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THERMAL DEGRADATION OF POLYETHYLENE CONTAINING ANTIOXIDANT AND HYDROPHILIC/HYDROPHOBIC SILICA

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High-density polyethylene, its composites with hydrophilic/hydrophobic silica and the antioxidant BHT (butylated hydroxytoluene) were studied using the thermogravimetric analysis. It has been shown that filling with silica as well as introducing BHT into the unfilled polymer increases the thermal-oxidative stability of the polymer. Immobilized BHT is inactive and it suppresses the stabilizing effect of hydrophobic silica surface in the processes of thermal oxidation at the initial stage. However, being gradually released from the surface antioxidant prolongs the resistance of the polymer against oxidation.

Keywords: *antioxidant, polyethylene, silica filler, thermal-oxidative degradation*

Introduction

High-density polyethylene (HDPE) due to its lightness, mechanical properties, cheapness and availability is known to be the main packaging material and is widely used for storage and transportation of food products [1]. However, polyolefines are oxidation-vulnerable, especially at high temperature. Introducing antioxidants is one of the most convenient and efficient means to preserve thermooxidative degradation of these materials. In such polymer systems the compounds with 2,6-di-*tert*-butylphenol groups are commonly used as antioxidants [2, 3]. For instance, 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) is used as food additive and antioxidant for rubbers, petrochemicals and plastics [4]. Thus, HDPE with BHT can be used as antibacterial packing for cereal food [5]. However, it turned out that low-molecular antioxidants are easily released from the polymer matrix due to migration, evaporation and extraction [6, 7]. BHT leaching from HDPE pipes, for instance, was observed and investigated in [8, 9]. Thus, the physical loss of antioxidants is the main problem with respect to environmental protection, safety measures and durability of polymeric materials.

On the one hand, scientific efforts are turned to synthesis of polymeric antioxidants whose application will allow one to prevent the physical loss of active substance and to improve the thermal stability of a material [10, 11]. Suitable approach to obtain such compounds is the copolymerization or homopolymerization of monomer antioxidants. For instance, by this technique it was possible to synthesize polymeric antioxidants based on acrylate derivatives [12–14] or those containing 2,6-di-*tert*-butylphenol functional groups [15].

On the other hand, embedding of inorganic nanoparticles with immobilized antioxidants into polymer matrix might be one of the easiest ways to solve the above-mentioned problem. Such approach allows the regulation of the antioxidant mobility and activity by variation of filler surface chemistry. Besides, polymers filled with just inorganic materials, for instance silica particles, in some cases demonstrate an improvement in mechanical and thermal characteristics [16, 17]. However, there is a contradictory data in literature regarding the influence of adsorbed stabilizers on the oxidative resistance of filled polymers. On the one hand, this influence is negative [18], on the other – filler promotes the composite stabilization which is assumed to be a consequence of controlled release of stabilizer from the filler surface [19, 20]. It is indicated [21] that at right combination of stabilizers, silica is able to improve the stability of HDPE films.

BHT adsorption on silica occurs with the participation of phenol group [22] which plays an essential role in stabilization mechanism. As a result, immobilization of this antioxidant may lead to its partial or full deactivation. The main idea of our work is that BHT immobilization on silica filler will decrease the release of this low-molecular antioxidant from the polymer matrix. At this, hydrophobization of silica surface, i.e. elimination of active silanol groups from the filler surface, might change the mechanism of BHT adsorption and correspondingly might prevent its deactivation.

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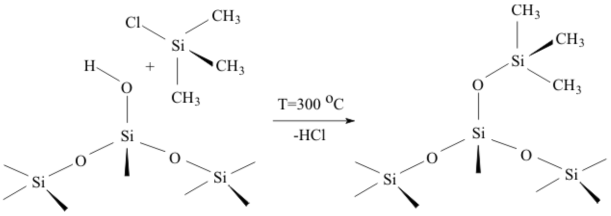
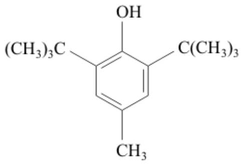
The present study is devoted to thermal degradation of HDPE–silica nanocomposites with or without BHT antioxidant immobilized onto filler surface. The aim was to reveal the peculiarities of HDPE thermal degradation depending on silica surface chemistry and the form of antioxidant BHT in polymer matrix (free and immobilized on filler surface).

Experimental

Fumed silica with a specific surface area of 200 $m^2 g^{-1}$ (Kalush, Ukraine) was used as an initial filler. Hydrophobization of silica surface was performed via gas-phase silylation using trimethylchlorosilane (Kremnepolimer, Ukraine) as a modifying agent (Scheme 1). Full substitution of isolated silanols by trimethylsilyl groups was confirmed by means of IR spectroscopy.



Silica surface trimethylsilylation via electrophylic substitution of proton in isolated silanol group



BHT

Scheme 1

BHT (Fluka) was immobilized onto the surface of initial or trimethylsilylated silica via the impregnation technique. In brief, BHT was dissolved in ethanol solution and the appropriate amount of silica powder was added into the mixture. After mixing for 0.5 h samples were dried at 60°C to remove the solvent. Then silica particles were embedded into HDPE matrix (TVK, Hungary) by means of forge-rolling at 160°C. The final HDPE–silica and HDPE–silica/BHT nanocomposites contained 1 mass% of filler and 0.1 mass% of the antioxidant.

Samples obtained were studied by means of thermogravimetric analysis (MOM, Paulik and Erdey, Budapest) in an interval of temperatures 20–1000°C at heating rate 10°C min^{-1}.

Results and discussion

In order to reveal the influence of the additives on individual stages of polymer thermal oxidation it is necessary to consider in details the process of thermal-oxidative degradation of the unfilled HDPE sample with the accent on the initial stages. Aerobic thermal oxidation of polyethylene is known to pass by the chain-radical mechanism and is divided into four main stages [23]. The splitting of peaks on DTG curves was performed taking into account these data in order to calculate the effective activation energy values for individual stages of the process (Fig. 1).

Calculations were performed using the Freeman–Carrol (Eq. (1)) [24] and graphical (Eq. (2)) methods [25] (Table 1):

$$\frac{\Delta \ln d\alpha/dt}{\Delta \ln(1-\alpha)} = n - \left(\frac{E}{R}\right)\frac{\Delta(1/T)}{\Delta \ln(1-\alpha)} \qquad (1)$$

$$E = \frac{R(T_{max})^2 (dm/dT)}{m} \qquad (2)$$

where α is the fraction of nondegraded or unreacted polymer at absolute temperature T, R is the universal gas constant, E is the activation energy, n is the reaction order, T_{max} is absolute temperature of a maximum mass loss rate (determined by splitting of DTG curve), m is the sample mass loss in temperature interval from split DTG peak beginning to T_{max}. The values $\Delta\ln(d\alpha/dt)$ and $\Delta\ln(1-\alpha)$ were taken at the regular $1/T$ interval.

According to data from the literature [26], initiation of chain thermal oxidation (Stage I) occurs mainly in amorphous parts of a polymer and its rate depends on the rate of oxygen diffusion into polymer bulk. For the samples under study the diffusion process is limited due to compact packing of macromolecules and oxidation passes in frontal regime from the sample surface predominately at the temperature higher than melting point (130°C, endo-effect on the DTA curve in Fig. 1). This process is not accompanied by mass loss up to 252°C and therefore this stage is hard to distinguish on the TG curve. At first stage of HDPE thermal oxidation the oxygen-stimulated chain breakage occurs resulting in accumulation of peroxide radicals (reaction 1, 2) which partly decay yielding the destruction products at the temperature above 252°C. The processes involved are accompanied by broad exo-effect starting at 207°C with the maximum at 285°C (Fig. 1, DTA curve). The mass loss may be also attributed to the passage of the processes 3–5 with activation energies of 66.9, 58.5 and 117 kJ mol^{-1}, respectively [27].

$$(1)\ RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet}\ (1^A)\ R^{\bullet} + HO_2^{\bullet} \rightarrow RO + HO^{\bullet}$$

$$(2)\ 2RH + O_2 \rightarrow 2R^{\bullet} + H_2O_2$$

where RH is the monomer unit ~CH$_2$–CH$_2$~

$$(3)\ \mathrm{RH}+{}^{\bullet}\mathrm{OH}\rightarrow\mathrm{R}^{\bullet}+\mathrm{H_2O}$$

$$(4)\ \mathrm{RH}+\mathrm{HO_2^{\bullet}}\rightarrow\mathrm{R}^{\bullet}+\mathrm{H_2O_2}$$

$$(5)\ \mathrm{RH}+{}^{\bullet}\mathrm{CHO}\rightarrow\mathrm{R}^{\bullet}+\mathrm{CH_2O}$$

The absence of mass loss during the passage of the main process (reaction 1) does not allow adequate evaluating of the activation energy of the initiation stage using the TG data. Along with the chain initiation stage the sample peroxidation occurs corresponding to the stage of chain propagation (Stage II).

Peroxidation occurs without essential degradation of the polymer and it also takes place in amorphous sites mainly at surface layer. At this, the activation energy of peroxides formation is about 70–100 kJ mol^{-1} [28]. Alcohols and ketones are the main products of HDPE degradation. As for the chain breakage with the monomer formation (depolymerization), this process is unlikely for polyethylene, however, in aerobic conditions vinylene groups may be produced during the disproportionation [29]. The chain breakage is also a result of recombination whose rate increases with an increase of the amount of macroradicals with terminal peroxide groups [23]. Because of the superposition of two stages of thermal oxidation with a prevalence of the chain propagation, the TG curve in the temperature interval 252–340°C was considered as the single stage of the process in order to evaluate the effective activation energy. According to the analysis of the DTG and DTA curves for the unfilled HDPE the interval of 207–340°C with a maximum at 340°C on the DTA curve was attributed to the stage of chain propagation. Within an interval 252–340°C the sample mass loss is negligible and its rate is constant which is typical for the first two stages. At chain propagation stage the mass loss is related to the removal of low-molecular products that are not bound into polymeric chain, as well as to the degradation of hydroperoxides (expressions 7^A, 7^B and 7^D) which are initially present in the material and formed according to the expression 7 or according to the schemes 6^A, 6^B. The value of reaction order calculated in an interval 281–321°C confirms superposition of several processes. Taking into account relatively low value of the activation energy (96–108 kJ mol^{-1}) at n=3 and the data on the activation energies of ketones and alcohols formation [29], the ketones formation predominates at this interval.

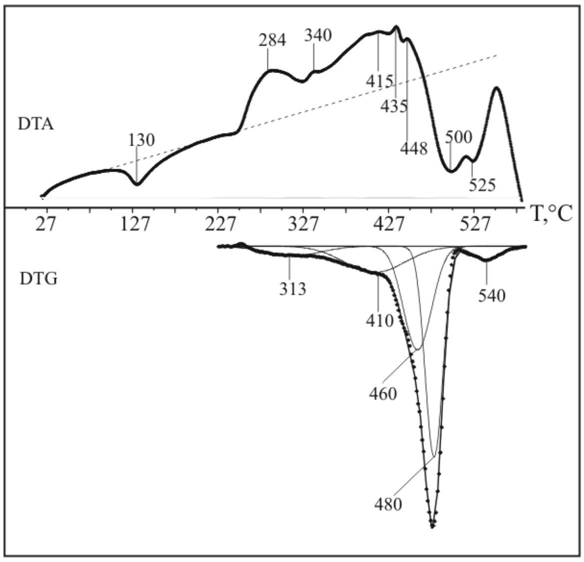


Fig. 1 DTA and DTG curves for the unfilled HDPE

A maximum on the DTG curve at 410°C is attributed to the stage of chain branching (Stage III). In an interval 323–435°C related to this stage there are several exo-effects on the DTA curve (Fig. 1). Here is the superposition of peroxides degradation (reactions 9, 10, 13) (main process) and polymer degradation via C–C breakage to produce macroradicals with subsequent chain transfer resulting in polymer

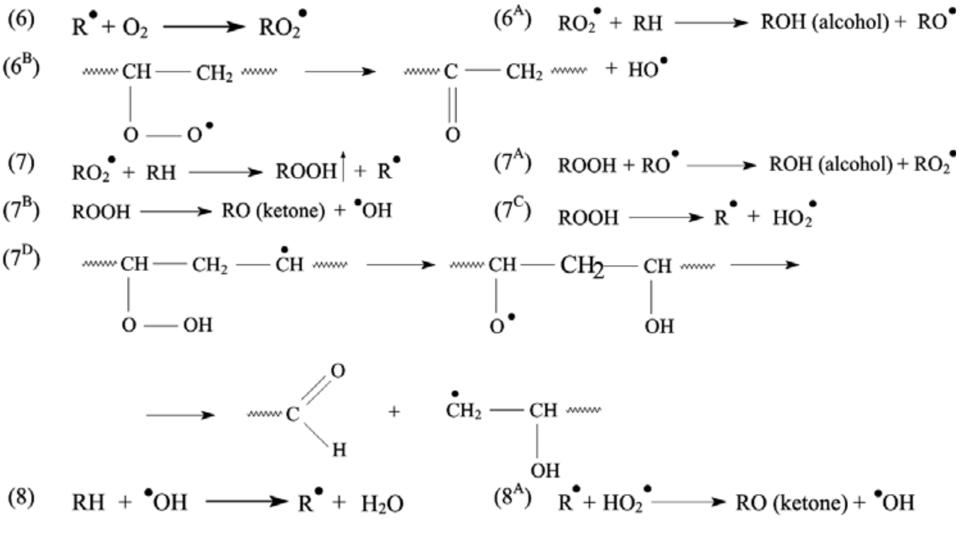
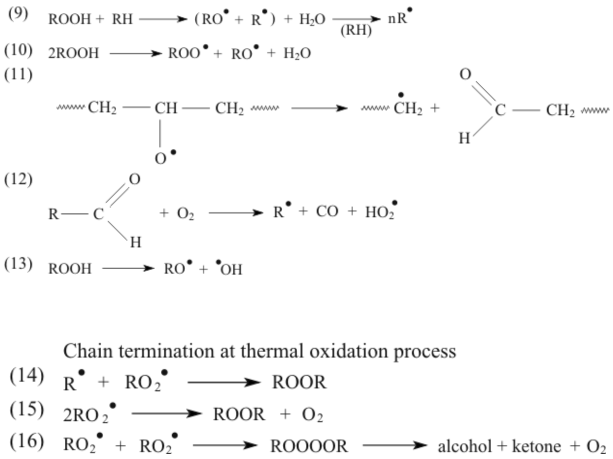


Table 1 Effective activation energy (E_a, kJ mol^{-1}) and reaction order (n) of thermal-oxidative degradation of HDPE and HDPE-based composites derived using DTG curve splitting (Graphic) and Freeman–Carrol methods

Sample	Graphic		Freeman–Carrol			Graphic		Freeman–Carrol			Graphic		Freeman–Carrol		
	T_{1max}/°C	E_a	T^*/°C	E_a	n	T_{2max}/°C	E_a	T^*/°C	E_a	n	T_{3max}/°C	E_a	T^*/°C	E_a	n
1	313	96.6	281–321	108.5	3	409	69.6	323–399	59.8	2.7	461	217.9	419–461	189.5	0.4
2	325	159.2	314–334	80.9	2.6	401	77.4	363–401	100.3	1.3	451	166.4	422–447	196.7	3
3	331	176.3	311–331	146.1	3	404	89.7	366–386	49.8	1.7	451	186.9	621–468	296.8	2.3
								366–404	77.8	2.5					
4	324	250.3	309–329	206.1	3	418	73.7	356–384	89.6	1.1	464	231.6	429–464	143.9	1.5
								356–402	109.2	3			429–484	176.2	0.7
5	375	73.5	327–356	79.9	3	437	109.2	412–430	145.2	2.3	464	262.4	430–450	153.5	1.1
			365–412	54.8	1.2								430–464	144.7	0.6

*Temperature interval of TG curve linearization in term of Freeman–Carrol equation with correlation coefficient (R^2) above 0.97

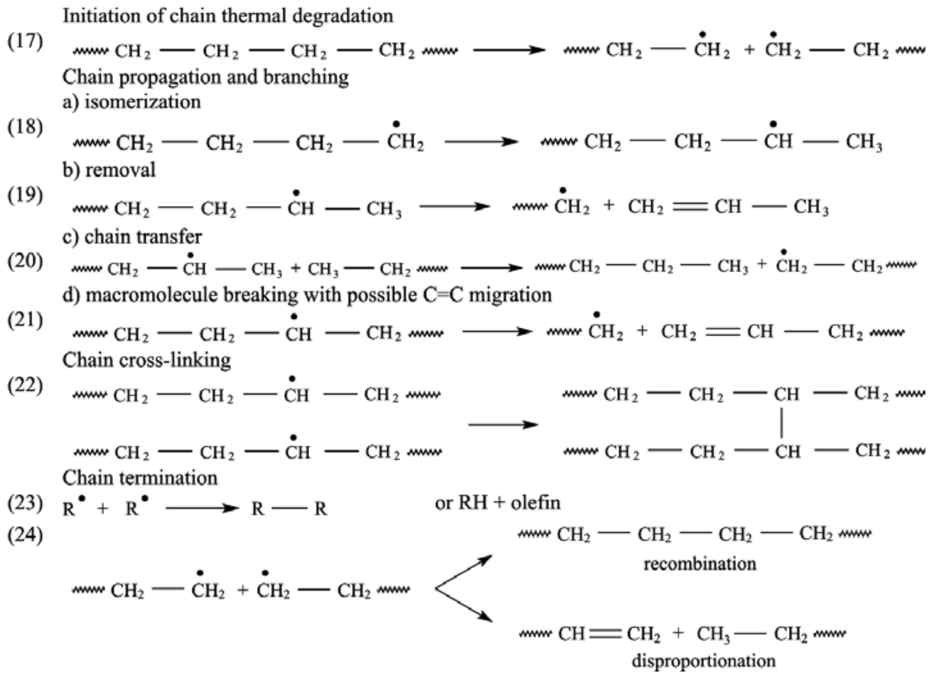


cross-linking and formation of branched bonds network (reactions 17–22). The frontal oxidation from the surface promotes this process. The char formation prevents the autocatalysis. Low oxygen concentration inside the polymer matrix and therefore, the presence of little amount of terminal peroxide groups increasing the rate of recombination leads to the polymer cross-linking, as well. The interaction between hydroxyperoxide groups and alcohol hydroxides is also possible. At this, the low energy of HDPE isomerization prevents easy-to-evolve formation of monomer; this is reflected in low mass loss rate [30]. As a result, the sample mass loss at maximum degradation rate at this stage is 13%. For this interval the intensity of the appropriate peak on the DTA curve is considerably increased which may be considered as indirect evidence of the polymer cross-linking process.

The activation energy calculated in an interval 323–399°C is 59.8–69.6 kJ mol^{-1}. According to a decrease in activation energy in comparison with the previous interval (Table 1) $HO_2^{\bullet}$ is the main attacking agent in oxidation processes at chain branching (58 kJ mol^{-1}) [31].

Exo-effect at 397°C is related to this process and the subsequent broad exo-effect peak is attributed to the reaction schemes 9–12. Low activation energy also indicates that hydroperoxides degradation passes predominantly via hydrogen removal from –ROOH according to the bimolecular mechanism (10) [27, 32]. The narrow exo-effect peak at 435°C and the next one at 448°C are in the temperature interval of the transition from the stage of chain branching to the stage of chain termination. On our opinion, the first peak is related to the autocatalysis with intensive evolution of the polymer oxidation products, the second one is caused by the oxidation of the polymer oxidation products. At these temperatures the mass loss rate increases considerably.

The stage of chain termination (Stage IV) is attributed to the maximum on the DTG curve at 460°C (Fig. 1). Within this stage the reactions of chain termination pass according to both thermal-oxidative (reactions 14–16) and thermal degradation (reactions 23, 24). The activation energy at this stage is maximum – 189.5–217.9 kJ mol^{-1} (commensurate with the energy of chain termination at anaerobic thermal decomposition [33]. Weakly expressed exo-effect peak (about 460°C) is noted on the DTA curve at transition to endothermic process (transition temperature is about 470°C) with subsequent broad endo-effect peak at 500°C. Therefore, chain termination is realized mainly via the mechanisms of macroradicals disproportionation and recom-



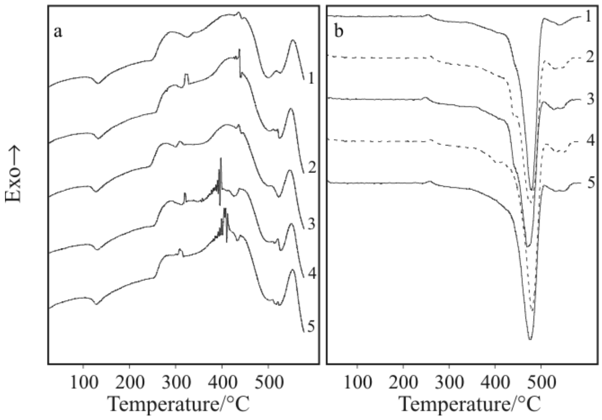


Fig. 2 a – DTA and b – DTG curves for the 1 – unfilled HDPE, 2 – HDPE-BHT, 3 – HDPE filled with unmodified silica, 4 – HDPE filled with trimethylsilylated silica and 5 – HDPE filled with trimethylsilylated silica containing immobilized BHT

bination (24). The contribution of peroxyradicals disproportionation as well as their regeneration and reactions involving $HO_2^•$ and $HO^•$ is less weighty [34]. This process results in formation of high- and low-molecular products removing from the material. The subsequent stage with maximum mass loss rate at 480°C corresponds to the degradation of high-molecular products formed at previous stages and the end of this stage is also attributed to the endo-effect peak at 500°C. At this stage the mass loss rate is a maximum. The shift of thermal effect into the region of higher temperatures relative to the maximum of mass loss is caused by char crust formation on the sample surface during its thermal degradation. The maximum on the DTG curve at 540°C may be attributed to the evolution of poor-volatile oxidation products [35]. The total sample mass loss is 99.6% and is reached at 575°C.

Inhibition of HDPE thermal oxidation at the presence of the BHT antioxidant (Sample 2) starts at the stage of peroxide radicals formation (reactions 27, 28) i.e. at the initiation stage (reactions 25, 26) [36]. It results in an increase in starting temperature of mass loss in comparison with the initial sample 1 (Fig. 2, curve 2). An increase in the activation energy of thermal oxidation at this stage is related both to the interaction of BHT with alkoxyl and alkyl radicals (reaction 31), disproportionation reaction between R-OH and $In^•$ and the change of the content of evaporating volatile products, in particular, the formation of vinyl- and vinylene groups is increased at reduced yield of alcohols [37].

The peroxidation exo-effect peak (313–329°C) (Fig. 2a, curve 2) narrows, becomes more intensive reaching the maximum at a higher temperature (323°C). The changes described on the DTA curve at the presence of the antioxidant allow one to attribute the exo-effect at 323°C to the kinetic chain termination involving the antioxidant (reactions 27, 28). At this, the effective activation energy grows. Also, at BHT presence the temperature maximum of mass loss at the stage of chain branching is shifted to the region of lower temperatures (DTG, Fig. 2b) and the corresponding exo-effect peak narrows reaching the maximum at 423°C indicating progress to the processes (32, 33).

(25) $RH + O_2 \longrightarrow R^• + HO_2^•$ (26) $R^• + O_2 \longrightarrow RO_2^•$

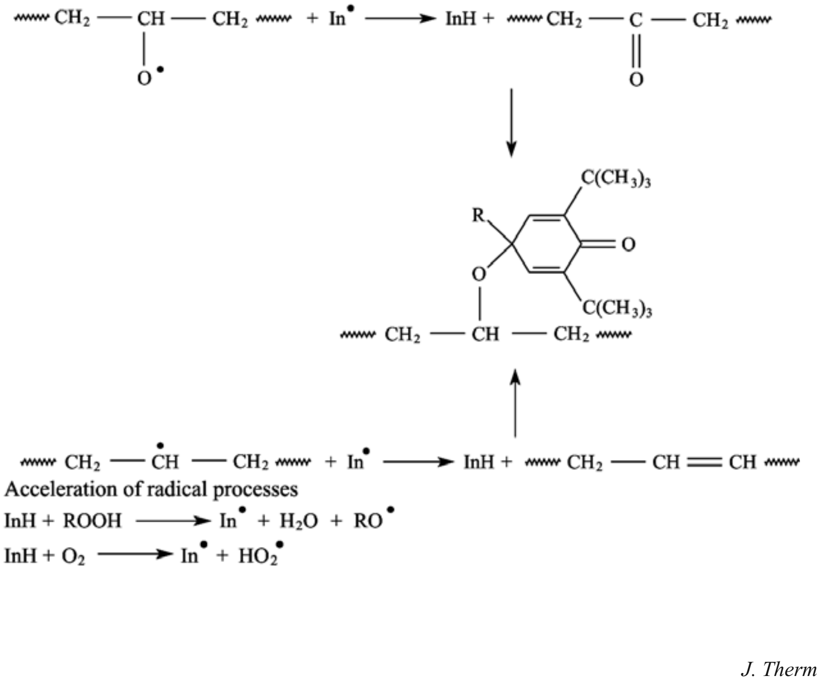
(27) $RO_2^• + InH \longrightarrow ROOH + In^•$ (28) $RO_2^• + In^• \longrightarrow ROOIn$

Antioxidant poisoning

(29) $In^• + RH \longrightarrow InH + R^•$

(30) $In^• + ROOH \longrightarrow InH + RO_2^•$

(31)



$$\sim CH_2-\underset{\displaystyle O^•}{CH}-CH_2\sim + In^• \longrightarrow InH + \sim CH_2-\underset{\displaystyle \| \atop O}{C}-CH_2\sim$$

$$\sim CH_2-\overset{•}{C}H-CH_2\sim + In^• \longrightarrow InH + \sim CH_2-CH=CH\sim$$

Acceleration of radical processes

(32) $InH + ROOH \longrightarrow In^• + H_2O + RO^•$

(33) $InH + O_2 \longrightarrow In^• + HO_2^•$

On the DTA curve the drastic transition at 437–444°C is observed. Such a transition is more typical for physical processes at phase transition but in this case its appearance is attributed to the growing contribution of the mechanism of thermal decomposition. The maximum of mass loss rate at the stage of chain termination (DTG, Fig. 2b) is also shifted into the region of lower temperatures and is accompanied by less intensive exo-effect on the DTA curve, however, this process occurs with less mass loss rate. This indicates the prevalence of thermal oxidation products with larger molecular mass in sample. It is confirmed by the appearance of the peak at 517°C and by the intensity growth of the endo-effect peak at 523°C on the DTA curve.

In the presence of unmodified silica filler (Sample 3) the activation energy of the processes increases considerably (Table 1). The starting temperature of thermal degradation is the same as in the case of the HDPE sample with the antioxidant, however, the exo-effect peak which we attributed to the peroxidation reactions has the maximum at 308°C and the drastic transition to endothermic processes at 438°C is not observed (Fig. 2, curves 3).

This may indicate that the filler binds the material structure thus preventing its mobility at phase transition. The mass loss rate for the Sample 3 corresponds to that for the Sample 2. Therefore, the filler, as well as the antioxidant, inhibits the oxidation but the mechanism of its action is different. It is related to involving of filler surface hydroxyl in reactions of oxidation and chain termination resulting in immobilization of macromolecules at surface layer of silica particles. An increase in activation energy is typical at polymer filling with inorganic particles [38, 28], but as opposed to the data [39, 28] an essential increase in degradation rate on stages III and IV was not observed for the composite under study.

A similar effect is also noted for the HDPE filled with fully trimethylsilylated silica (Sample 4) but with more considerable increase in the activation energy at all thermal oxidation stages (Table 1). It indicates the prevalence of thermal reactions of macroradicals formation (low oxygen penetrability) at the initial stages and growing contribution of disproportionation and recombination reactions resulting in the polymer cross-linking. The narrow peak on the DTA curve at 391°C (the stage of chain branching) testifies to the passage of highly exothermic process – presumably fast oxidation (Fig. 2a, curve 4). A similar effect is possible at polymer thermal oxidation in the presence of radical process initiator. Therefore, this effect corresponded to autocatalysis as a result of the reaction (13). Thus, the methylated filler surface promotes fast autocatalytic reactions in narrow temperature interval. At this, an increase in the mass loss rate is not observed indicating the formation of the high-molecular oxidation products in the material. An increase in the mass loss rate as compared with the Sample 3 occurs only after 50% of polymer transformation. The exo-effect split at about 430°C into 410 and 440°C observed on the DTA curve is the evidence that the mechanism of HDPE thermal oxidation changes in the presence of the modified silica filler in comparison with Sample 3. An increase in the HDPE thermal stability at the presence of modified silica is explained by a decrease in the molecular mobility in polyethylene amorphous regions containing filler particles [40].

In the case of HDPE filled with trimethylsilylated silica containing the immobilized antioxidant (Sample 5) the starting temperature of mass loss decreases to 258°C and within the interval 258–327°C the rate of this process is constant (Fig. 2b, curve 5). At this, the activation energy of thermal oxidation is decreased considerably at the stages of chain initiation and propagation and is increased at the stages of chain branching and termination. The DTA curve is identical to that for Sample 4 indicating the similarity of the processes occurring in the sample at thermal oxidation and the prevailing role of the surface in comparison with the antioxidant action. However, the intensity of exo-effect peaks is changed demonstrating the prevalence of reflex at 410°C corresponding to the stage of chain branching. Presumably, cross-linking of the surface polyethylene layer at stage II results in retention of the BHT molecules near the filler surface and the deactivation effect of the silica surface is more evident. The smoothing of stage transitions is observed on the DTG curve indicating many simultaneous reactions. Here, the mass loss rate slightly increases up to 50% of polymer transformation and then decreases.

Summarizing the results it should be noted that in spite of the expected material loosening an increase in starting mass loss temperature is observed for the filled HDPE samples. It is related to the effect of the silica filler which might be explained as follows. During the degradation process macromolecules immobilized on particles surface divide into more high-molecular and therefore, less volatile fragments. Direct participation of surface groups in thermal oxidation reactions is also possible. For the unmodified silica filler the mechanism of antioxidant action may be similar to the action of hydroxyl groups of BHT molecules. In the case of trimethylsilylated silica the hydrophobic interactions between the surface groups and macromolecules could play the determining role in change of near-surface layer structure. Besides, the compatibility between methylated silica and the polymer matrix is higher than in the case of unmodified silica, thus, more uniform distribution of particles in polymer bulk and therefore, higher effectiveness of filler stabilizing effect is achieved. Owing to this, the thermal stability of the HDPE composite containing hydrophobic silica is higher than that of the composite containing hydrophilic silica. So, the surface groups of silica filler and the hydroxyl group of the antioxidant BHT play an inhibiting role in thermal oxidative degradation of HDPE since filling with silica and introduction of BHT into unfilled HDPE lead to similar changes in characteristic temperatures of the material thermal oxidation (at the initial stage). However, filling of HDPE with fully trimethylsilylated silica containing immobilized BHT gives not synergistic but antagonistic effect resulting in worsening in the thermal stability of the polymer. We assume that the effect observed is related to blocking of active sites responsible for the antioxidant activity of silica filler by adsorbed BHT which, in turn, looses its antioxidant activity in immobilized state. At this, the loosened structure is more vulnerable to the action of diffusing oxygen than that of the unfilled polymer. It is evident when comparing the parameters of the samples thermal oxidative degradation. As the temperature rises, the antioxidant releases slowing down the oxidation process and the considerable increase in the activation energy at the stage of chain branching with the maximum mass loss rate at 437°C is the evidence for this.

The above-mentioned statements are confirmed by the results of the analysis of $dW/d\tau=f(1-W)$ curves (Fig. 3a) (W and τ are the mass loss (%) and the process time (min), respectively) [41]. In general, thermal-oxidative degradation of the samples has the similar mechanism: the main process passes by random scission mechanism, at the stage of chain branching in the interval 340–415°C the process is described by both random scission and step-by-step mechanisms, the latter prevails within the interval 210–291–340°C (up to 15% mass loss). The greatest contribution of step-by-step mechanism of depolymerization up to 15% mass loss (stages I–III) is noted for Sample 4. Therefore, the structure formed at the presence of trimethylsilylated silica contains some terminal groups of macromolecules which are not bound into polymeric chain. At the same time, the degradation process' higher 15% of mass loss passes according to the random scission mechanism confirming the statement on stabilizing action of the surface of silica filler owing to more compact packing of macromolecules, strengthening of oxidation-vulnerable bonds or retention of oxidation products in the material.

It should be noted that on the curve $dW/d\tau=f(1-W)$ (Fig. 3a) for the Sample 5 in the interval up to 15% of mass loss the step is expressed weakly which indicates the prevalence of random scission at the initial stage and therefore the macromolecules' ends are protected from the oxidation. Subsequent oxidation, as in the previous case, passes according to the random scission mechanism indicating structural uniformity; however, a decrease in the molecular mass of removing fragments is observed which means that degradation occurs to produce the high-molecular products. Presence of the antioxidant in surface layer of modified silica decreases the length of evaporating fragments in comparison with the polymer filled with modified silica only, however, this length is larger than in the case of the composite containing the unmodified silica filler (Sample 3). Besides, for the composite with unmodified filler the process of the oxidation products removal is more restricted. The prevalence of step depolymerization, especially at the stage of chain termination (more than 20% of mass loss) confirms the above-mentioned statement on limited oxygen penetration into the

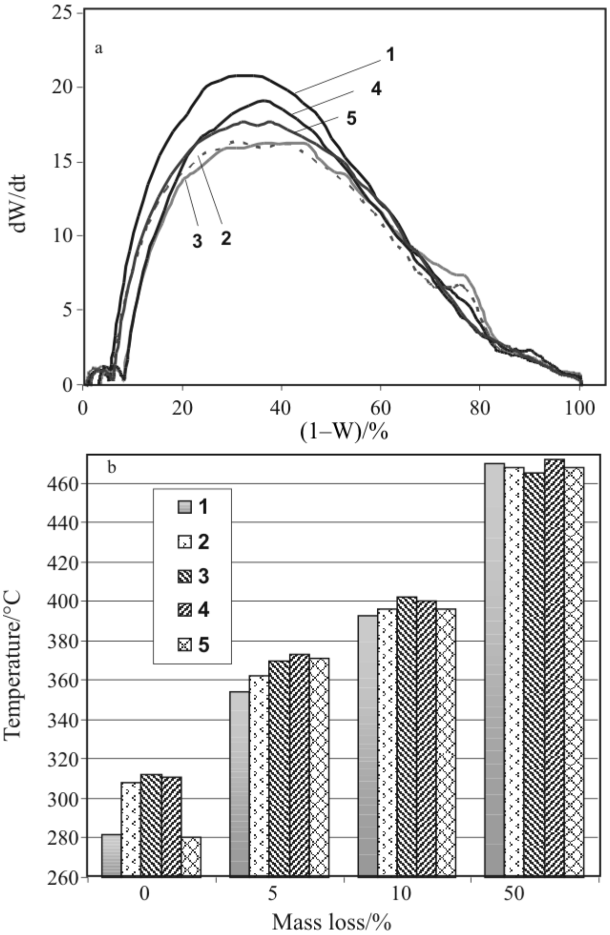


Fig. 3 a – Thermal oxidation rate *vs*. degradation degree; b – the temperature at the beginning of the thermal oxidation process and at 5, 10, 50% of mass loss. 1 – initial HDPE; 2 – HDPE with BHT; 3 – HDPE filled with unmodified silica; 4 – HDPE filled with trimethylsilylated silica; 5 – HDPE filled with trimethylsilylated silica containing immobilized BHT

polymer bulk (as well as diffusion of thermal oxidation products from the bulk, though) and on the processes involving oxygen occurring predominately at surface layer of the sample. Though, such curve form may be the evidence of structural non-uniformity, as well. Thus, at the presence of the unmodified silica filler within the interval 257–360°C two phases are noted: 257–308°C and 312–360°C which according to the curve form are related to step depolymerization. For the unfilled polymer in this interval only one process is observed starting at higher temperature. Also, at the presence of the unmodified filler within 509–576°C (corresponding to the degradation of the products of thermal oxidation) three phases are noted: 509–537°C – chain termination according to the random scission mechanism, the process of step depolymerization occurs simultaneously (506–521°C) and random scission depolymerization completes the carbonization reaction (538–576°C). It is interesting to note that at the presence of the unmodified silica the processes in high temperature region start at earlier temperatures of the polymer transformation than in the case of the unfilled polymer. Therefore, the filler slows down the carbonization process. The antioxidant and silica filler with immobilized antioxidant have no such effect.

Similar to Sample 3 but more smoothed curve was obtained for Sample 2 confirming the similarity in the action of antioxidant and unmodified silica surface in HDPE thermal oxidation processes. The maximum rate of thermal-oxidative degradation, as compared with Sample 1, is achieved at less mass loss and this value is less; this may be the evidence of a decrease in length of removing fragments. Also, the thermal-oxidative stability of HDPE composites with and without antioxidant was evaluated by comparison analysis of temperatures of 5, 10, 50% sample mass loss [42]. Comparing samples 1 and 2 reveals an increase in temperature of 5 and 10% mass loss for Sample 2 and a decrease in that of 50% (Fig. 3b). It indicates that introduction of silica slows down the polymer degradation process by the mechanism of side-group elimination (initial stage of the process). Further it promotes the degradation by random scission mechanism (main stage of the process). The influence of silica surface modification is not observed at this stage of the process since the degradation characteristics for the Samples 2 and 4 are similar. Introducing of modified filler with BHT antioxidant into polymer decreases the initial as well as 5 and 10% degradation temperature keeping the same the temperature of 50% mass loss. It indicates that immobilized antioxidant worsens inhibiting filler effect on the process of thermal degradation at the initial stage. At the same time, the presence of the antioxidant in unfilled polymer increases the initial (by 30°C) and 5% (by 10°C) degradation temperature (Samples 1, 6). It should be also noted that the characteristics of the unfilled polymer with antioxidant only slightly differ from those for the polymer containing modified silica with immobilized antioxidant except of the initial degradation temperature. Thus, filling with silica increases the thermal stability of HDPE even more efficiently than the presence of the antioxidant BHT, free and immobilized onto the filler surface.

Conclusions

- Filling with hydrophilic/hydrophobic silica (1 mass%) as well as introduction of BHT antioxidant (0.1 mass%) into unfilled polyethylene increases its thermal-oxidative stability. At this, the presence of silica filler changes the mechanism of the polymer decomposition from the prevalence of the chain scission to the prevalence of step depolymerization or the chain scission on the macromolecules' ends.
- Immobilized BHT suppresses the stabilizing effect of hydrophobic silica surface in the processes of polyethylene thermal oxidation at the initial stage. However, being gradually released from the surface, antioxidant prolongs the resistance of the polymer against oxidation.
- Silica surface irrespectively to its nature (hydrophilic or hydrophobic) suppresses the antioxidant activity of immobilized BHT in the process of HDPE thermal oxidation. Nevertheless, it is possible to control the antioxidant activity of BHT by varying its mobility which depends essentially on the nature of filler surface.

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