Some Features of Phenolic Inhibitor Consumption in Oxidized Polypropylene in the Presence of Synergists–Hydroperoxide Decomposers

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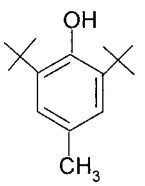
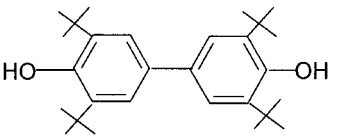
ABSTRACT: The influence of sulfur and phosphors containing substances, hydroperoxide decomposers, on the kinetics of the consumption of two phenolic antioxidants in polypropylene (PP) was studied. The induction periods of PP autoxidation at 130°C were measured in the presence of inhibiting compositions that consisted of phenolic inhibitors and decomposers of hydroperoxide. The obtained results indicated that the influence of the hydroperoxide decomposer became significant when the concentration of the phenolic antioxidant became close to a critical value. It was shown also that the influence of the hydroperoxide decomposer significantly depended on the mechanism of the phenolic inhibitor transformation: first of all, on the nature of its transformation products. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 2226–2229, 2003

Key words: poly(propylene) (PP); antioxidants; degradation

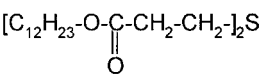
It is well known that simultaneous addition of a phenolic inhibitor and a decomposer of hydroperoxide (sulfide, phosphite) to a polymer during the oxidation process results in synergism and allows increase of the time of polymer protection from degradation. The mechanism of the interaction of substances, synergists with hydroperoxides, has also been well investigated.[1–3] However, details of the interaction or simultaneous action of a phenol and a synergist–decomposer of hydroperoxides remain, in many respects, not absolutely clear. Therefore, we found it necessary to return to this problem and, for our research, 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, dilaurylthiodipropionate (DLTP) and tris(2,5-di-*tert*-butyl)phosphite (called phosphite in the following). Phenol 1 was chosen as an inhibitor, as it the most well-investigated mechanism of transformation in oxidized substrates.[4,5] Besides, this phenol is often used as a standard antioxidant during kinetic experiments. Phenol 2 was chosen as a substance that provides a very long induction period of polypropylene (PP) oxidation owing to the synergism of phenol–quinone, the last substance being a product of the transformation of this bisphenol during inhibited oxidation[6]:



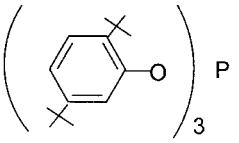
Phenol 1



Phenol 2



DLTP



Phosphite

Experimental part

EXPERIMENTAL

Isotactic PP as a powder (Himont Co., USA, ProFax 6501) with a molecular mass of M_w = 164,400 and M_w/M_n = 3.8, was used after washing away of inhibitor traces in a Soxhlet apparatus (Himont Inc., Wilmington, DE). All samples were oxidized in sealed ampules at 130°C. For measurement of the antioxidant concentration, a kinetic method was used. The inhibitor was extracted from the polymer samples, and after addition of this extract to a mix of the initiator and the oxidizing substrate (cumene), the induction period was measured using a manometer gauge. Then, the concentration of the antioxidant in the poly-

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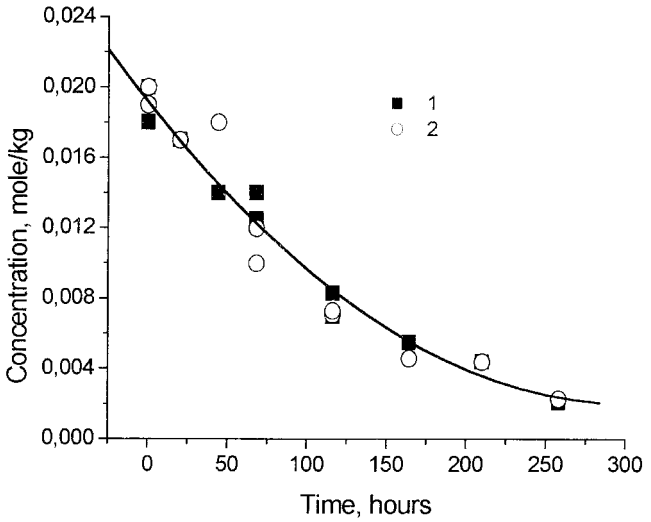


Figure 1 Kinetics of phenol 2 consumption in PP in the presence of 10^{-2} mol/kg of (1) phosphite and (2) without it. T = 130°C, air.

mer sample could be calculated. The details of the procedures of sample preparation, oxidation of the polymer, measurements of the antioxidants and the diphenoquinone concentrations, and also measurements of the induction periods of polymer oxidation were described in our previous works.[6,7] The procedures for chlorobenzene and cumene purification were given in ref. 8. The low molecular weight components were purified by crystallization from ethanol and heptane.

RESULTS AND DISCUSSION

In Figures 1 and 2, data on the kinetics of phenol 2 consumption and formation of diphenoquinone—the

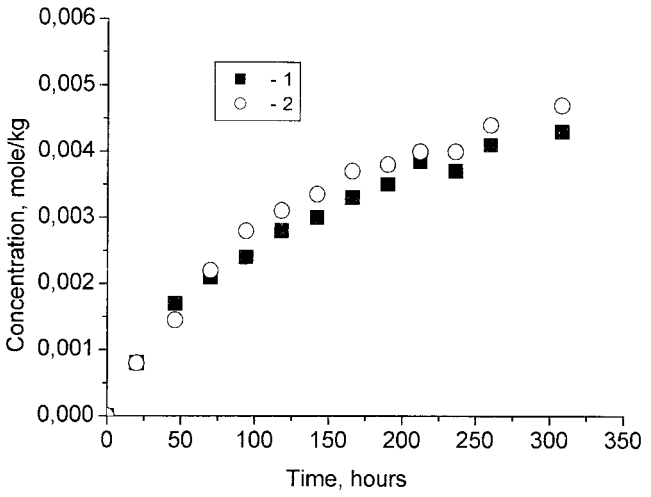


Figure 2 Kinetics of diphenoquinone accumulation in PP in the presence of 10^{-2} mol/kg of (1) phosphite and (2) without it. T = 130°C, air. Initial concentration of phenol 2: 2×10^{-2} mol/kg.

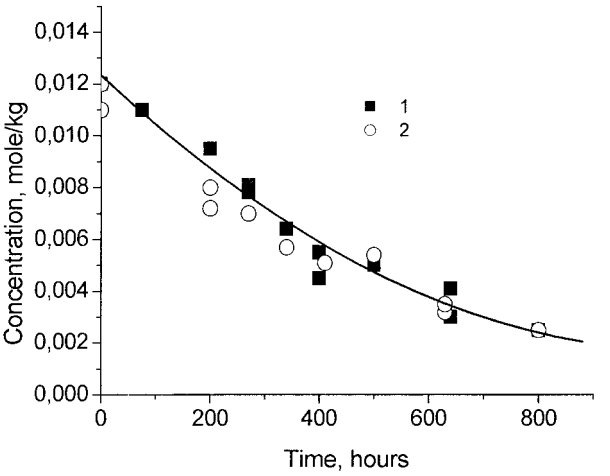


Figure 3 Kinetics of phenol 1 consumption in PP: (1) without sulfide; (2) in the presence of 10^{-2} mol/kg of DLTP. T = 130°C, air.

product of its transformation—in the presence and in the absence of phosphite are presented.* As follows from these data, phosphite practically 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 the induction period. In Figure 3, data on the kinetics of the consumption of phenol 1 in the presence and in the absence of DLTP are shown. The conclusion is the same one—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 are presented in Figure 4 and Table I. From these data, it follows that DLTP gives a more essential effect than does phosphite, and in the case of phenol 1, the effect of the introduction of hydroperoxide decomposers is more noticeable.

The obtained results showed 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 it was possible to measure it using our method. Apparently, these substances 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: The concentration of phenol becomes low, close to a critical one, and linear chain termination becomes less probable.) This fact is in good agreement with the well-known data, that

*These data differ a little from those published in our previous work[6] because polymers with different characteristics were used.

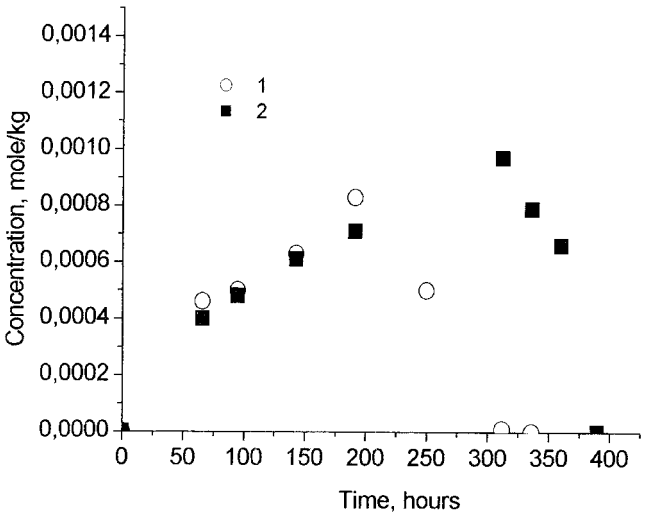


Figure 4 Kinetics of diphenoquinone accumulation in PP of (1) without phosphite and (2) in the presence of 5×10^{-3} mol/kg of phosphite (low concentrations). $T = 130$°C, air. Initial concentration of phenol 2: 5×10^{-3} mol/kg.

exactly during this period accumulation of hydroperoxide starts, which finally results in the ending of the induction period. At this stage, the influence of the synergist on the process of oxidation–suppression of the radical decomposition of hydroperoxides becomes significant, and as a result, prolongation of the induction period can be observed.

The mathematical description of this situation was given in ref. 9. The influence of the synergist (S) can be described with the parameter γ, having following structure:

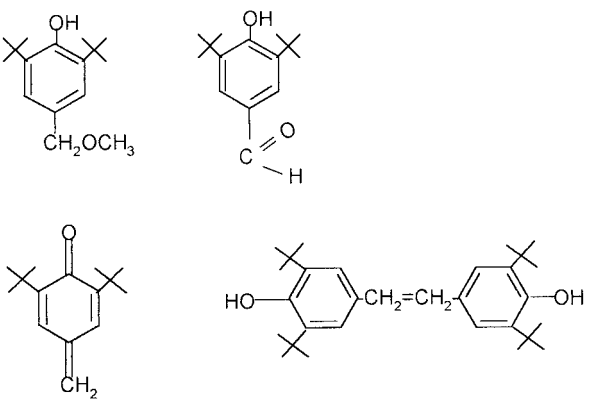
$$\gamma = k_3/(k_3 + k_4[S])$$

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

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

where f characterizes the cage effect at the 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 $\gamma \rightarrow 0$ and $[\mathrm{PhOH}]_{\mathrm{crit}} \rightarrow 0$, 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 a synergist.

The degree of the 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; the formation of new inhibitors is of low probability. The assumption that diphenoquinone is practically the only product of this phenol transformation has been confirmed by study of the UV spectra of heptane extracts after the washing out of phenol and its products from an oxidized polymer. It is necessary to say that different routes of phenol transformation will lead to the same product—diphenoquinone: Among them are the reaction of the hydrodiphenyloxy radical with the peroxy radical, the oxidation of the hydrodiphenyloxy radical with the oxygen of air, disproportionation, and reactions of quinolide peroxides. 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, which behave as strong ones in the presence of a synergist–can explain

TABLE I
Induction Period and Synergy Effect of Inhibiting Systems

Inhibiting system	Induction period (h)	Synergy effect
Phenol 1 (4×10^{-3} M)	140	
Phenol 1 (2×10^{-3} M)–DLTP (2×10^{-3} M)	1500	10.7
Phenol 1 (2×10^{-3} M)–phosphite (2×10^{-3} M)	250	1.8
Phenol 2 (4×10^{-3} M)	280	
Phenol 2 (2×10^{-3} M)–DLTP (2×10^{-3} M)	650	2.3
Phenol 2 (2×10^{-3} M)–phosphite (2×10^{-3} M)	400	1.4

the more considerable effect of synergists in the case of phenol 1. It is possible also to suppose, in the case of phenol 2, which shows a very high inhibiting activity as a result of the synergy between the phenol and its transformation product—diphenoquinone—that addition of another synergist, even of an absolutely other nature, cannot be very effective.

The fact that the synergists start to influence the process only during the period close to the end of the induction period allows one to make some conclusions: For example, it is possible to propose that the observation of the effect of a synergist has to depend, among others, on the concentration of the main inhibitor. If we will deal with the ideal inhibiting scheme without side reactions, the synergy effect will become less with an increasing inhibitor concentration. It will be so because of a decrease of the relative contribution of the transition period to the total duration of the induction period. In severe conditions, for example, at high temperatures, the role of synergists will become more significant. Of course, for the real process with side reactions and the possibility of the formation of new inhibitors, this situation will not be so simple. But this conclusion is in good coincidence with the fact that the one of main purposes of introducing an inhibiting system into polyolefins is to protect these polymers during processing.

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