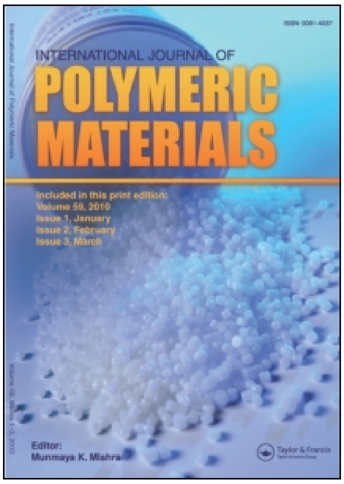

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Shanina, E. L. and Zaikov, G. E.(1996) 'Antioxidant Consumption in Stabilised LDPE-PP Composition', International Journal of Polymeric Materials, 33: 1, 57 — 60
To link to this Article: DOI: 10.1080/00914039608028607
URL: http://dx.doi.org/10.1080/00914039608028607

Intern. J. Polymeric Mater., 1996, Vol. 33, pp. 57–60
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Antioxidant Consumption in Stabilised LDPE-PP Composition

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(Received July 20, 1995)

Method for investigation of inhibited oxidation process and evaluation of antioxidant efficiency in polymer is proposed. This procedure is based on the analyses of antioxidant consumption curves. As an example data for consumption of Nonox WSP in the PP-PE blend are analysed.

KEY WORDS Oxidation, antioxidant efficiency, polymer blend.

1. INTRODUCTION

When considering the problem of service stability of polymer materials, their stability towards thermooxidation is one of the most important factors. To enhance their stability, special additives—antioxidants—are usually incorporated into polymers or composites. During processing and use, the concentration of antioxidant decreases and if a critical low value is reached, the additive becomes ineffective.

Antioxidant consumption is a complex process that usually includes physical losses as well as chemical reactions. The number of such chemical reactions is usually much higher than it is possible to take into consideration. For example, during inhibited oxidation of polymer and as a result of oxidation of the antioxidant itself, the formation of new antioxidants is possible and these new antioxidants participate in the process.[1] Besides, formation of initiators—for example quinolide peroxides—is also possible. To solve the problem of polymers protection it is, therefore, necessary to take into account not only the starting antioxidant activity but also the one of its transformation products. One possibility to obtain the complete information about antioxidant behaviour is to analyse its consumption curve which can be obtained by means of the kinetic method of antioxidant concentration control.[1] An example of this method application is given below.

2. RESULTS AND DISCUSSION

In most cases it is impossible to measure the concentration of all antioxidants in the system. It is, however, possible to evaluate the total inhibiting potential of the system,

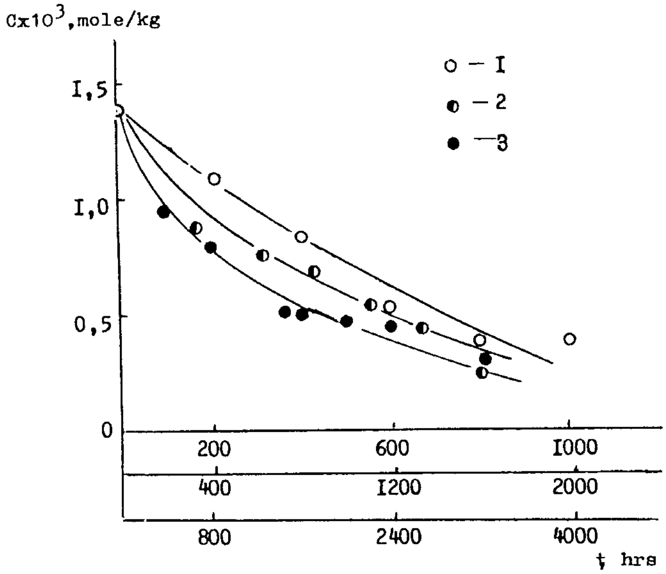

FIGURE 1 Kinetic curves of Nonox WSP consumption in the PE-PP blend at 60° (1, t_{max} = 4000 hrs), 80° (2, t_{max} = 2000 hrs) and 105° (3, t_{max} = 1000 hrs).

involving the starting antioxidants as well as their transformation products possessing antioxidative activity. This method which is rather simple and does not require expensive equipment is described below.

The method of analysis includes: 1) the extraction of antioxidant from polymer, using an inert oxidation resistant solvent, in our case—chlorobenzene; 2) the addition of chlorobenzene solution of initiator—dinitrile of azo- bis-isobutiric acid and cumene (oxidising substrate) to the extract; 3) the measurement of cumene oxidation induction period, using special highly sensitive pressure gauge.

By taking probes of oxidizing polymers and measuring the antioxidant concentration in these pores it is possible to obtain consumption kinetics for this antioxidant. Of course this scheme can be used also for the measurement of antioxidant concentration in the liquid phase. We previously used this method for the investigation of the oxidation kinetics of some phenols in chlorobenzene and also for their consumption in polymer during oxidation.[2]

The goal of the present work was to study the consumption kinetics of phenolic antioxidant Nonox WSP (2,2′-Methylene-bis-[4-methyl-6-(1-methylcyclohexyl-1)-phenol]) in the stabilised polymer composition: LDPE (158–10 K) (80%) containing 2% soot and PP (20%) (Silpon 4), modified with rubber. Thermooxidation of samples was conducted in the thermostat at three different temperatures: 60, 80 and 105°C in the air. The losses of the antioxidant due to physical processes were excluded because samples were placed in the sealed tubes. The samples had the rod shape of 5 mm diameter. For the analysis a thin surface layer (≈0.5 mm) was used to avoid possible influence of oxygen diffusion process.

Figure 1 shows the kinetic cuves of antioxidant consumption in the above mentioned composition at different temperatures. These curves cannot be described using simple kinetic laws, but their initial parts (up to 40–50% conversion) can be satisfactorily linearized in the first order kinetic equation co-ordinates. In one of our earlier papers[2] we have shown, that the initial part of phenolic antioxidant consumption curves in the polymer at rather high initial concentration reflects predominantly the direct oxidation of inhibitor with oxygen from air. This process is of the first order law with effective constant k $[O_2]$. On this basis, the calculated values of effective constants for Nonox WSP in the blend are as follows:

Temperature, °C	Constants × 10^7, 1/sec
60	0.56
80	1.5
105	3.9

The activation energy of antioxidant consumption process, calculated for initial rates at three temperatures is 11.5 ± 0.5 kcal/mole.†

The kinetics of antioxidant consumption in PP—one of blend components—was also studied at 105°C. Results are given below.

Time, hrs	0	400	770	1200
Concentration × 10^3, mole/kg	3.4	3.0	2.8	2.0

The initial rate of antioxidant consumption in PP is 2.8×10^{-10} mole/kg·sec at the initial concentration 3.4×10^{-3} mole/kg. In the blend, the initial rate at 105°C is 1.5×10^{-9} mole/kg·sec at the initial concentration 1.4×10^{-3} mole/kg. Assuming that the initial consumption rate of the antioxidant is proportional to its concentration, it follows that during the initial stage in the blend the antioxidant is consumed at a higher than tenfold rate, than in the one of its constituents. Because of too low antioxidant concentration in PE it was impossible to obtain reliable results. For comparison, however, it is possible to use results of the other sample of LDPE, containing 3.2×10^{-3} mole/kg of the same antioxidant. For this sample at 105°C, the initial consumption rate is 3.8×10^{-10} mole/kg sec and this value is also much lower than in the blend. It is necessary to point out, that the consumption rate in PE is higher than in PP and it can be attributed to rather high oxidation temperature which is close to melting point for PE.

Thus, the antioxidant is consumed in the blend at a rather high rate, higher than in each of its constituents. This indicates a higher rate of blend oxidation in comparison with the separate constituents. A few reasons for such nonadditivity chemical and structural can be put forward. One of the reasons can be that the system, composed of two unmiscible polymers is not at equilibrium with the energy excess in the interphase layers, where the oxidation is most likely to begin.

The data obtained permit us to make some evaluations of the time of full antioxidant consumption at different temperatures. For such evaluation it is necessary to

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†In this case value of activation energy has not any physical sense and is given only for convenience of possible inter- and extrapolations. It is necessary to mention yet, that very far extrapolations in the case of such complicated process as antioxidant consumption can lead to mistake.

know the value of critical concentration of the antioxidant in PP (i_{cr}). For rough evaluation it is possible to use the following formula[3]:

$$i_{cr} = \frac{\delta k_2[RH]}{fk_7}$$

where δ = initiation efficiency during hydroperoxide formation, f = stoichiometric coefficient of inhibition, k_2 = rate constant of chain propagation process, k_7 = rate constant of reaction of peroxy radical with phenol, $[RH]$ = monomer links concentration.

In the calculation process one has to use the data for PP, because for the blend, the kinetic information is rather scarce. With these assumptions the following parameters values at 60°C: $k_2 = 10^{-2}$ kg/mole·sec[4], $k_7 = 1.6 \times 10^4$,[5]‡ $\delta = 0.1$,[5] $f = 4$, $[RH] = 23.4$ mole/kg critical concentration value about 10^{-6} magnitude are obtained. Taking the above given value of the rate constant for antioxidant consumption at 60°C it is possible to evaluate the time interval during which initial antioxidant concentration would decrease to its critical value. Considering the approximate character of evaluation this value is about four years. This value should be considered as the lower limit, because the data in Figure 1 show that the consumption rate deviates with time from the first order law, becoming slower (possibly, because of secondary antioxidants formation).

Although the above example is only semiquantitative, the obtained result can serve as a reference point in the process of material service life evaluation. It is also necessary to note that the above described method provides the possibilities for comparing the efficiency in polymers of different antioxidants.

Acknowledgment

The authors would like to acknowledge with gratitude the financial support of ISF.

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‡The value for structurally analogous antioxidant—2246 is taken. It appears possible because of levelling of different antioxidants k_7 values in the solid polymer. In the liquid phase k_7 value for Nonox WSP is slightly higher than for 2246.[5]