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Effects of some secondary amines on the oxidation of ethylene–propylene elastomers

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Abstract

The oxidative degradation of ethylene–propylene elastomers (EPDM and EPR) in the presence of some secondary amines was studied. The stabilization efficiency of these additives was assessed by oxygen uptake performed in air at 180°C and normal pressure. The oxidation induction times and the oxidation rates were obtained for polymer systems containing low amounts (0.05 and 0.1 phr) of additive. Some considerations concerning the effects of the chemical structure of the compounds added to EPDM and EPR on the thermal stability of elastomers are presented. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Thermal stability studies on thermoplastics are one of the main options for lifetime assessment. Many factors can affect the thermal degradation: chemical structure of polymer matrix, nature and concentration of additive, history of material, operation and environmental conditions.

There is an abundence of studies on the stabilization effects of various classes of antioxidants such as phenols [1–5], amines [6–10] and triazines [11–13]. The oxidation retardation requirements of antioxidants concern the length of oxidation induction time and the rate of oxidation; these two parameters are often referred to in the efficiency qualification.

In this paper a new set of antioxidants is studied. They belong to the amine class, but they have different chemical structures in comparison with "classical" stabilizers. A previous study on the thermal and photostability of polyethylene has revealed a certain antioxidant activity of some compounds belonging to this series of synthetic derivatives [14].

2. Experimental

2.1. Materials

Elastomeric materials [ethylene–propylene copolymer (EPR) and ethylene–propylene–diene terpolymer (EPDM)] were supplied by ARPECHIM Piteşti (Romania). They have the same quantitative ratio between ethylene and propylene units (3:2). The terpolymer contained 3.5% ethylidene norbornene. Chemical characteristics of these synthetic rubbers were mentioned in a previous paper [15].

Secondary amines were synthetized by catalytic reactions in liquid phase. The full procedure and the level of purity have been presented earlier [14]. The compounds used in this work are shown in Fig. 1.

2.2. Sample preparation

Elastomers were purified in order to avoid any synergistic effects involving the studied compounds and the small amounts of factory stabilizer. To each hot polymer solution in o-xylene amounts of cold methanol were gently added. The precipited material was filtered and washed with acetone to remote the retained solvent. Then a light drying in an oven at 30°C followed until o-xylene odour could not be detected. The purified elastomers were finally transferred to $CHCl_3$ solution.

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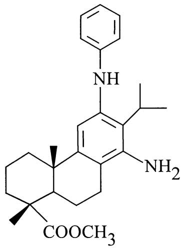
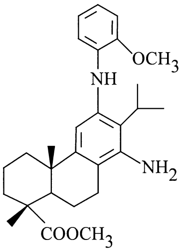
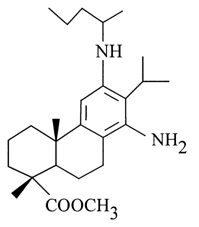
Samples of stabilized elastomers were separately prepared by the addition of suitable amounts of secondary amines to obtain 0.1 phr or 0.05 contents in these compounds. Thin homogenous films were obtained in aluminum trays by solvent removal.



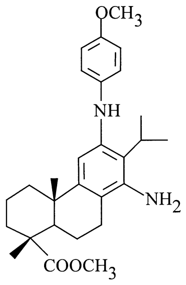
A 08. Methyl 12N-(phenyl)amino-14-amino-dehydroabietate



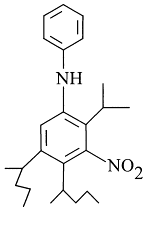
A 09. Methyl 12N-(2-methoxyphenyl)amino-14-amino-dehydroabietate



A 10. Methyl 12N-(1-methylbutyl)amino-14-amino-dehydroabietate



A 11. Methyl 12N-(4-methoxyphenyl)amino-14-amino-dehydroabietate



A 12. Methyl 12N-(phenyl)amino-14-nitro-dehydroabietate

Fig. 1. The additives used in this paper.

2.3. Oxygen measurements

Oxidation was performed under isothermal and isobaric conditions; the apparatus was described previously [16]. For the estimation of the kinetic parameters of thermal degradation the following oxidation parameters were selected: temperature: 180°C; pressure: 1 atm.

3. Results and discussion

Thermal degradation of ethylene–propylene elastomers can be characterized by two main kinetic parameters: oxidation induction time and maximum oxidation rate attained in the propagation stage of oxidation. Table 1 lists these values for both additive concentrations. It can be remarked that all of the studied compounds are antioxidants in the matrix of ethylene–propylene copolymer, while only some of them (A 08 and A 09) inhibit the oxidation of ethylene–propylene terpolymer. The other three compounds (A 10, A 11 and A 12) are pro-oxidants when they are present in EPDM. In contrast, EPR shows very efficient thermal stabilization. In the cases of the copolymer stabilized

Table 1
Some kinetic characteristics of thermal oxidation obtained for ethylene–propylene rubber/secondary amine systems

Polymer	Additive	Additive concentration (%)	Oxidation induction time (min)	Oxidation rate (mol g^{-1} s^{-1})×10^{6}
EPDM				
	Free		57	1.61
	A08	0.10	380	2.96
		0.05	170	4.75
	A09	0.10	271	2.74
		0.05	214	1.27
	A10	0.10	34	1.76
		0.05	37	1.54
	A11	0.10	41	1.51
		0.05	36	2.13
	A12	0.10	35	1.68
		0.05	40	1.22
EPR				
	Free		73	1.21
	A08	0.05	288	2.87
		0.10	> 800	–
	A09	0.05	136	1.41
		0.10	> 800	–
	A10	0.05	122	1.95
		0.10	208	2.15
	A11	0.05	> 800	–
	A12	0.05	219	1.77
		0.10	527	2.02

with 0.1 phr of secondary amines the measured induction periods were longer than 800 min; this means that the stability of this material is twice that of the corresponding control.

Fig. 2 presents two different ways in which the same compound can behave in different materials. Thus, the thermal degradation of ethylene-propylene terpolymer that contained initially 3.5% ethylidene norbornene starts earlier than the control. Under the same conditions, ethylene–propylene copolymer (Fig. 2a) is efficiently stabilized over long induction periods. However, during the propagation stage of oxidation the rates of oxygen consumption are higher than the control. It means that when the existing reactive site concentrations are different enough, the action routes of these compounds are unlike. This can be considered as a consequence of various intermediates appearing during degradation of secondary amines. Besides, large differences between the two selected concentrations of additives in EPDM obtained for A 08 and A12 (Fig. 3 and Table 1) presume the existence of several chemical forms in which these compounds can react.

During the first stage of oxidative degradation the breaking of weaker bonds and the formation of free radicals occur. A competition between molecular oxygen and stabilizer for reaction with free radicals determines the progress in damaging material. The mechanism of degradation and stabilization depends on the rate of bond breaking, the accumulation of intermediates, the rate of oxygen diffusion, the capability of additive to trap free radicals and the rates of other processes involving modifications in additive molecules. Basic mechanism of hydrocarbon oxidation was formulated by Bolland and Gee [17] and two ways for chain breaking processes would be foreseen: the trapping of radicals and/or decomposition of hydroperoxides.

The structures of the studied secondary amines can promote radical scavenging on both nitrogen atoms. Similar reactions occur with quinoneimines and quinonediimides [18]. It is also possible that a nitroxide intermediate would be formed. In a recent study on hindered amine stabilizers [19], Gijsman has stated that

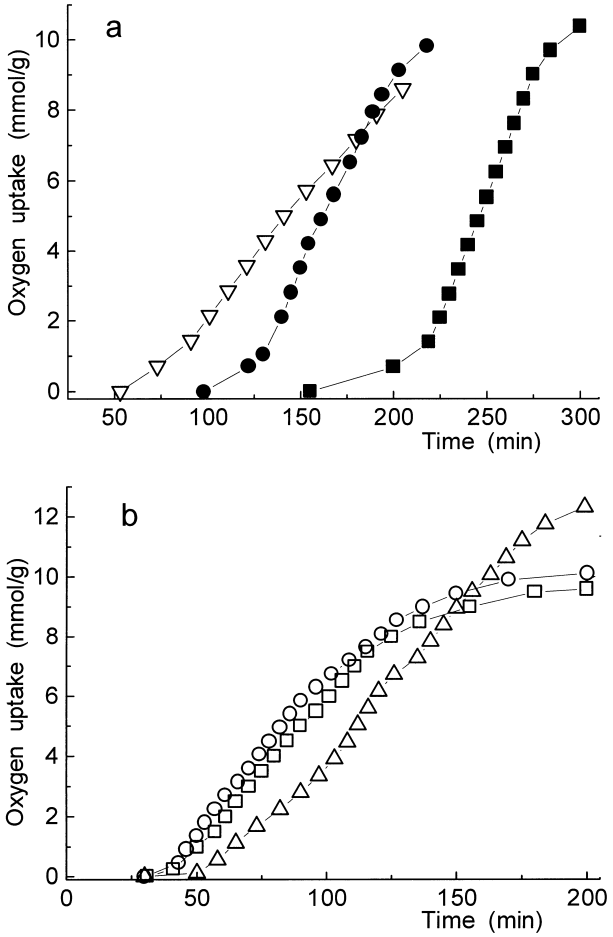


Fig. 2. Time dependencies of oxygen uptake for ethylene–propylene elastomers in the presence of A10 compound: (a) EPR; (b) EPDM. (■,●) additive concentration 0.05 phr; (□,○) additive concentration 0.10 phr; (△) control.

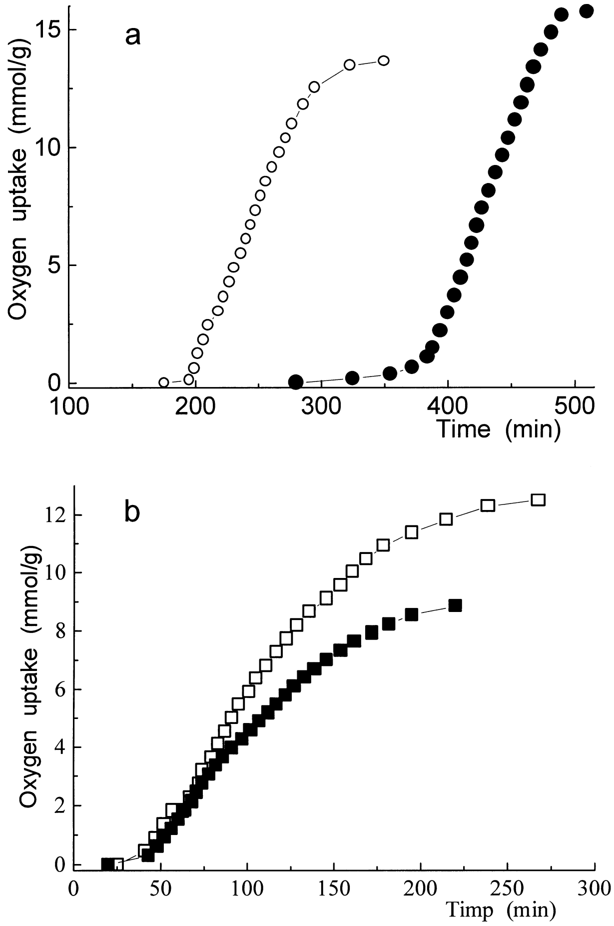


Fig. 3. Time dependencies of oxygen uptake for ethylene–propylene terpolymer in the presence of (a) A 08 and (b) A 12 compounds. (□,○) 0.05 phr; (■,●) 0.10 phr.

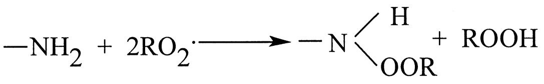
the influences of the amine and the nitroxide on the oxidation rate of hydrocarbons are comparable due to conversion of the amine into the nitroxide. The behaviour of secondary amines in ethylene-propylene elastomers has suggested the mechanism presented in Fig. 4. A confirmation of this proposal can be found in [20].

It is probable that the C–N bond is broken easier because its energy of 13.3 kJ/mol is less than the bond energy of N–H (20 kJ/mol) [21]. During oxidation a nitroxid group can be formed due to low energy requirement (14.6 kJ/mol) [21]. The stabilization activity would be diminished when nitroso group is created because of its high stability (25.8 kJ/mol) [21].

A simplified scheme of stabilization involving the secondary amines may be presented on the basis of energetic considerations. It is suggested that they react as chain breaking acceptors.

$$>\mathrm{N}^{\cdot} + \mathrm{R}^{\cdot} \longrightarrow\ >\mathrm{N{-}R} \quad (1)$$

$$=\mathrm{NO}^{\cdot} + \mathrm{R}^{\cdot} \longrightarrow\ =\mathrm{NOR} \quad (2)$$



$$-\mathrm{NH_2} + 2\mathrm{RO_2}^{\cdot} \longrightarrow -\mathrm{N}\begin{smallmatrix}\mathrm{H}\\ \mathrm{OOR}\end{smallmatrix} + \mathrm{ROOH} \quad (3)$$

$$>\mathrm{NH} + 2\mathrm{RO_2}^{\cdot} \longrightarrow\ >\mathrm{NOOR} + \mathrm{ROOH} \quad (4)$$

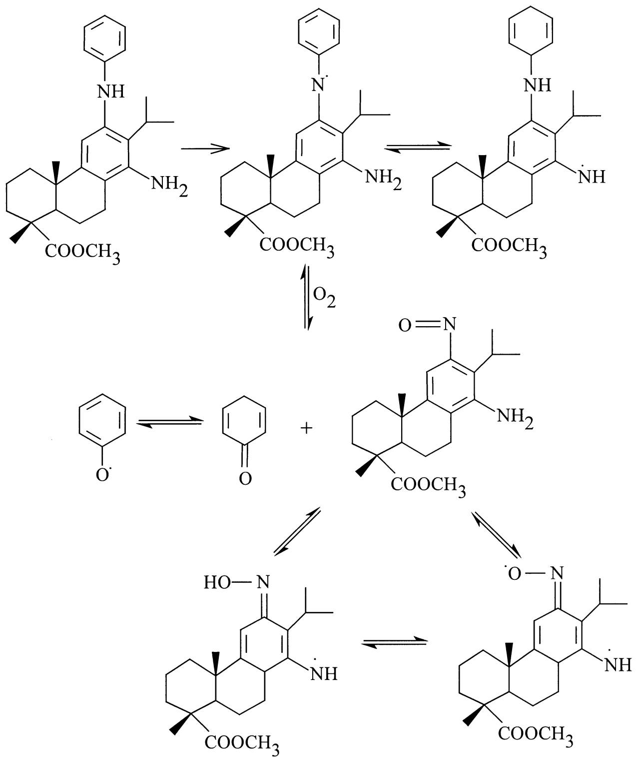


Fig. 4. Scheme of the proposed chemical changes of secondary amines during thermal oxidation of ethylene–propylene elastomers.

Of course, the preponderance of these last four reactions depends in a large extent on the size and electronic effects of substituents. The differences in the stabilization efficiency of secondary amines in ethylene–propylene elastomers can be explained by the difference in thermal stability of host materials [22]. On the other hand, the pro-oxidative behaviour of A 10, A 11 and A 12 suggests that a fast consumption of this additive takes place at the testing temperature.

4. Conclusions

In the present work a new series of secondary amines was studied. Their activity in thermal stabilization of ethylene–propylene elastomers was satisfactory for the most representative of this set of additives at low concentrations. This class of compounds would be considered suitable for the prevention of oxidation in ethylene–propylene copolymer, while terpolymer exhibited only a moderate oxidation induction times, comparable with some of less hindered phenols. It would be expected that remarkable results would be obtained by coupling these secondary amines with phenols like Ionox 330 or other commercial products.

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