

Influence of Synergists: The Influence of Hydroperoxide Decomposers on Phenolic Inhibitors Consumption in Oxidized Polypropylene

E. L. SHANINA,¹ G. E. ZAIKOV,¹ L. K. FAZLIEVA,² S. V. BUKHAROV,² N. A. MUKMENEVA²

¹ N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygin Str., Moscow 117977 Russia

² Kazan State Technological University, 68 Karl Marx Str., Kazan 420015 Tatarstan, Russia

Received 2 November 2001; accepted 27 November 2001

ABSTRACT: The influence of sulphur- and phosphorus-containing substances (hydroperoxide decomposers) on the kinetics of the consumption of two phenolic antioxidants in polypropylene (PP) was studied. The induction periods of PP autoxidation at 130°C were measured in the presence of inhibiting compositions that consisted of phenolic inhibitors and decomposers of hydroperoxide. Obtained results indicated that the influence of the hydroperoxide decomposer became significant when the concentration of the phenolic antioxidant became close to critical value. It also was shown that the efficiency of the hydroperoxide decomposer significantly depended on the mechanism of the transformation of the phenolic inhibitor; and first of all on the nature of its transformation products. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2239–2243, 2002

Keywords: additives; antioxidants; polypropylene; stabilization

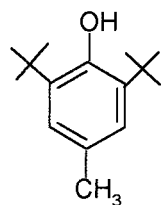
INTRODUCTION

It is well known that the simultaneous addition of a phenolic inhibitor and a hydroperoxide decomposer (sulphide, phosphite) to a polymer during the oxidation process results in synergism, allowing us to increase the time of the protection of the polymer from degradation. The mechanism of interaction of synergistic substances with hydroperoxides has also been thoroughly investigated.^{1–3} However, the detailed interaction or simultaneous action of phenol and a synergist—the decomposer of the hydroperoxides—remain in many

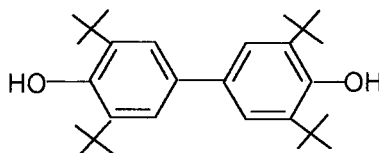
respects not absolutely clear. Therefore, we have found it necessary to return to this problem; for our research, we selected two phenolic inhibitors, 2,6-di-tert-butyl-4-methylphenol (phenol 1) and 4,4'-bis (2,6-di-tert-butylphenol) (phenol 2), and two synergists, dilauryl-thio-dipropionate (DLTP) and tris(2,5-di-tert-butyl) phosphite (phosphite). Phenol 1 was chosen because it is the inhibitor with the most well investigated mechanism of transformation into the oxidized substances; in this process, new antioxidants appear, and they are less active than the initial ones.^{4,5} This phenol is often used as a standard antioxidant during kinetic experiments. Phenol 2 was chosen because it has a very long induction period of polypropylene (PP) oxidation, owing to synergism phenol–diphenoquinone, which is a product of the transformation of this bisphenol during inhibited oxidation.⁶

Correspondence to: G. E. Zaikov (chembio@sky.chph.ras.ru).

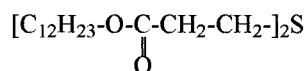
Journal of Applied Polymer Science, Vol. 85, 2239–2243 (2002)
© 2002 Wiley Periodicals, Inc.



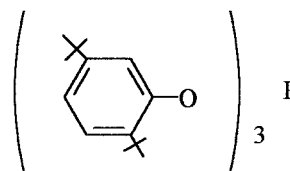
Phenol 1



Phenol 2



DLTP



Phosphite

Experimental part

EXPERIMENTAL

Isotactic polypropylene as a powder (Himont Co., Wilmington, DE, ProFax 6501), with molecular mass $M_w = 164,400$, $M_w/M_n = 38$, was used after washing away traces of the inhibitor in the Soxhlet apparatus. The oxidation of the polymer, measuring of antioxidants and diphenoquinone concentrations, and measuring of the induction periods of polymer oxidation have been described in our previous works.^{6,7} The procedures of chlorobenzene and cumene purification were also described earlier.⁸ The low molecular weight components were purified by crystallization from ethanol and heptane.

RESULTS AND DISCUSSION

In the data in Figures 1 and 2, the kinetics of phenol 2 consumption and on the formation of diphenoquinone—the product of its transformation—in the presence and in the absence of phosphite are presented. (These data differ a little from the published ones in our previous work⁶ because polymers with different characteristics were used.) As follows from these data, phosphite basically does not influence the kinetics of the consumption of phenol 2 and the accumulation of

diphenoquinone during the induction period of oxidation in the range far from completion of induction period. In Figure 3, data on the kinetics of the consumption of phenol 1 both in the presence and in the absence of DLTP are shown. The conclusion is the same in both situations: At least while the concentration of phenol 1 remains high enough, the synergist does not influence the consumption process. At the same time, the induction periods of PP oxidation become longer in the presence of synergists. The corresponding data

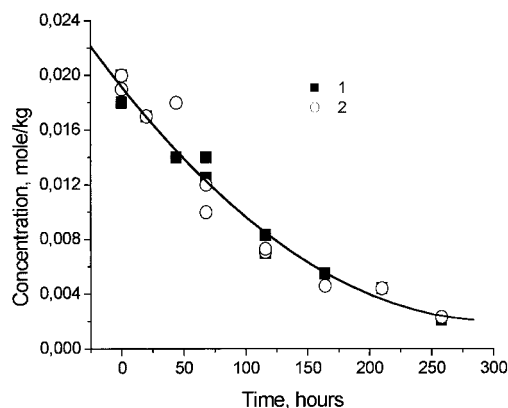


Figure 1 Kinetics of phenol 2 consumption in polypropylene both in the presence of 10^{-2} mole/kg of phosphite (1) and without it (2). $T = 130^\circ\text{C}$, air.

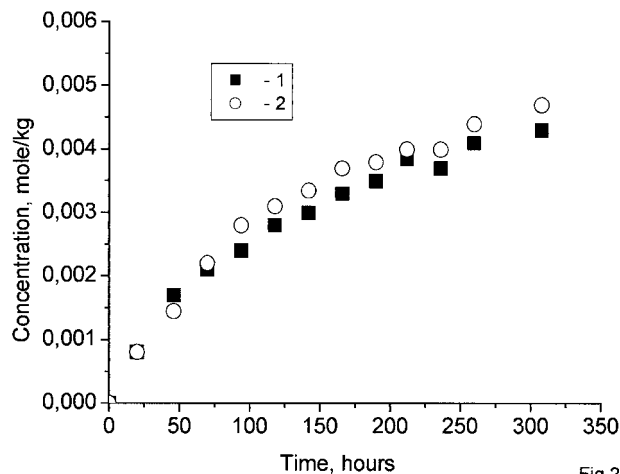


Figure 2 Kinetics of diphenoquinone accumulation in polypropylene both in the presence of 10^{-2} mole/kg of phosphite (1) and without it (2). $T = 130^{\circ}\text{C}$, air. Initial concentration of phenol 2 is 2×10^{-2} mole/kg.

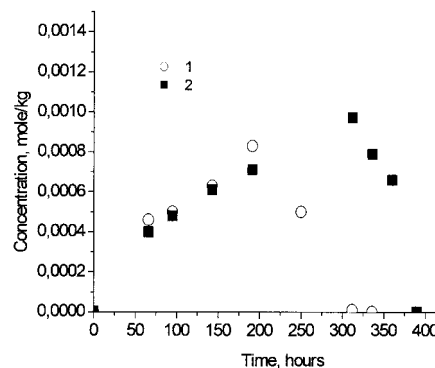


Figure 4 Kinetics of diphenoquinone accumulation in polypropylene both without phosphite (1) and in the presence of 5×10^{-3} mole/kg of phosphite (2) (low concentrations). $T = 130^{\circ}\text{C}$, air. Initial concentration of phenol 2 is 5×10^{-3} mole/kg.

are presented in Figure 4 and in Table I. From these data, it follows that DLTP is more efficient than phosphite and that, in the case of phenol 1, the effect of introducing hydroperoxide decomposers is more noticeable.

The obtained results show that hydroperoxide decomposers did not influence the process of phenol consumption at that stage of the process, when the concentration of the phenolic inhibitor was rather high, and that it was possible to measure this concentration using our method. Appar-

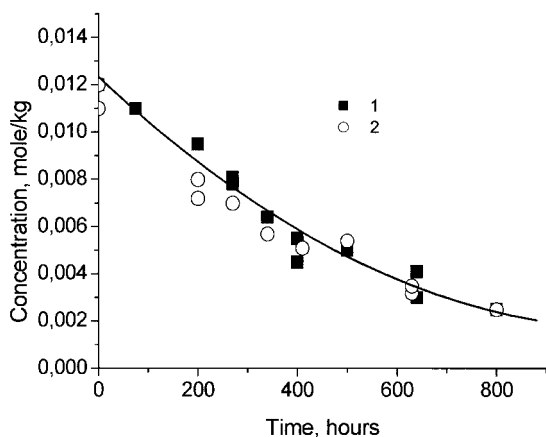


Figure 3 Kinetics of phenol 1 consumption in polypropylene (1) without sulphide and (2) in the presence of 10^{-2} mole/kg of dilauril-thio-dipropionate. $T = 130^{\circ}\text{C}$, air.

ently, these decomposers start to influence the process of inhibited oxidation only when the possibilities of the main inhibitor, phenol, are already practically exhausted and the character of the process begins to change. (Usually, we determine this period of oxidation as a transitional one: concentration of phenol becomes low, close to critical, and linear chain termination becomes less probable.) This is in good agreement with well known data, which indicate that it is exactly during this period that accumulation of hydroperoxide starts, which finally results in the end of the induction period.

At this stage, the influence of the synergist on the process of oxidation—suppression of the radical decomposition of the hydroperoxides—becomes significant, and as a result, the prolongation of the induction period can be observed. The mathematical description of this situation was given earlier.⁹ The influence of the synergist (S) can be described with parameter γ , having the following structure:

$$\gamma = k_3/[k_3 + k_4(S)],$$

where k_3 is the rate constant of hydroperoxide decomposition without the synergist and k_4 is the rate constant of the interaction of the synergist and hydroperoxide. It is clear that the case $\gamma = 1$ corresponds to absence of synergism and that at $\gamma = 0$, synergism is maximum. In the presence of the synergist, the critical concentration of phenolic antioxidant can be defined by

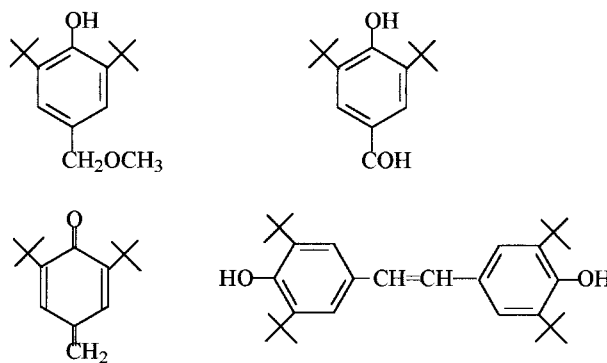
Table I Induction Periods of PP Oxidation with Different Inhibiting Compositions

Inhibiting System	Induction Period, Hours	Synergy Effect
Phenol 1 ($4 \times 10^{-3}\text{M}$)	140	
Phenol 1 ($2 \times 10^{-3}\text{M}$)–DLTP ($2 \times 10^{-3}\text{M}$)	1500	10.7
Phenol 1 ($2 \times 10^{-3}\text{M}$)–Phosphite ($2 \times 10^{-3}\text{M}$)	250	1.8
Phenol 2 ($4 \times 10^{-3}\text{M}$)	280	
Phenol 2 ($2 \times 10^{-3}\text{M}$)–DLTP ($2 \times 10^{-3}\text{M}$)	650	2.3
Phenol 2 ($2 \times 10^{-3}\text{M}$)–Phosphite ($2 \times 10^{-3}\text{M}$)	400	1.4

$$[PhOH]_{crit} = 2 \gamma f k_2 [RH] / [k_7 (1 - 2\gamma f)],$$

where f characterizes the cage effect at hydroperoxide decomposition, k_2 is the rate constant of chain propagation, and k_7 is the rate constant of the interaction of the peroxide radical and phenol. From this expression, it follows that in the limit case, when $\gamma \rightarrow 0$, $[PhOH]_{crit} \rightarrow 0$ and the interval of inhibitor concentration at which the process is a stationary one becomes unlimitedly wide. It is also clear that in the presence of the synergist, the critical concentration of the inhibitor has to decrease and, as a result, the nonstationary process becomes stationary. Thus, a weak inhibitor begins to behave as a strong one in the presence of the synergist.

The degree of synergist influence should strongly depend on the mechanism of transformation of the phenol inhibitor, namely, on the set of its transformation products. For phenol 2, the formation of diphenoquinone is very advantageous from the energy standpoint, and the probability of the formation of new inhibitors is low. The assumption that diphenoquinone is practically the only product of these bisphenol transformations has been confirmed by the study of the ultraviolet spectra of heptane extracts from oxidized polymers after washing out the phenol and reaction products. It is necessary to say that different routes of bisphenol transformation will lead to the same product: diphenoquinone. These routes include the reaction of the hydrodiphenyloxy radical with the peroxy radical, the oxidation of the hydrodiphenyloxy radical with the oxygen in the air, disproportionation, and the reactions of quinolide peroxides. The transformation of phenol 1 results in the formation of new inhibitors, some of them are shown below.^{3,4}



The influence of these new inhibitors—products of the transformation of phenol 1—that behave as strong (highly efficient) ones in the presence of the synergist can explain the more considerable effect of the synergists in the case of phenol 1. It is possible also to suppose that, in the case of phenol 2, this influence is less significant because of its very high inhibiting activity as a result of synergy between the bisphenol and its transformation product, diphenoquinone: the addition of another synergist—even one of an absolutely different nature—cannot be very effective.

That fact that the synergists start to influence the process only during the period close to the end of the induction period allows us to form some conclusions. For example, it is possible to propose that observing the effect of the synergist has to depend on, among other things, the concentration of the main inhibitor. If we deal with an ideal inhibiting scheme without side reactions, the synergy effect will become less as the inhibitor concentration increases. This will be because of the decreasing of the relative contribution of the transition period to the total duration of the induction period. In severe conditions (e.g., at high temperatures), the role of synergists will become more significant. Of course, for a real process with side reactions and the possi-

bility of the formation of new inhibitors, this situation will not be so simple. But this conclusion is in good agreement with the fact that the main purpose of introducing an inhibiting system into polyolefins is to protect these polymers during processing.

REFERENCES

1. Levin, P. I., Mikhailov, V. V. *Uspekhi Khimii* 1970, 39, 1687.
2. Pobenimsky, D. G. *Uspekhi Khimii* 1971, 40, 254.
3. Yachigo, S., Sasaki, M., Kojima, F. *Polym Degrad Stab* 1992, 35, 105.
4. Popova, G. S. *Cand Sci (Chemistry) Thesis*. Investigation of the mechanism of the antioxidative action of 2,6-di-tert-butyl-4-methylphenol. Leningrad, 1975.
5. Taimr, I., Pospisil, J. *Angew Makromol Chem* 1974, 39, 189.
6. Shanina, E. L., Zaikov, G. E., Mukmeneva, N. A. *Polym Degrad Stab* 1996, 51, 51.
7. Shanina, E. L., Belyakov, V. A., Zaikov, G. E. *Polym Degrad Stab* 1990, 27, 309.
8. Belyakov, V. A., Vasiliev, R. F., Fedorova, G. F. *Khimiya Vysokhikh Energii* 1978, 12, 247.
9. Roginsky, V. A. *Phenol Antioxidants. Reactivity and effectiveness*. Moscow: Nauka, 1988; p. 230.