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Determination of Algorithm: Phenolic Antioxidants as a Route to Improve Mechanical Properties of Polymeric Materials

A. P. KRYSIN, V. P. FADEEVA, O. N. NIKULICHEVA, A. A. NEFEDOV

N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Russia, Novosibirsk

E-mail: kap@nioch.nsc.ru

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Abstract

For the first time, consecutive steps of algorithm solution, such as phenolic antioxidants in the improvement of mechanical properties of polymers were proposed. The first step begins with the studies of thermokinetic characteristics of thermolysis reactions of phenolic antioxidants accompanied by the determination of their kinetic constants (activation energy, E, and pre-exponent, Z). Modifiers of the main group of antioxidants can be distinguished according to the ratio of these constants. Polymer modification effect by them was determined at the second step. It appears in the temperature of the beginning of modifier decomposition under polymer thermal processing conditions and in parameters of an increase in product service time under extreme operating conditions. Examples are given of modification and stabilization of properties of polymer-derived composites.

Keywords: phenolic antioxidants, thermogravimetric analysis, polymers, stabilizers, modifiers, structure-properties algorithm, glass-filled polyamide, mechanical strength

INTRODUCTION

The chemistry of stable states of matter in our extreme oxygen world and its long-term normal functioning over time are fundamentally related to the chemistry of antioxidants. As revealed by the development of polymer science, without the addition of antioxidants, the duration of the existence of matter in the initial state is sharply reduced.

Currently, a new trend for the creation and production of durable, various by nature, graft-polymers containing stabilizing fragments grafted to the structure is rapidly developing. Due to this, there ensures the required performance of organic products under extreme conditions (space, irradiation, high and low temperatures, mechanical loads, and action of water and solvents).

Solving the tasks of the chemistry of sustainable development in relation to the development of new polymer materials required the search for mathematical laws that allow separating from the hundreds of known antioxidants those that can be vaccinated to polymers, and also determining conditions that ensure efficient interaction of additives with polymers. Particular attention is given to the exploration of chemical properties of products formed in thermal processes of antioxidant cleavage.

ISSUES OF POLYMERS STRENGTH

Reinforcement of polymeric materials is usually carried out using fillers [1]. Polymeric properties modification observed under their action is explained by changes in the chemical structure: cross-linking polymeric chains with the formation of new C–C bonds, as well as binding individual polymer units with sulphur or oxygen [2].

The retention of mechanical properties of polymeric products over time is a function of antioxidants [3]. However, negative opinion has been formed in recent years regarding a role of antioxidants in filled polymers: “They may have a strong negative impact even on the best modifiers of polymer properties” [1]. It is known that increasing strength characteristics of polymers is ensured by radical cross-linking its polymer chains or binding with generating atomic bridges between the chains. However, antioxidants are “aimed” by their nature at destroying the radical density over the polymer, taking it upon themselves [3]. They eventually inhibit reactions leading to polymer reinforcement [1].

In recent years, there are materials of Russian scientific meetings dealing with single examples of the use of antioxidants that are able to only extend the service life of polymer products but also improve their mechanical properties. Such properties were revealed for nanomatrix-bound organophosphorus compounds [4], hydrazine derivatives [5, 6], and also for sulphur spatially hindered phenols [7, 8]. The causes of their multi-factorial actions were not disclosed in detail.

MATHEMATICAL SOLUTION OF THE PROBLEM

According to V. A. Roginsky [9], the issues of stabilization and projected changes in properties of polymer materials may be removed by developing and solving a number of algorithms, He considered an algorithm that determines a relationship between the antioxidant efficiency of the additive and changes in the mechanical strength of the polymer during its ageing as the most important of them [9].

The purpose of our work was to develop materials with new properties. Within the task set, it was required to find an approach towards a number of theoretical problems. The solution of a new algorithm has become the crucial one whereof: phenolic antioxidants as the improvement of mechanical properties of polymers.

The general plan for solving algorithms proposed by V. A. Roginsky in 1988 [9] is taken as the keystone. It is based on: 1) the investigation of the behavior of antioxidants in polymers, which is related to the research by academician N. M. Emanuel and his school; 2) creating a theory using the kinetic parameters of individual thermolysis reactions; 3) solving problems of materials science.

The theory of retention of properties of the organic medium by phenolic antioxidants is based on fundamental Emanuel’s equation:

$$\mathrm{ArOH} + \mathrm{R}^{\bullet} = \mathrm{ArO}^{\bullet} + \mathrm{RH} \qquad (1)$$

where phenolic antioxidant reduces the radical contained in the medium to form the low-activity phenoxyl species, wherein the radical density is weakened by the redistribution along the molecule [10]. It is known that the dissociation energy of the O–H bond in molecules of phenolic antioxidants is 82–85 kcal/mol [11].

To solve the algorithm, we acquired in two steps thermokinetic parameters of thermolysis of phenolic antioxidants in a wide temperature range.

In the first phase, thermal analysis of phenolic antioxidants was carried out using Q-1000-D derivatograph (MOM, Hungary) and an STA 409 PC Luxx synchronous thermal analyzer (Netzsch company). The use of these devices allows simultaneously recording sample mass changes (TG and DT), as well as determining the characteristic temperatures and heat phase transitions (DTA). To acquire kinetic characteristics of thermolysis, samples with the same mass were heated in a platinum crucible in helium flow from 20 to 500 °C with different heating rates (3, 5, 10, 15, 20 °C/min).

Kinetic performance of the antioxidants was determined during their thermogravimetric investigation. Since thermolysis of samples proceeds in a melt, the equation describing the kinetics of homogeneous processes is applicable:

$$\mathrm{d}\alpha/\mathrm{d}t = Z\exp\,(-E/RT)(1-\alpha)^n \qquad (2)$$

where α is substance transformation degree, t is time, min; Z is pre-exponential factor in Arrhenius equation; E is activation energy, kJ/mol; n is reaction order; T is temperature, K.

Calculations of the thermokinetic parameters of the sample were performed according to differential methods on the basis of the bend point of the thermogravimetric curve (TG) at different heating rates [12].

According to performance time, a completely different technique using developed Thermograph software is more efficient [13]. It is used to determine the numerical values of thermokinetic parameters of antioxidants in equation (2) that coincided with the calculations carried out according to the differential method.

This work, as the second step of algorithm solution, is performed for the mathematical description of regularities of thermolysis of a large group of phenolic antioxidants [14].

When plotting the chart of the dependence of E parameters on ln Z, two almost parallel regularities were revealed (Fig. 1). The rate of decomposition during thermolysis for one group of antioxidants is three orders of magnitude higher than that for the other group [14], which points to significant differences between chemical processes, that limit the stage of thermolysis of samples for each of **A** and **B** groups [15, 16].

Group **A**, most numerous, includes phenolic antioxidants **1–15**, thermolysis of which proceeds according to dealkylation and decarboxylation reactions preserving the molecular frame [16] (Scheme 1).

The latter in a series of compounds **B** (**16–22**) is split accompanied by generating active species that react with the sole antioxidant present in the medium [15].

Thermolysis of *tert*-butyl phenol derivatives of group **A**, as shown earlier [16], proceeds according to Emanuel's rule and begins with dissociation of the ArO–H bond.

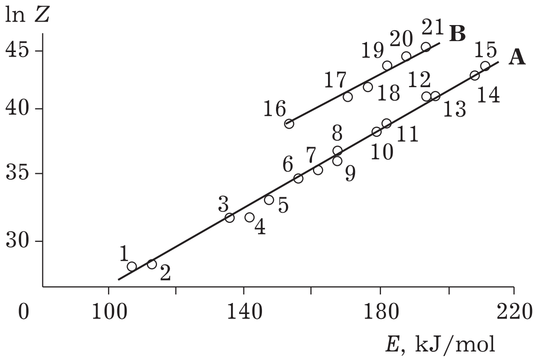
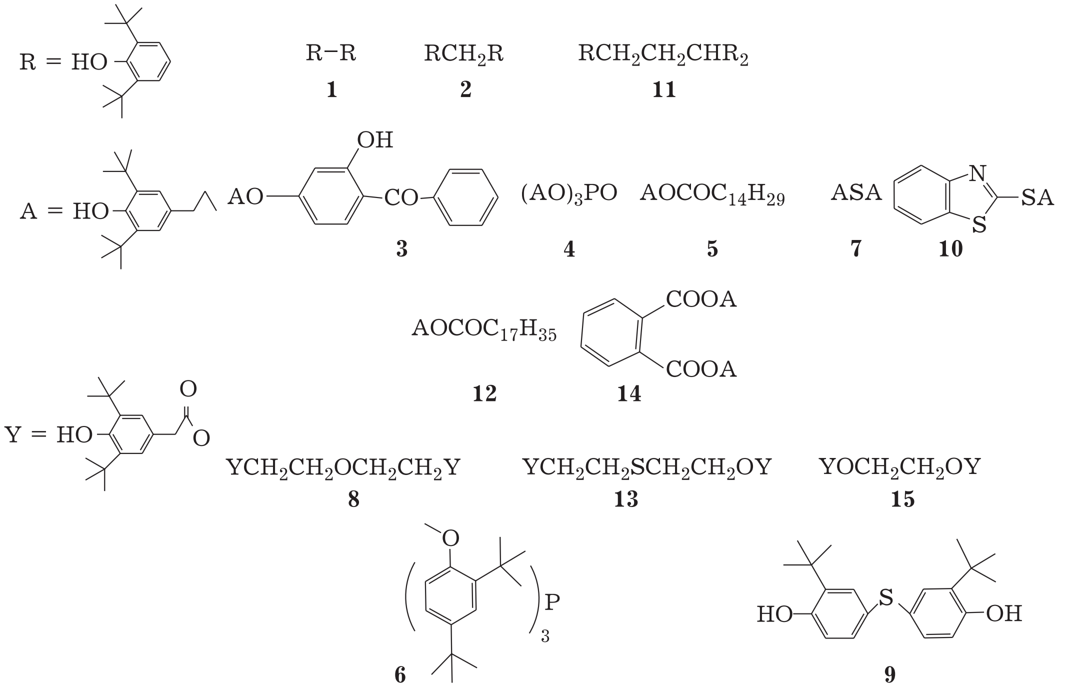


Fig. 1. Activation energy (E) of sterically hindered phenols group **A** (**1–15**) and **B** (**16–22**) versus logarithm of pre-exponential factor (Z).

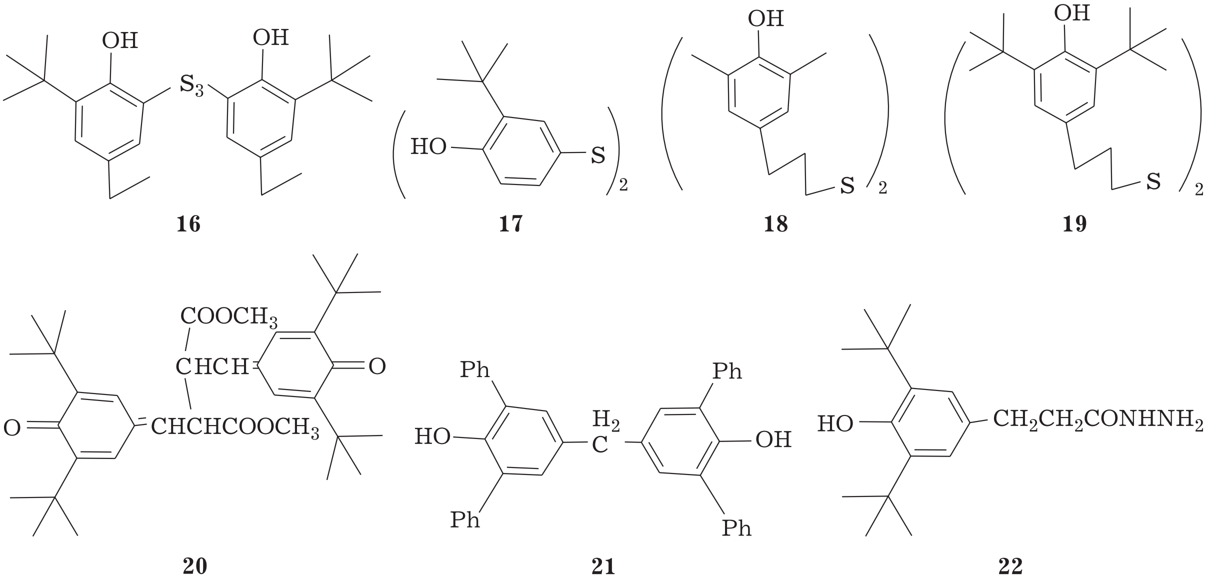
Thermal dissociation of the group **B** compounds proceeds as an exception to Emanuel's rule, and a radical is generated in a remote place from the hydroxyl group in the structure of a thermally torn molecule (Scheme 2).

THERMOLYSIS CHEMISTRY OF PHENOLIC ANTIOXIDANTS

Thermolysis of methylphenols clearly demonstrates these two trends: one of them with molecular core retention, as observed in



Scheme 1.



Scheme 2.

the case of de-*tert*-butylation of 4,4′-methylene-bis-2,6-di-*tert*-butylphenol **2** [16]. However, a modifier of polyamides, 4,4′-methylene-bis-2,6-diphenylphenol **21**, thermally splits along the skeleton and there are generated volatile products: 2,6-diphenylphenol and 4-methyl-2,6-diphenylphenol [17].

Generating two identical radicals was recorded during splitting compound **20** by heating [18] already at 60 °C. 2-(4-Hydroxy-3.5-di-*tert*-butylphenyl)-propionic acid **22**, derived hydrazides, are the known modifiers of caoutchouc [6, 19].

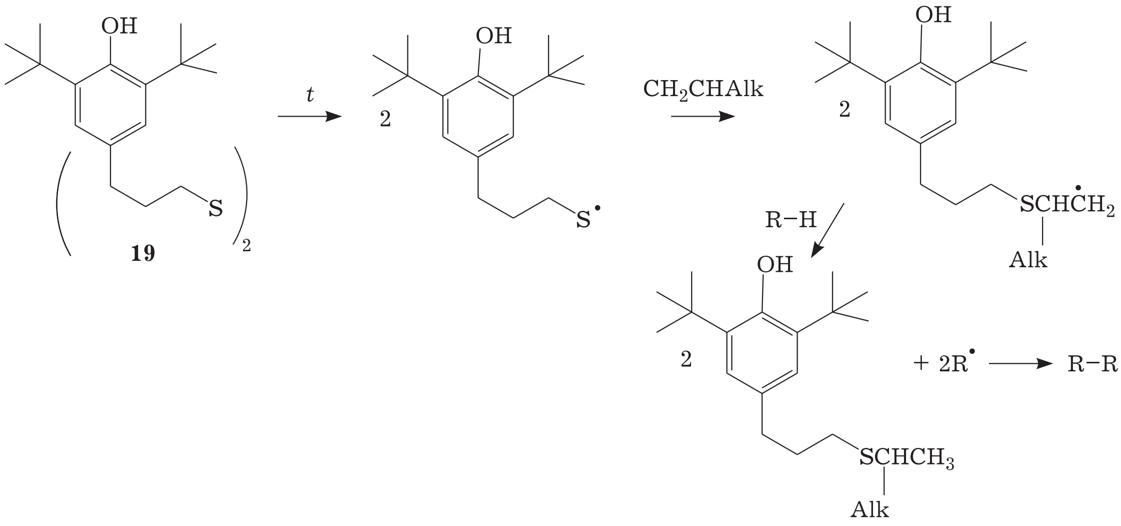
There are two different schemes of splitting molecules along the frame in thermolysis bis-3,3′-[(4-hydroxyphenyl-2,6-hydroxyphenyl) propyl]disulphide **3** with the involvement of the S–S bond. There is the process of formation of two radicals structurally identical on the structure sulphur-containing radicals of by 85 % and C–SSAlk bond rupture between carbon and sulphur by 15 % [20].

The activation energy of the breakup of Alk–S–S–Al and S–C bonds varies within 60–70 kcal/mol. In aryldisulphides and hydrazine derivatives, it is lower, 40–50 kcal/mol [11], which is significantly less than that in the ArO–H bond collapse (82–85 kcal/mol) for phenolic antioxidants with generating phenoxyl radicals [9]. It is the formation of radicals of chemically different nature that determines the unusual properties of innovative modifiers and antioxidants.

The nuances of the interaction of particles formed during thermolysis of disulphide **19** with polyolefins are traced for the model reaction of *n*-hexane and hexane with products of its thermolysis. Products of antioxidant linking to the double bond of the olefin were determined. According to [3], chemical linking the antioxidant to the polymer significantly increases the service life of the products made therefrom (3–5 times compared to the use of the antioxidant as an additive) (Scheme 3).

Processes of linking olefin molecules accompanied by generating C–C and C–S–C bonds proceed in parallel. With regard to the polyolefin, they are polymer modification processes. The processes of reduction of the produced radicals by phenolic antioxidants and the composition of their oxidation products during these transformations are described in detail in [20].

The final step of the practical application of the algorithm is carried out using the standard shopfloor and analytical equipment. It involves manufacturing parts from modified polymers processed under the conditions of decomposition of the selected modifier (or at any higher temperature of the process). The required analytical support of the process to determine indicators of mechanical properties and



Scheme 3.

stability time of the resulting polymer composite is carried out [21].

Performing the sequence of steps of the algorithm appears to be a long-time process. However, it is much easier, if all researchers provide TG, DTG, and DTA curves of a sample of the antioxidant using thermal analysis. Another procedure that involves borrowing these data from literature is acceptable too.

Afterwards, their mathematical processing is carried out using the Thermograph software. According to its results, it becomes clear, whether the antioxidant has the property of modifying polymers under its thermal decomposition conditions, or not.

At the decomposition temperature (140–160 °C), an antioxidant-modifier with low dissociation energy of the ARS–SAr bond (50 kcal/mol) becomes universal for all traditional polymers processed at this or higher temperature of their melt. For instance, the modifier thioalkaphene B (TAB) that is based on compound **17**, and also trisulphide **16** refer to such universal additives.

PRACTICAL APPLICATION OF MODIFIED POLYMER MATERIALS

It is worth noting one peculiarity of polymeric materials initially containing an antioxidant-modifier. With prolonged heating, the melt flow index does not increase due to their decay but rather decreases, which is easy to explain by linking chains.

It is known that conventional supplements/antioxidants are removed from the polymer under one or another influence. Manufactured parts of the modified polymer that contains a sewn antioxidant may work for a long time without a significant loss of properties: in high vacuum and at elevated temperatures, in water, organic solvents, biosystems, and other extreme conditions. The problems of sewing the antioxidant to the polymer are easily solved under thermal polymers processing conditions (chemistry without solvents).

Where could these materials be used? It is known that (thermal shock, absolute vacuum, cosmic radiation, solar radiation, and plasma) contribute to the migration of additives to the polymer surface and their evaporation accompanied by the loss of the required technical performance of polymer products under cosmic impact conditions. It is advisable to use phenolic stabilizers sewed to polymer chains under these conditions [22].

All compounds of group **B** proved to be active components-modifiers of physical and mechanical properties of glass-filled polyamide-based composition [23] in terms of modification of properties of polyamides at high temperature during their processing (260 °C). This caused an increase of 1.5 times in the service life of the products under extreme conditions of their operation. Table 1 gives data on the effectiveness of compounds **16** and **19**.

As can be seen, a significant improvement of properties of glass-filled polyamide occurs in case of a 0.5–1.0 % modifier. Herewith, a new quality of polymer products is reached under standard composite processing conditions.

It has become necessary to increase the amount of TAB modifier (a mixture of di- and trisulphides based on 2-*tert*-butylphenol and other components) from 0.5 to 2 % [24] to develop a reliable adhesion of the coating to current-carrying elements of the device during creating an epoxy resins-based protective coating for microelectronics devices from external impacts. [25].

The moisture resistance of coatings made of epoxide resins substantially increased using TAB stabilizer [26]. It has shown excellent results as a stabilizing and modifying additive to radiation and peroxide-based plastics [21].

Disulphides **18** and **19** approved themselves as excellent modifiers/stabilizers by surpassing the known stabilizer Irganox 1010 according to the stability properties three times [27].

The use of modifiers and antioxidants is carried out using standard equipment. They are generally selected according to thermal decomposition temperature considering thermal conditions of manufacture of the polymer composite and its processing conditions. The lower this temperature is, the more pronounced are the initial stages of chemical modification: modifier decomposition with sewing its fragments to the polymer (as the first step) followed by processes of polymer stabilization. As a whole, this gives a positive result of modification and stabilization of the new properties of the polymer.

Modern inoculating antioxidants (mercaptans and acid esters with an activated double bond) to caoutchouc during manufacturing petrol-resistant materials assumes its mechanical decomposition in the presence of an initiator for free radical reactions of ROOR′. The mechanism and conditions of such sewing are known [22]. Bonds in the polymer could preliminarily be destroyed too by irradiation, the action of ozone and other reagents. The complexities of such a process are obvious, both in terms of reagents used and in their implementation conditions. The proposed modification principle is based not on polymer decomposition but on thermolysis of antioxidant fragment-containing additive, which is much more processible.

In general, to reach success, it is required to advance the initial rupture of structural bonds of the modifier compared to the higher thermal stability of bonds of antioxidants with the ArY–H structure, where Y = O; NR.

CONCLUSION

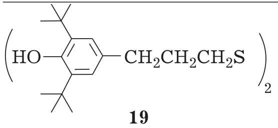
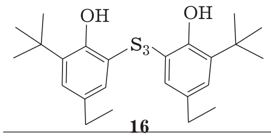
1. There has been proposed an approach towards obtaining polymers with new properties through the use of phenolic stabilizers/modifiers.

2. A series of innovative phenolic antioxidants as modifiers of polymer materials have been determined during theoretical research.

3. The mechanism of their action has been determined. As demonstrated, the modification property of each of them depends on the

TABLE 1

Changes in mechanical properties and stability of products made of glass-filled polyamide containing modifiers **16** and **19**

Used di- or trisulphide (modifier)	Content of modifier, %	Impact strength, kJ/m^2	Breaking stress, MPa, at stretching	Breaking stress, MPa, at bending	Number of sample destruction cycles
 **19**	–	47	225	157	10 645
	0.5	53	242	170	14 900
	1.0	54	244	186	15 800
 **16**	0.5	53	247	169	15 700
	1.0	54	252	174	16 500

energy of breaking bonds in the modifier structure. This has made it possible to determine the modifier selection principle, having agreed the temperature of its thermolysis with that of polymer processing. There have been revealed a number of modifier additives suitable for modification of properties of the majority of polymer composites in the range of their processing temperatures of 140–250 °C. The order of actions on the identification of modifiers from the common group of phenolic antioxidants is presented.

4. The order of actions directed to the elucidation of a modifier from the general group of phenolic antioxidants is presented.

5. A thermal route of sewing on antioxidant fragments to the polymer matrix has been found. It is based on the available and low-toxic disulphides of sterically hindered phenols. The chemistry of the resulting polymers with inoculated antioxidants without solvents has become a part of polymer technology.

For this reason, the preliminary breaking of bonds in the polymer with a purpose of its modification by oxidizing agents, radiation exposure, thermolysis, or mechanical breakdown is no longer appropriate.

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