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NATURAL ANTIOXIDANTS FOR THERMO-OXIDATIVE STABILIZATION OF ELASTOMERS

Gheorghe IVAN,[a*] Maria GIURGINCA,[b] Nicoleta IFTIMIE[b] and Aurelia MEGHEA[b]

[a]Tofan Grup International S.A., 35-37 Olteniței St, RO-041293, Bucharest, Roumania
[b]University "Politehnica" of Bucharest, 1 Polizu St, RO-011061 Bucharest, Roumania

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Stabilization against thermo-oxidative degradation is an important requirement for the performance of elastomer-based products. The addition of antioxidants is a common way for increasing material resistance and service life in atmospheric conditions. This paper presents the effects of thermo-oxidation and peroxidation on saturated (IIR) and unsaturated (IR, BR, SBR) rubbers protected by natural (vitamins A and E) and usual synthetic antioxidants (BHT).

INTRODUCTION

Degradation and stabilization of commercial elastomers bring to mind the main features of some biological systems. Compatibility of the antioxidant with the substrate and the aggressiveness of the intermediary or final products resulting from metabolic processes limit the acceptable structures of the protecting agents.

For certain products (*e.g.*, rubber products intended for children toys, dolls, etc., rubber goods coming in contact with food or beverages and packages with a given service life where specific requirements are imosed for sanitary and/or ecological purposes), some vitamins and natural products with flavonoid structure were introduced to the family of antioxidants with possible technical applications.[1,2]

The α-tocopherol is a suitable protecting agent encountered in natural products as well as in medical/pharmaceutical practice. Studies conducted during the last decades[3-5] have confirmed that the antioxidant activity of α-tocopherol is the result of its ability to capture alkylperoxy radicals, quite similar to the behaviour of commercial chain breaking antioxidants. Thus, vitamin E (α-tocopherol) introduced into polypropylene has demonstrated a higher efficiency in comparison with the phenolic antioxidants (*e.g.*, Irganox 1010) even at much lower dosages.[4] Based on these data, some authors have proposed[5] a co-operative mechanism in the presence of phenolic and phosphitic antioxidants. Previous investigations have found similar products to α-tocopherol during processing of polyphenols at 180 ºC.[6,7]

Vitamin E was also utilized in stabilizing the low density polyethylene (LDPE) used for packaging in the food industry; LDPE protected by addition of vitamin E has demonstrated higher durability performance in comparison with phenolic antioxidants even at lower concentrations (0.025–0.050 %); at higher concentrations (0.1–0.2 %) a photostabilization effect was observed.[8,9]

The interest in utilizing vitamins as protecting agents in rubbers started with ethylene-propylene elastomers. Thus, α- and δ-tocopherol and β-caroten (provitamin A) have been used in stabilization of EPM and EPDM (with 42% polypropylene and 3.5% ENB) in comparison with phenolic antioxidants BHT and 2246. Physical and physico-chemical tests accompanied by kinetic evaluation and evolution of gel content, all revealed that α-tocopherol is more efficient in comparison to δ-tocopherol and provitamin A.[10]

* Corresponding author: gheorghe.ivan@tgint.ro

Though vitamin C is well known for its antioxidant capability in biologic media[3] by having a high ability to capture free radicals of oxygen (*e.g.*, singlet oxygen) as well as to inactivate oxigenated free radicals like $RO_2^{\bullet}$ and $HO^{\bullet}$, so far it hasn't been used in practical applications involving compounds exposed to thermo-oxidative degradation due to its rapid modification of the structure accompanied by significant loss of antioxidant capability.[11] Even though this phenomenon is well known, some investigation on LDPE stabilization with vitamin C was conducted at 170–190 °C using the oxyluminescence technique.[12]

In our experimental programme, thermooxidative degradation was performed in the 100–160 °C temperature range and peroxidation was conducted using the couple luminol + $KO_2^{\bullet}$. The protective effect was evaluated by spectral measurements in the IR domain as well as with the chemiluminescence technique; for kinetic evaluation of the antioxidant activity, variation of the carbonyl band (1720 cm^{-1}) and time variation of chemiluminescence intensity have been used.

RESULTS AND DISCUSSION

Determination of antioxidant activity of vitamins was conducted by the chemiluminescence method using the following chemiluminescence systems luminol (LH) + H_2O_2, radiolized acridine + $KO_2^{\bullet}$, acridine + NaOH. The antioxidant activity was calculated by the relation

$$\%AA = \frac{I_0 - I_s}{I_0}.100$$

where: I_0 represents the maximum intensity of chemiluminescence for standard at time t = 5 s;

I_s maximum intensity of chemiluminescence for sam[ple at time t = 5 s.

The results (Table 1) show that vitamin C has the highest antioxidant activity, confirmed also by the lag period determined in the system LH + H_2O_2.

Table 1

Antioxidant activity of vitamins

Vitamins	AA (%)			Lag (s)
	Acridine + $KO_2^{\bullet}$	Acridine +NaOH	LH + H_2O_2	
A	57.4	43.6	81.1	35.0
C	98.6	81.8	92.3	75.0
E	31.6	43.7	75.9	40.0

After the thermo-oxidative ageing in the temperature range 90–120 °C, the vitamins antioxidant activity decreased and the loss of activity was more significant for vitamin C (Table 2). The activation energy (E_a) was calculated based on chemiluminescence measurements (after exposure at different temperatures, using the reaction rate constant for each temperature) following the well known procedure.[13] It is worth mentioning as well that at 120°C, the antioxidant activity of vitamins A and E increases approximately by 10–15% compared to their exposure to 100°C, probably due to formation of dimeric/trimeric and quinonic structures with properties reminding the behaviour of antioxidants with the structure of hindered phenols.[2]

Table 2

Antioxidant activity of vitamins after termo-oxidation

Vitamins	AA (%) at 100 °C	AA (%) at 120° C	E_a (kJ/mol)
A	30.8	45.6	3.61
C	57.3	22.8	27,65
E	47.1	59.3	9.78

The chemiluminescence results were confirmed by spectral investigation in IR and UV-Vis-NIR domains indicating major modifications of the initial structure only for vitamin C. The process begins by modifications of the OH and C=C groups revealed by a significant decrease of the appropriate absorption bands νOH (3500–3200 cm^{-1}), δOH (1250–1000 cm^{-1}), and νC=C (3010 cm^{-1}), followed by appearance of conjugated carbonyl structures clearly confirmed by the 386 nm band in UV-Vis spectrum, and accompanied by a significant colour intensification (Figs. 1 and 2; Table 3). The CIE – Lab programme (DIN 6174, CIE – Lab, 1976) was used for computing L*C*H* colour parameters.

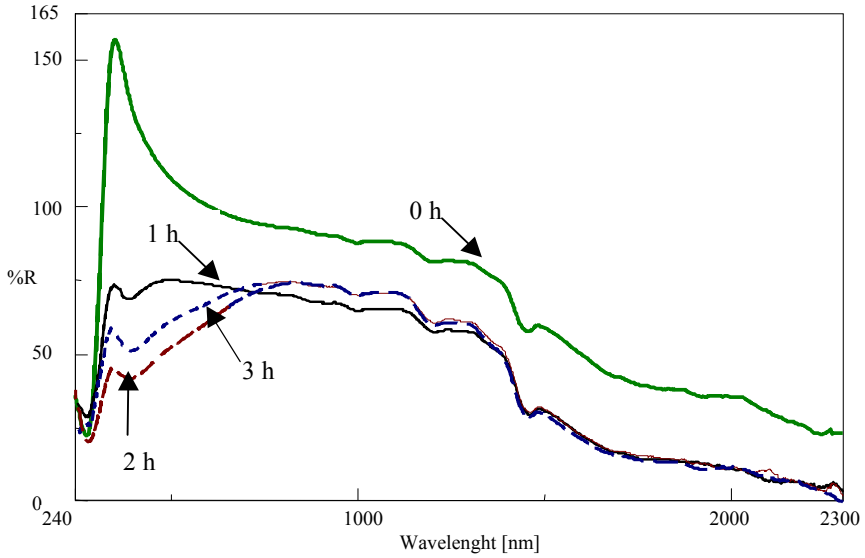

Fig. 1 – UV-Vis-NIR spectra of vitamin C before and after thermo-oxidative degradation at 120°C.

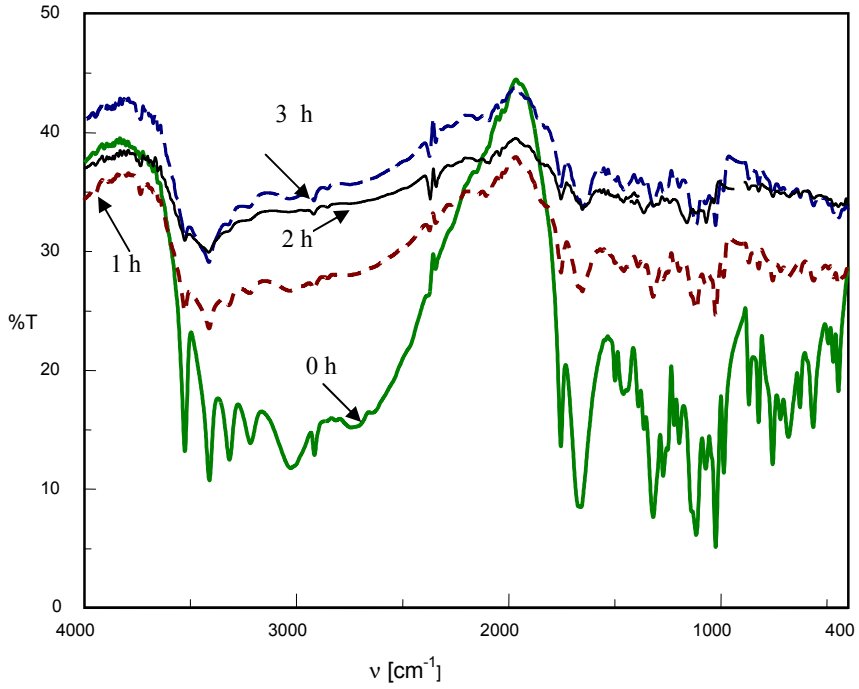

Fig. 2 – IR spectra of vitamin C before and after the termo-oxidative degradation at 120 °C.

Table 3

Variation of colour of vitamin C according to temperature

Time / temperature	L^*	a^*	b^*	C^*	H^0
Initial	101.49	0.19	- 8.04	8.05	- 88.65
2 h × 100° C	93.89	- 0.86	- 5.48	5.54	- 98.97
4 h × 100° C	88.18	- 0.66	- 6.55	6.59	- 95.77
6 h × 100° C	88.72	- 0.91	- 5.25	5.30	- 99.90
1 h × 120° C	89.06	- 1.15	0.28	1.18	166.27
2 h × 120° C	84.51	0.65	7.19	7.22	84.80
3 h × 120° C	80.51	1.80	9.86	10.03	79.65

L^*, a^*, b^* – trichromatic parameters, C^* – chromaticity, H – nuance angle

Based on the information obtained regarding the antioxidant performance, only vitamins E and A were tested in elastomer protection; the same vitamins were also tested in the system LH: $KO^{\bullet}_2$ (4:1) . The test results (Fig. 3) revealed that the vitamins antioxidant capability, even at lower concentrations, is higher in comparison with phenolic antioxidant BHT.

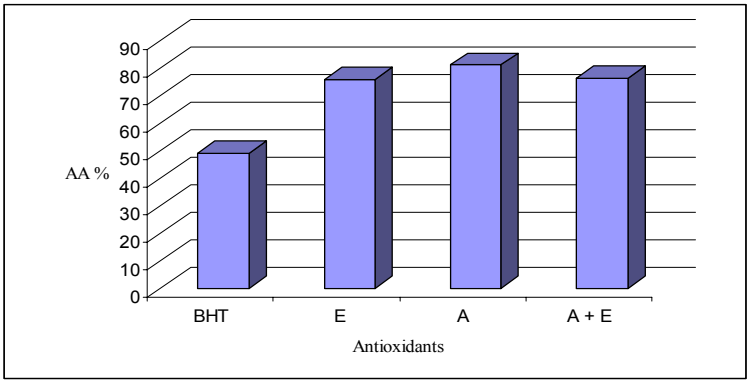

Fig. 3 – Antioxidant activity (AA %) of the investigated antioxidants.

The comparison of the elastomers protected by vitamins in the presence of the couple LH + $KO^{\bullet}_2$ is presented in Table 4. For all investigated systems, the superior protective capability of vitamins can be noticed.

The thermo-oxidation behaviour of the elastomer + antioxidant systems was also monitored by IR spectroscopy and the results are presented in Table 5. The evolution of the absorption band at 1720 cm^{-1} (νCO) was used to evaluate the main characteristics of the process: induction period, reaction rate constant and activation energy. The results of the IR measurements have been used for calculation of activation energy according to the known method.[14]

Table 4

Antioxidant activity of vitamins determined by chemiluminescence

Elastomer + antioxidants	Antioxidant activity, AA (%)	Elastomer + antioxidants	Antioxidant activity, AA (%)
IR	82.8	SBR	84.5
IR + A	91.8	SBR + A	88.2
IR + E	98.4	SBR + E	91.2
IR + A + E	96.2	SBR + A + E	97.6
IR + BHT	51.2	SBR + BHT	54.0
BR	89.9	IIR	93.5
BR + A	97.0	IIR + A	94.8
BR + E	98.9	IIR + E	95.9
BR+ A + E	97.9	IIR + A + E	94.9
BR + BHT	53.0	IIR + BHT	60.0

For all investigated systems, regardless of the degree of unsaturation of the elastomers, the best protection is ensured by vitamin E and by the couple of vitamins E + A, in both circumstances:

- in the presence of the free radicals with short life of the luminol + $KO^{\bullet}_2$ system;
- in the presence of hydrocarbon and oxigenated free radicals $R^{\bullet}/RO^{\bullet}/RO^{\bullet}_2$ appearing during thermo-oxidative destruction of the elastomers.

Table 5

Characteristics of the thermo-oxidative process

Elastomer + antioxidants	Induction time (h) at		Activation energy (kJ/mol)
	100 °C	*150 °C*	
IR + A	2.0		108.4
IR + E	5.0		112.0
IR + A + E	4.5		113.0
IR + BHT	0.5		105.2
BR + A	2.7		125.2
BR + E	6.0		131.0
BR + A + E	8.0		133.2
BR + BHT	1.8		122.0
SBR + A	4.0		126.0
SBR + E	6.5		136.0
SBR + A + E	9.0		137.2
SBR + BHT	3.0		121.4
IIR + A		4.8	140.4
IIR + E		5.5	145.0
IIR + A + E		6.2	148.0
IIR + BHT		2.5	125.2

The low level of antioxidant capability of BHT in the elastomers included in our experiments could be due to pro-oxidant free radicals generated in the presence of KO^{*}_2; the support for such an assertion is presently not certain enough and this aspect is now under scrutiny.

EXPERIMENTAL

The following elastomers were used during the experiment: isoprene rubber (SKI 3, Russia, with 96% *cis*-1,4 units), butadiene rubber (SKD II, Russia, with 91% *cis*-1,4 units), styrene-butadiene rubber (SBR 1502, Romania, with 27% styrene content), and butyl rubber (BK 1652, Russia, with 2% isoprene content), all containing phenolic stabilizers. Commercial rubbers were purified by successive precipitation with methanol from benzene solutions in order to remove the residues of polymerization systems, the gel content and the added stabilizers.

Our experimental programme used natural antioxidants such as vitamins A and E (Merck, Germany) and synthetic antioxidant BHT (2,6-di-t-butyl-p-methylphenol, Sumitomo, Japan) as a reference. The dosage used was (p – mass parts): 100 p elastomer + 0.04 p vitamin E + 0.004 p vitamin A and 100 p elastomer + 1 p BHT for the chemiluminescence analysis and 100 p elastomer + 0.6 p vitamin E + 0.06 p vitamin A for IR analysis.

Thermal oxidation was carried out in an air-circulating oven (Caloris, Romania). Spectral measurements for the IR domain were taken with a FT-IR 620 equipment (Jasco, Japan). The modification of the vitamins antioxidant activity in reaction with radiolised acridine and H_2O_2, $KO^{\bullet}_2$ in the presence of luminol was investigated by chemiluminescence using a chemiluminometer type TD 20/20 (Turner Design, USA).

CONCLUSION

Vitamin A (β-carotene) and vitamin E (α-tocopherol), as well as their couple, are effective protecting agents against thermo-oxidative degradation of elastomers with various degrees of unsaturation, exceeding the protective capability of the classic synthetic antioxidant BHT.

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