, at α = 56–74.2%; with straight DCP MFI = 2.8 g/10 min and α = 84.4% (Table 3, entries 3, 12, 14, 16).

Among the tested carborane-containing peroxides, the most thermostable is silylcarborane **III** (T_{od} = 135°C), which can be simultaneously considered as a peroxide monomer owing to the presence of two vinyl groups; however, under the experimental conditions (0.15 and 0.3 wt %) it is the least efficient initiator of MA grafting to LDPE (Table 3, entries 8, 10; α = 18.4 and 29.1%, respectively). This is probably due to partial consumption of radicals generated by decomposition of **III** for initiation of oligomerization of the carborane-containing fragment via double bonds and its grafting to polyethylene macromolecules. This processes can be represented as follows [12, 13].

Thermal decomposition of peroxide:

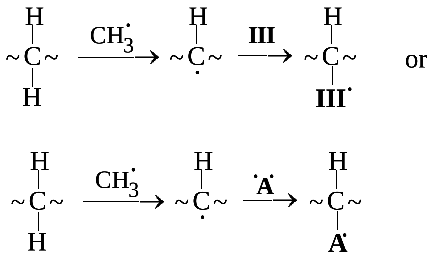


$$+\ 2(CH_3)_3CO^\bullet \xrightarrow{\text{Fragmentation}} 2CH_3^\bullet + 2(CH_3)_2C{=}O. \qquad (1)$$

Oligomerization of peroxide:

$$\mathbf{III} \xrightarrow{CH_3^\bullet} \mathbf{III}^\bullet \xrightarrow{\mathbf{III}} \mathbf{III}\text{–}\mathbf{III}^\bullet \xrightarrow{x(\mathbf{III})} \mathbf{III}\text{–}(\mathbf{III})_x\text{–}\mathbf{III}^\bullet. \quad (2)$$

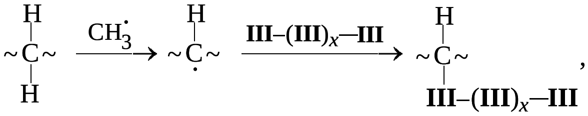
Grafting of peroxide to LDPE macromolecules:



$$\sim\overset{H}{\underset{H}{C}}\sim \xrightarrow{CH_3^\bullet} \sim\overset{H}{\underset{\bullet}{C}}\sim \xrightarrow{\mathbf{III}} \sim\overset{H}{\underset{\mathbf{III}^\bullet}{C}}\sim \quad \text{or}$$

$$\sim\overset{H}{\underset{H}{C}}\sim \xrightarrow{CH_3^\bullet} \sim\overset{H}{\underset{\bullet}{C}}\sim \xrightarrow{{}^\bullet\mathbf{A}^\bullet} \sim\overset{H}{\underset{\mathbf{A}^\bullet}{C}}\sim \qquad (3)$$

Grafting of oligoperoxide:



$$\sim\overset{H}{\underset{H}{C}}\sim \xrightarrow{CH_3^\bullet} \sim\overset{H}{\underset{\bullet}{C}}\sim \xrightarrow{\mathbf{III}\text{–}(\mathbf{III})_x\text{–}\mathbf{III}} \sim\overset{H}{\underset{\mathbf{III}\text{–}(\mathbf{III})_x\text{–}\mathbf{III}}{C}}\sim, \qquad (4)$$

It should be noted that biradical $^\bullet$**A**$^\bullet$ owing to steric hindrance is low-mobile and should not exhibit appreciable initiating power as compared to $^\bullet OC(CH_3)_3$ and $^\bullet CH_3$. Therefore, oligomerization of peroxide **III** by scheme (2) is improbable. Hence, grafting to LDPE of oligomeric fragments of **III** [scheme (4)] is also improbable. The most probable pathway is formation of products with monomolecular grafted fragments of peroxide **III** [scheme (3)].

The noticeably higher MFI (18.5 and 20.3 g/10 min) of the sample obtained with silylcarborane **III**, as compared to the initial LDPE (MFI 16.9 g/10 min) (Table 3, entries 1, 8, 10) indicates that a material with new physical (rheological) characteristics is formed. The higher MFI of LDPE-*graft*-MA obtained in the presence of silylcarborane **III** may be due to

Table 4. DTA data for the polymeric materials prepared

Entry	Initial composition, wt %	T_{od}	T_{10}	T_{50}	T_{ox}
		°C			
1	LDPE	360	390	445	170
2	LDPE/MA + 0.3DCP	360	385	440	160
3	LDPE/MA + 0.3(DCP + **I**)	358	380	445	162
4	LDPE/MA + 0.3(DCP + **II**)	351	380	455	162
5	LDPE/MA + 0.3(DCP + **IV** + **V**)	360	375	450	175
6	LDPE/MA + 0.3(**VI** + **VII**)	362	397	442	180
7	LDPE/MA + 0.3(**III**)	360	388	450	190

Note: (T_{od}, T_{10}, T_{50}, T_{ox}) temperatures of the onset of degradation, 10 and 50% weight loss, and onset of oxidation, respectively.

degradation of the macromolecules, which is hardly probable [9], or to the lubricating effect of grafted (and nongrafted) organosilicon fragments in the polymer melt. It is known [16] that organosilicon compounds are good lubricants. Therefore, the increase in MFI on grafting in the presence of **III** should be mainly due to the lubricating effect of the thermolysis products of **III**.

The use of carborane-containing peroxides (straight or mixed with dicumyl peroxide) noticeably enhances the resistance of LDPE-*graft*-MA to thermal oxidative degradation as compared to the material prepared in the presence of DCP (Table 4). Thermal oxidation of functionalized polyethylene prepared using a mixture of diperoxy alcohols **VI** + **VII** (0.3 wt %, Table 4, entry 6) and a mixture of **IV** + **V** with DCP (0.3 wt %, entry 5) is accompanied by the weight gain in the TG curve, with the onset at 180 and 175°C, which is 15–20°C higher compared to the material prepared with DCP (Table 4, entry 2). The material prepared with peroxide monomer **III** exhibits the highest resistance to thermal oxidative degradation: Its thermal oxidation starts only at 190°C, which is 30°C higher than the onset temperature of oxidation of the functionalized polyethylene formed in the presence of DCP. Presumably, the thermostabilizing effect of carborane-containing peroxides is due to grafting of carborane-containing fragments to polyethylene macromolecules. This effect is especially characteristic of **III**.

CONCLUSIONS

(1) The performance of peroxides containing carborane fragments in initiation of grafting of methylenebutanedioic acid to low-density polyethylene macromolecules depends on the chemical structure of the peroxides.

(2) Initiation of grafting with a mixture of diperoxy alcohols **VI** + **VII** containing alkylperoxy groups ensures formation of the functionalized polymer with the grafting efficiency comparable to that attained with dicumyl peroxide initiator, with the appreciably reduced degree of cross-linking of the macromolecules.

(3) Peroxide silylcarborane monomer **III** used as initiator allows preparation of the material with the melt flow index 10–20% higher than that of the initial LDPE.

(4) Functionalized low-density polyethylene prepared in the presence of carborane-containing peroxides exhibits enhanced resistance to thermal oxidative degradation as compared to the product obtained in the presence of dicumyl peroxide.

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