

CHEMISTRY AND TECHNOLOGY OF ORGANIC SUBSTANCES, MATERIALS AND GOODS

УДК 678.675

A. G. Liubimau¹, V. V. Yurachka²

¹Belarusian State Technological University

²Institute of Chemistry of New Materials of the National Academy of Sciences of Belarus

POLYETHYLENE ANTIOXIDANTS BASED ON AROMATIC ACID HYDRAZIDES

Hydrazides of aromatic acids were synthesized and used as stabilizers of polyethylene. The thermal stability of polyethylene compositions was studied by methods thermogravimetry and infrared spectroscopy. The activation energy of thermal oxidative degradation of modified polyethylene was calculated. The optimal concentration of synthetic antioxidants was determined. It was shown that hydrazones of aromatic acids exhibit thermostabilizing properties.

Key words: antioxidant, polyethylene, energy of thermal oxidative degradation.

Introduction. The main mechanical characteristics of the polymer are dependent on the chemical nature of the polymer, its molecular weight and crystalline structure (if the polymer crystallizes). Therefore, affecting these properties, it is possible to control the mechanical characteristics of the material. To modify the chemical nature of polyolefins is most effectively at the synthesis stage, but it is very difficult, because the synthesis is an ongoing process and it is technologically complicated.

Therefore, it is more rational to influence the processes that lead to changes in molecular weight and crystalline structure.

Thermo-oxidative degradation is the main process leading to a change in molecular weight of the polymer, it occurs during the processing of polymers and the use of the products from them. By varying the speed of thermal oxidative degradation reactions, we can influence changes in molecular weight and thus control the mechanical properties of the polymer.

Technically it is simply impossible to get “absolutely pure” polymer. It is impossible to eliminate structural defects and impurities. Moreover, in the first stage of processing, such as extrusion, injection molding and blow molding, peroxide radicals are formed by reaction with molecular oxygen under conditions of heat and mechanical shear. Then, the peroxide radicals are transformed into hydroperoxides by the separation of hydrogen off the chain. Decomposition of hydroperoxides occurs with the formation of alkoxy and hydroxyl radicals. Therefore, as the temperature increases the reaction rate increases too. This reaction is also accelerated by light or by the presence of metal ions [1].

The processing of the polyethylene can result either in reduced molecular weight or chain branching, or even cross-linking and gelation [1]. The behavior of the polymer depends on the processing conditions such as shear and temperature, as well as on the specific macromolecule structure, in particular on the number of terminal vinyl groups [2–4]. The ability to resist oxidation and thermal deterioration of polymer properties, in general, depends on the ease of peroxide formation. Thus, the oxidation resistance of the polymer is related to the rate of the hydrogen abstraction from the carbon atom in the main chain or in side groups. In semi-crystalline (crystallizable) polymers, in particular polyolefins, decomposition under thermal-oxidative aging process is heterogeneous. The morphology of the polymer affects the solubility and diffusion of oxygen, which occurs mainly in the amorphous regions of polyolefins. Since the mechanical properties of these polymers to a large extent are determined by the interweaving of the binding molecules, the oxidative degradation of these areas leads quickly to the loss of strength [1, 5].

One of the methods to inhibit the thermo-oxidative degradation reactions of the polymer is the use of heat stabilizers. Heat stabilizers are substances which inhibit degradation processes during the processing of the polymeric material, as well as during the use of the product obtained from it. Inhibition is due to thermal stabilizer functional groups that can act as hydrogen donors [6, 7], radical acceptors [8, 9], hydroperoxide destroyers [10].

Main part. High-density polyethylene (HDPE) of 15803-020 grade produced by the “Polymir” plant (JSC “Naftan”) was used as a polymeric

matrix: melt flow index (190°C/2.16 kg) – 2.0 g/10 min; density – 0.918 g/cm³; breaking strength (σ_{bs}) – 12.2 MPa; elongation at break (ϵ_{eb}) 550%; tensile yield strength (σ_{ts}) – 9.3 MPa; melting point – 103°C.

Synthesis, identification of the structure and properties of aromatic acids hydrazides are described in detail in the article [11]. Compounds shown in Fig. 1 were used as heat stabilizers. For uniform distribution of heat stabilizers in the polymer, polyethylene based compositions with different contents of substances were prepared by milling: 0.1; 0.3; 0.5 wt % and the control composition of pure polyethylene. The temperature of the hot mill roll – 190°C, milling time – 2 min. Thereafter the milled stock was pressed into a film. The temperature of the upper and lower press plates was 190°C, pressing force – 5 t.

Then the film was cut into standard samples, 10×150 mm in size, part of the samples was placed in an oven and the accelerated thermal aging was performed at 80°C in the following time interval: 0; 24; 96; 150 hours. As a result of thermal oxidative degradation the polyolefin macromolecules

begin oxidizing to carboxylic acids and ketones. The characteristic absorption band for the carboxyl group is observed in the region 1,720 cm⁻¹. Fig. 1 shows the IR spectra of pure polyethylene. We can see that, even without being subjected to the accelerated thermal aging, pure polyethylene after milling and pressing already contains carboxylic acids and ketones in its composition, as is evidenced by the presence of absorption bands at 1,720 cm⁻¹. The remaining absorption bands correspond to alkanes.

When aromatic acids hydrazones are added into polyethylene, the appearance of the absorption bands characteristic of ketones and carboxylic acids is not observed (Fig. 2, 3), indicating the inhibition of oxidative destruction processes.

IR spectra of compounds containing heat stabilizers in their composition, have no absorption bands at 1,720 cm⁻¹. These absorption bands appear only marginally after 150 hours of aging at 80°C in compositions containing 0.3 wt % of N,N'-bis[3-hydroxy-4-methoxybenzylidene]-biphenyl]-4,4'-dicarbohydrazide and N-(4-hydroxy-3-methoxybenzylidene)biphenyl-4-carbohydrazide.

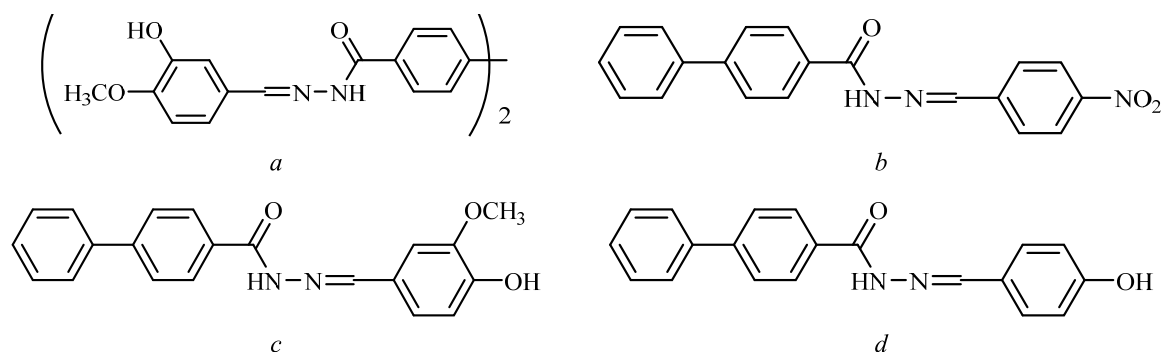


Fig. 1. Structural formulas of heat stabilizers:

a – N,N'-bis[3-hydroxy-4-methoxybenzylidene]-biphenyl-4,4'-dicarbohydrazide;

b – N-(4-nitrobenzylidene)biphenyl-4-carbohydrazide;

c – N-(4-hydroxy-3-methoxybenzylidene)biphenyl-4-carbohydrazide;

d – N-(4-hydroxybenzylidene)biphenyl-4-carbohydrazide

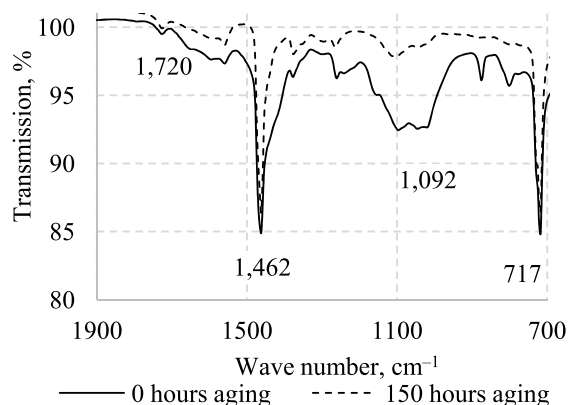


Fig. 2. IR spectra of polyethylene

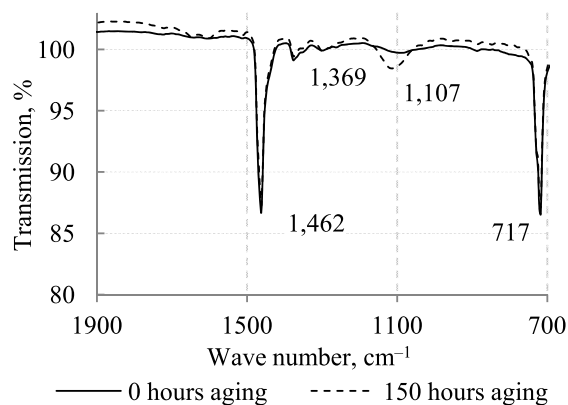


Fig. 3. The IR spectra of PE compositions containing 0.3 wt % antioxidant (see Fig. 1, *d*)

In addition, the absorption bands of heat stabilizers themselves appear in the IR spectra of modified compositions, values for the absorption bands of the stabilizers are shown in [11]. The remaining absorption bands correspond to alkanes [12].

Even a small change in the chemical composition and molecular weight of the polymer can cause a significant reduction in its mechanical properties [13].

Investigations by thermogravimetry (TG) have been carried out. The results of TG analysis show that the addition of 0.3 wt % of heat stabilizer (see Fig. 1, *a–d*) at the initial stage of aging (0 hours) has almost no effect on the onset temperature of

degradation. However, the TG analysis of samples, which have been aged for 150 hours, demonstrates a decrease in thermal stability of pure polyethylene, in contrast, compositions comprising heat stabilizers, conversely have higher start temperature of degradation. This may indicate the course of structuring processes, as well as the effects of heat stabilizers.

One of the most effective ways to assess the effect of heat stabilizers is to calculate the activation energy of thermal oxidative degradation (E_a) according to the results of TG analysis. Calculation method is described in [14], the results of the calculation are presented in Table 1.

Table 1

The activation energy of thermal oxidative degradation

Polymer compound composition	E_a , kJ/mol	
	0 hours aging	150 hours aging
Polyethylene (films)	58.31	104.91
Polyethylene, 0,3 wt % of N,N'-bis[3-hydroxy-4-methoxybenzylidene]-biphenyl-4,4'-dicarbohydrazide (see Fig. 1, <i>a</i>)	59.21	132.16
N-(4-nitrobenzylidene)biphenyl-4-carbohydrazide (see Fig. 1, <i>b</i>)	60.99	126.74
N-(4-hydroxy-3-methoxybenzylidene)biphenyl-4-carbohydrazide (see Fig. 1, <i>c</i>)	65.89	118.83
N-(4-hydroxybenzylidene)biphenyl-4-carbohydrazide (see Fig. 1, <i>d</i>)	54.59	121.40

Table 2

Changes in mechanical characteristics of polyethylene depending on the content of heat stabilizer and aging time

Composition	Concentration, wt %	Time, h	σ_{ts} , MPa	ϵ_{ct} , %	σ_{bs} , MPa	ϵ_{cb} , %	E , MPa
HDPE	0	0	7.0	12	9.5	442	147
		24	7.8	12	8.2	277	154
		96	8.2	10	7.1	171	176
		150	6.8	9	3.0	56	161
HDPE N,N'-bis[3-hydroxy-4-methoxybenzylidene]-biphenyl-4,4'-dicarbohydrazide (see Fig. 1, <i>a</i>)	0.1	0	8.1	13	11.0	633	174
		24	8.1	12	8.8	308	171
		96	8.9	12	7.5	388	180
		150	7.7	11	5.2	117	142
	0.3	0	8.2	11	8.4	418	188
		24	8.2	11	8.4	418	188
		96	7.9	13	9.2	499	156
		150	8.1	12	6.3	226	153
	0.5	0	7.9	11	10.7	494	192
		24	7.9	14	10.8	544	145
		96	9.0	13	7.3	283	141
		150	7.8	14	8.2	450	115
HDPE, N-(4-nitrobenzylidene)-biphenyl-4-carbohydrazide (see Fig. 1, <i>b</i>)	0.1	0	7.9	13	12.1	650	152
		24	7.5	14	8.1	448	115
		96	7.4	11	4.9	290	158
		150	8.0	11	11.0	346	150
	0.3	0	6.5	17	10.3	561	82
		24	7.3	13	9.5	503	131
		96	7.3	17	9.2	626	89
		150	7.5	17	10.4	529	105
	0.5	0	6.2	15	11.3	711	105
		24	6.7	14	10.5	528	113
		96	8.0	14	12.2	605	131
		150	6.9	13	7.5	387	118

End of Table 2

Composition	Concentration, wt %	Time, h	σ_{ts} , MPa	ε_{ct} , %	σ_{bs} , MPa	ε_{cb} , %	E , MPa
HDPE, N-(4-hydroxy-3-methoxybenzilidene)biphenyl-4-carbohydrazide (see Fig. 1, c)	0.1	0	7.8	12	5.8	504	150
		24	7.4	11	4.7	162	142
		96	7.0	10	4.7	139	166
		150	7.8	9	6.5	282	215
	0.3	0	6.1	11	8.8	434	133
		24	7.0	14	9.8	586	129
		96	7.5	14	9.4	516	133
		150	6.5	12	5.4	261	137
	0.5	0	6.6	11	9.6	435	142
		24	6.9	15	6.1	300	101
		96	6.8	12	10.4	564	162
		150	5.6	11	6.0	256	119
HDPE, N-(4-hydroxybenzilidene)biphenyl-4-carbohydrazide (see Fig. 1, d)	0.1	0	6.4	9	7.9	344	170
		24	7.1	12	9.5	511	147
		96	7.4	13	9.9	430	144
		150	7.5	13	8.4	250	130
	0.3	0	7.2	15	9.4	446	107
		24	6.2	11	5.4	215	117
		96	7.3	14	7.2	300	135
		150	7.0	15	8.5	406	97
	0.5	0	6.1	10	6.9	357	127
		24	6.8	11	4.7	99	130
		96	7.0	11	4.7	119	127
		150	6.5	11	5.6	192	139

The increase of the activation energy values of thermal oxidative degradation with time of aging appears to be related to the processes of cross-linking in the polyethylene and the action of heat stabilizers, the most effective heat stabilizer being N-(4-hydroxy-3-methoxybenzilidene)biphenyl-4-carbohydrazide.

Study changes in the mechanical characteristics of polyethylene depending on the content of heat stabilizers and the time of aging have been carried out. The results are shown in Table 2.

Changes in the chemical composition and molecular weight influence the mechanical characteristics. The most significant is to estimate the influence of thermal aging and heat stabilizers on the mechanical properties of polyethylene by the values of elongation at break (ε_{tr}).

The experimental results show that the most effective heat stabilizer is N-(4-hydroxy-3-methoxybenzilidene)biphenyl-4-carbohydrazide (0.3 wt %). This is consistent with TGA and the calculated values of the activation energy of thermal oxidative degradation. The absence of a monotonic change in mechanical characteristics of polyethylene in the

aging time in the presence of heat stabilizers is caused by the occurrence of several processes: thermo-oxidative degradation, cross-linking, the secondary crystallization, relaxation of internal stresses. Relaxation of the internal stresses increases the deformation characteristics of the polymer, the remaining processes lead to their decrease [15].

Conclusion. The change in the chemical composition of polyethylene by IR spectroscopy according to the optimum aging time and heat stabilizer content has been investigated. It is shown that heat stabilizers prevent the formation of carbonyl and ketone groups in the polyethylene in the aging process.

The change in the thermal stability of polyethylene by TG has been studied. Activation energy values of thermal oxidative degradation have been calculated.

The optimum content of heat stabilizers (0.3 wt %) has been identified. It is shown that when there is such a content, a decrease in values of breaking elongation (ε_{cb}) 2 times does not occur. This demonstrates the effectiveness of aromatic acids hydrazones as heat stabilizers of polyolefins.

References

1. Zweifel H., Maher R. D., Schiller M. *Dobavki k polimeram. Spravochnik* [Polymer additives. Directory]. St. Petersburg, Professiya Publ., 2010. 1144 p.

2. Halim Hamid S. Handbook of polymer degradation. Taylor & Francis, 2000. 800 p.
3. Gensler R., Plummer C. J. G., Kausch H.-H., Kramer E., Pauquet J.-R., Zweifel H. Thermo-oxidative degradation of isotactic polypropylene at high temperatures: phenolic antioxidants versus HAS. *Polym. Degrad. Stab.*, 2000, vol. 67, pp. 195–208.
4. Reich L., Stivala S. S. Autoxidation of hydrocarbons and polyolefins. New York, Marcel Dekker, 1969. 527 p.
5. Pospisil J., Nespurek S., Zweifel H. The role of quinone methides in thermostabilization of hydrocarbon polymers. *Polym. Degrad. Stab.*, 1996, vol. 54, no. 1, pp. 7–21.
6. Zweifel H. Effect of stabilization of polypropylene during processing and its influence on long-term behavior under thermal stress. *Polymer Durability*, 1996, no. 249, p. 375.
7. Pospisil J., Nespurek S., Zweifel H. The role of quinone methides in thermostabilization of hydrocarbon polymers II. Properties and activity mechanisms. *Polym. Degrad. Stab.*, 1996, vol. 54, pp. 15–21.
8. Beckwith A. L. J., Bowry V. W., Ingold K. U. Kinetics of the nitroxide radical trapping. Solvent effects. *J. Am. Chem. Soc.*, 1992, vol. 114, pp. 4983–4992.
9. Gladyshev G. P. Polymer stabilization by oxygen acceptors. Ninth annual international conference on advances in the stabilization and controlled degradation of polymers. Luzern, 1987. P. 119–132.
10. Ruger C., König T., Schwetlick K. Phosphororganische antioxidation. Einfluss cyclischer phosphite auf die radikalisch initiierte oxidation von kolenwasserstoffen und polymeren. *Acta Polymerica*, 1986, vol. 37, no. 7, pp. 435–438.
11. Yurachka V. V., Yuzhik L. I., Tarasevich V. A., Ol'khovik V. K. Arylhydrazones synthesis of 4,4-biphenyl dicarboxylic acid. *Izvestiya NAN Belarusi (seriya khimicheskikh nauk)* [Proceedings of the National Academy of Sciences of Belarus. Series of Chemical Sciences], 2012, no. 4, pp. 80–82 (in Russian).
12. Kuptsov A. Kh., Zhizhin G. N. *Fur'e spektry kombinatsionnogo i infrakrasnogo pogloshcheniya polimerov. Spravochnik* [Fourier spectra of Raman and infrared absorption in polymers. Directory]. Moscow, Fizmatlit Publ., 2001. 656 p.
13. La Mantia F. Handbook of plastics recycling. Shrewsbury UK, Rapra Technology, 2002. 441 p.
14. STB 1333.0-2002. Products polymeric for construction. Method for determining the durability of energy activation thermal oxidative degradation of polymeric materials. Minsk, Ministry of Architecture Publ., 2002. 11 p. (In Russian).
15. Tager A. A. *Fiziko-khimiya polimerov* [Physical chemistry of polymers]. Moscow, Nauchnyy mir Publ., 2007. 576 p.

Information about the authors

Liubimau Alexandr Gennadevich – junior researcher, Department of Technology of Petrochemical Synthesis and Polymer Materials Processing. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: Lubimov@belstu.by

Yurachka Vladimir Vladimirovich – junior researcher, Laboratory Surface of Bioactive Substances. The Institute of Chemistry of New Materials of the National Academy of Sciences of Belarus (36, F. Skorrina str., 220141, Minsk, Republic of Belarus). E-mail: uozh@ichnm.basnet.by

Received 04.02.2015