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Controlled Degradation of Polymeric Composites Stabilized with Natural Antioxidants

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The aim of our studies is to assess the effect of tert-butylhydroquinone, α-naphthoflavone and lawsone on the stabilization of ethylene-propylene copolymer. Owing to the presence of hydroxyl groups, their number and position in a molecule of naphthoquinone derivatives, these compounds show various anti-oxidizing properties. In a first step we investigated the antioxidant properties of selected compounds.

The examination of the electrochemical properties of compounds oxidation on a platinum electrode was performed in order to assess the mechanism of electrode reactions of these compounds to select the most effective antioxidant. The optimized structures of the molecules and the frontier molecular orbital energies of the Highest Occupied Molecular Orbital (HOMO) for each compound calculated. Fourier transform *infrared* (*FTIR*) spectroscopy was *used* to study structural characterization of components. Thermal stability of their was evaluated by using thermogravimetry analysis (TGA). The antioxidants tested included *tert*-butylhydroquinone and lawsone that were incorporated into ethylene-propylene copolymer. EPM vulcanizates were then subjected to UV(A) and thermal ageing. Based on the changes in deformation energy (K coefficient), OIT (oxygen induction time), the anti-oxidative efficiency of compounds in the protection of polymers against photodegradation and thermooxidation was determined.

Keywords: Antioxidants; Naphthoquinone derivatives; Cyclic voltammetry; Degradation of polymers; Ageing,

1. INTRODUCTION

Polymeric materials are widely used in various branches of industry and the demand for them is continually growing. Currently, they come second after steel among the most important groups of materials. It is considered that in the 21st century their amount used in industrial branches can amount to 50% of all materials [1-4]. Therefore their long-term stability is of paramount importance. During long-term use polymers continually interact with the environment. Their structure and properties change with time, while the range of these changes depends of both the original polymer structure and environment [5-7]. In other words polymeric materials undergo ageing. There are two types of ageing that lead to changes in the chemical and physical properties of polymers. The deterioration in polymer properties is due to the process of oxidation and hence most stabilizers consist of antioxidants. More detailed terms such as “antiozonant”, “UV-absorber” or “metallic deactivator” relate to the counteraction against various, often superimposing oxidation mechanisms [8].

Almost all synthetic polymers require stabilization. The incorporation of stabilizers into polymeric materials facilitates their processing, but first of all it protects them against degradation processes during the storage, transport and use of final products [9-10]. In the past years, there have been no significant changes in polymer stabilization methods [11]. Most investigations have focused on structural improvements to increase the effectiveness of the Hindered Amine Light Stabilizers (HALS)-type anti-oxidants used [12-13]. From the available literature on stabilization of polymer materials it shows that stabilizers should be sought such as oxygen. Substituted phenols [14-16]. The activity of anti-aging substances in the polymer depends on its ability to decompose hydroperoxide and peroxy radicals, and their compatibility with polymer [17].

Currently, commercial antioxidants are used as additives for polymers are hindered amines, substituted phenols, phosphorus compounds. Most of these are carcinogenic [18]. Undoubtedly, used natural derivatives for stabilization of polymers are interesting resolution. Naphthoquinone is a class of organic compounds derived from naphthalene [19]. We have been interested in the chemistry of naphthoquinones due to their interesting structure and antioxidant activities [20, 21]. Naphthoquinones, considered to be potential antifungal drugs, are produced by many plants that belong to the Caryophyllales families [22]. 1,4-Naphthoquinones in particular are widely distributed phenolic compounds in nature and they are reported to exhibit diverse pharmacological properties including antibacterial, antifungal, antiviral, anti-inflammatory and antipyretic effects, even including anticancer activity [23, 24].

Electrochemical techniques have been shown to be excellent procedures for the sensitive determination of organic molecules, including drugs and related molecules in pharmaceutical dosage forms and biological fluids [25-29]. As a rule, many active compounds in dosage forms, in contrast to excipients, can be readily oxidized or reduced. The advance in experimental electrochemical techniques in the field of analysis of organic molecules is due to their simplicity, low cost, and relatively short analysis time compared with the other techniques. Electrochemical methods are used to study the electrochemical properties, evaluation of antioxidant capacity and the mechanism of oxidation of organic compounds, including flavonoids [30-34]. Half-wave potential ($E_{1/2}$) is a useful parameter providing information about the antioxidant activity of the test compound [35]. It has been shown that flavonoids with less positive oxidation potential: higher susceptibility is electrochemical oxidation, possess higher radical scavenging activity [36, 37]. We described in this paper was determination tert-butylhydroquinone, α-naphthoflavone and lawsone electrochemical behavior in the process of its electrooxidation at platinum electrode in non-aqueous media. Analytical tests confirmed that the three tested compounds show high antioxidant activity. Furthermore, the application of compounds to polymeric materials (ethylene-propylene copolymer) was investigated. Aim of the study was to use environmentally friendly investigated compounds as anti-aging substance for polymers.

2. EXPERIMENTAL

2.1. Chemicals

The object of study was tert-butylhydroquinone (2-(1,1-dimethylethyl)-1,4-benzenediol, $C_{10}H_{14}O_2$), α-naphthoflavone (2-phenylbenzo[h]chromen-4-one, $C_{19}H_{12}O_2$), lawsone (2-hydroxy-1,4-naphthoquinone, $C_{10}H_6O_3$). It was obtained from Sigma-Aldrich GmbH.

These compounds were supplied by Sigma-Aldrich GmbH. Solutions were prepared with of the following compounds:

1. Acetonitrile (CH_3CN) pure p.a. from POCH Gliwice, Poland,
2. Tetrabutylammonium perchlorate ($(C_4H_9)_4NClO_4$) from Fluka was used a supporting electrolyte.

The compositions of the prepared mixes were as follows: The ethylene-propylene rubber (EPM, Dutral CO- 054) used in study was from Mentedison Ferrara – Italy (100 phr). Dicumyl peroxide, DCP (from Fluka) was used as cross-linking agent (2 phr), 1,3,5-Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (from Sigma-Aldrich Chemie GmbH) as co-agent of cross-linking (0,5 phr) and hexadecyltrimethylammonium bromide, CTBA (from Sigma-Aldrich Chemie GmbH) as dispersing agent (2 phr). Areosil 380 silica (from Degussa) was used as filler (30 phr). The anti-ageing substances used included the following compounds: tert-butylhydroquinone, lawsone (1phr) and 1,4-naphthoquinone (1phr).

2.2. Methods of Experimental Investigation

In order to assess the mechanism and kinetics of electrochemical oxidation of the compounds under investigation, the cyclic voltammetry (CV) and differential pulse (DPV) methods were used, employing an *Autolab* analytical unit *(Ecochemie, Holland).* A three-electrode system was used for the measurements with platinum test and auxiliary electrodes. The potential of the tested electrode was measured in relation to a ferrocene reference electrode *(Fc^+/Fc)* whose standard potential is defined as zero, independent of the solvent used. Prior to measurements, all the solutions were deoxidised with argon. During measurements an argon atmosphere was maintained over the solution. An effect of scan rate on the naphthoquinone derivatives electrooxidation in an non-aqueous medium was determined.

The quantum chemical calculations were performed using the AM1 method with HyperChem program packages. The molecular structures of compounds in gas phase were fully optimized by using ab-initio quantum chemical calculations at the restricted Hartree–Fock (RHF) level of theory.

FTIR spectra were tested in the range of 3000 – 700 cm^{-1} using an FTIR Nicolet 6700 FTIR (Thermo Scientific). The measurement parameters were as follows: 280 scans; resolution was set to 8

cm^{-1}; DTGS/KBr detector was employed. The FTIR spectrum of the compound was also recorded in the range of 3500 – 1000 cm^{-1}.

The thermogravimetric analysis (TGA) was using Mettler Toledo (Mettler-Toledo, Schwarzenbach, Switzerland). Samples with a total weight in the 7-10 mg range were placed into alumina crucibles and subjected to a temperature program used from 20 to 500 ºC at a heating rate of 10 ºC min^{-1} in an nitrogen atmosphere (flow rate of 50 mL min^{-1}).

The oxygen induction time (OIT) test was performed on a Mettler Toledo DSC instrument. Samples with a mass of 4 mg were heated from room temperature to the test temperature, 260 ºC, at a rate of 20 ºC/min under a nitrogen atmosphere. After 5 min at 260 ºC, the gas was switched from nitrogen to air at a flow rate of 60 ml/min. When all antioxidants are consumed, the sample starts to oxidise, producing a deviation in the baseline. The OIT was measured as the time between the switch to air flow and the intersection with a tangent from the maximum derivative after oxidation has started. Two analyses of each sample were performed to ensure the accuracy of the results.

Rubber blends were prepared by means of a laboratory mixing mill with rolls of the following dimensions: length L = 330 mm, diameter D = 140 mm. The speed of rotation of the front roll was V_p = 20 rpm, friction 1.1, the average temperature of rolls was about 40 ^{o}C.

The vulcanization of rubber blends was carried out with the use of steel vulcanization molds placed between the shelves of electrically heated hydraulic press. A teflon film was used as spacers preventing the adherence of blends to the press plates. Samples were vulcanized at a temperature of 160 ^{o}C, under a pressure of 15 MPa for 30 min.

The tensile strength of vulcanizates was tested according to standard PN-ISO 37:1998 by means of a ZWICK tester, model 1435, for dumbbell w-3.

Ageing characteristics were determined according to standard PN-82/C-04216. Samples were subjected to the action of air at elevated temperature (353 K) for 7 days in a dryer with thermo-circulation. UV ageing was performed by means of an UV 2000 apparatus from Atlas. The measurement lasted for 120 h and consisted of two alternately repeating segments with the following parameters: daily segment (radiation intensity 0.7 W/m^2, temperature 60 ºC, duration 8h), night segment (no UV radiation, temperature 50 ºC, duration 4 h). The ageing coefficient was calculated according to the relationship: $S= [TS'\times EB']/[TS\times EB]$, where TS – tensile strength, EB – elongation at break, TS’, EB’ – corresponding values after ageing.

3. RESULTS AND DISCUSSION

3.1. Electrochemical properties of naphthoquinone derivatives

Cyclic voltammetry is frequently used for the characterization of electroactive systems. The antioxidant properties of tert-butylhydroquinone, α-naphthoflavone and lawsone (Fig.1) were tested by electroanalytical methods were studied by cyclic voltammetry.

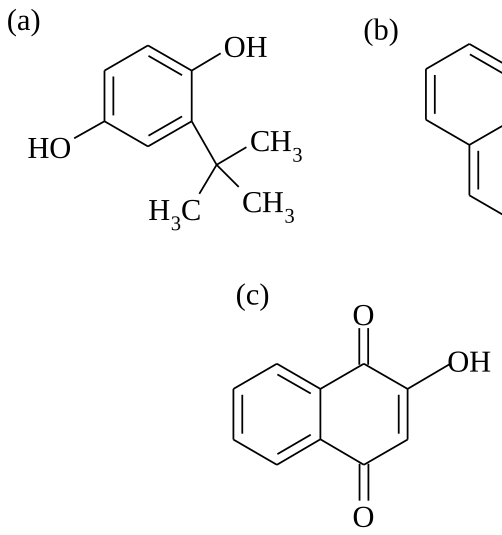


Figure 1. Structure of compounds: (a) – tert-butylhydroquinone, (b) – *α*-naphthoflavone, (c) – lawsone.

The dependence of current on the electrode potential provides information about the electrochemical reactions proceeding on the electrode tested. Exemplary cyclic voltammograms of compounds electrooxidation are presented in Figure 2.

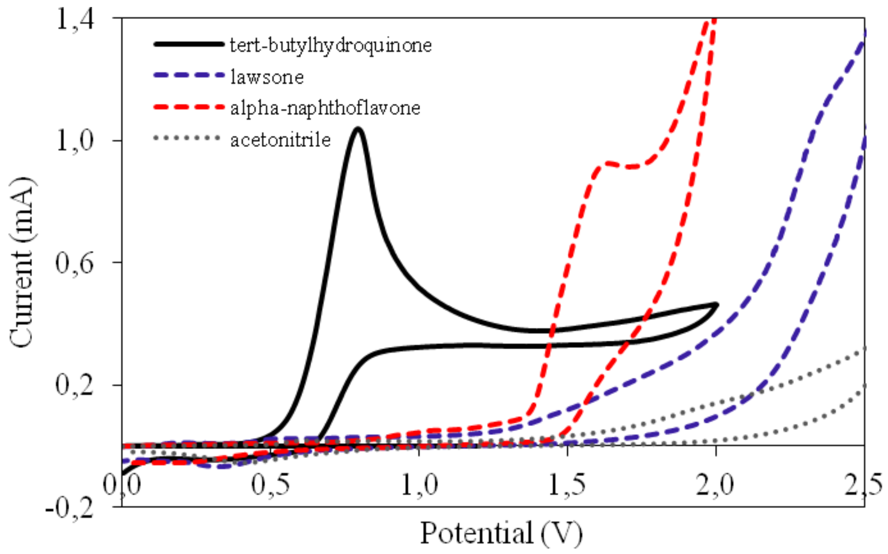


Figure 2. Cyclic voltammograms of tert-butylhydroquinone, α-naphthoflavone and lawsone oxidation at Pt electrode; c = 2.0 mM in 0.1 M $(C_4H_9)_4NClO_4$ in acetonitrile, v = 0.1 V s^{-1}.

From the relationship shown in Figure 2 it follows that test compounds are irreversibly oxidized in at least one electrode stage within the range of lower potentials than the electrolyte decomposition potential.

Within the potential range tested, in which one can observe the electro-oxidant peak of the compounds on the platinum electrode, the basic electrolyte, beside charging the double electric layer, does not show any peaks; it is only characterized by a low capacity current. Peak potential (E_{pa}), half-peak potential ($E_{pa/2}$) and half-wave potential ($E_{1/2}$) for the first step of naphthoquinone derivatives electrooxidation was determined from recorded voltammograms.

Useful information involving a electrochemical mechanism generally can be acquired from the relationship between peak and scan rate [38-40]. Therefore the voltammetric behaviour of compounds at different scan rates was studied using cyclic voltammetry. The linear dependence of ln i_p vs. ln v indicates that the investigated compounds electrooxidation reactions there are diffusion controlled.

If the electrode process proceeds under linear diffusion condition, then anodic transition coefficient (βn_β) and heterogeneous rate constant (k_{bh}) for the electrode process can be calculated from the following equations [41, 42]:

$$\beta n_\beta = \frac{1.857RT}{F\left(E_{pa} - E_{pa/2}\right)} \qquad (1)$$

$$E_{pa} = -1.14\frac{RT}{\beta n_\beta F} - \frac{RT}{\beta n_\beta F}\ln\frac{k_{bh}^0}{D_{red}^{1/2}} + \frac{RT}{2\beta n_\beta F}\ln \beta n_\beta v \qquad (2)$$

$$k_{bh} = k_{bh}^0 \exp\left(\frac{-\beta n_\beta FE}{RT}\right) \qquad (3)$$

where: D_{red} – diffusion coefficient of reduced form, $cm^2\ s^{-1}$,

v – scan rate, $V\ s^{-1}$,

F – Faraday constant (96,487 C mol^{-1}),

R – universal gas constant (8.314 J K^{-1} mol^{-1}),

T – Kelvin temperature (K),

k_{bh}^0 – heterogeneous rate constant at a peak potential vs. SCE (cm s^{-1}).

Heterogeneous rate constant (k_{bh}) determined for a specified potential E characterizes transfer rate of electron through electrode-solution interface. The electron transition coefficient characterizes symmetry of the activated barrier of an electrode reaction (Table 1).

The diffusion coefficient was estimated according to Hayduk and Laudie's equation [43]:

$$D = \frac{13.26 \times 10^{-5}}{\mu^{1.4}\, V_o^{0.589}} \qquad (5)$$

where μ is viscosity of a solvent (centipoises) and V_o is molar volume ($cm^3\ g^{-1}\ mole^{-1}$).

The parameters determined (E_p and $E_{1/2}$) are confirmed by quantum-chemical calculations. The energies of the frontier molecular orbitals HOMO are important parameters of the molecular electronic structure, because are taking part in the chemical reaction. The molecule that has the lower HOMO energy has the weakest donating electron ability; otherwise, a higher HOMO energy implies that the molecule is a good electron donor. Energy of HOMO is useful diagnostic criterion for oxidation. It has been reported that negative value of HOMO energy (equal to ionization potential) is directly proportional to oxidation potential [44, 45]. The E_{HOMO} molecular orbital energies were calculated using the AM1 method in HyperChem program (Table 1). The observed peak potentials should be linearly dependent on the energy of the HOMO [46, 47]. The HOMO orbitals of all investigated molecules are π like orbital and they are mainly localized on the phenyl groups and just partly distributed over the ring. The HOMO orbitals of the investigated compounds are shown pictorially in Figure 3.

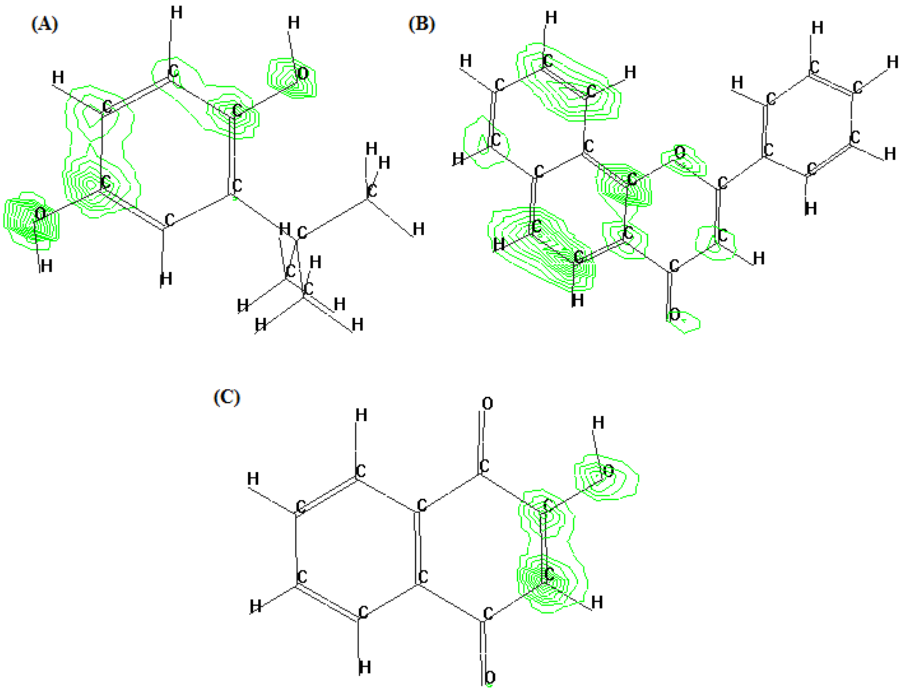
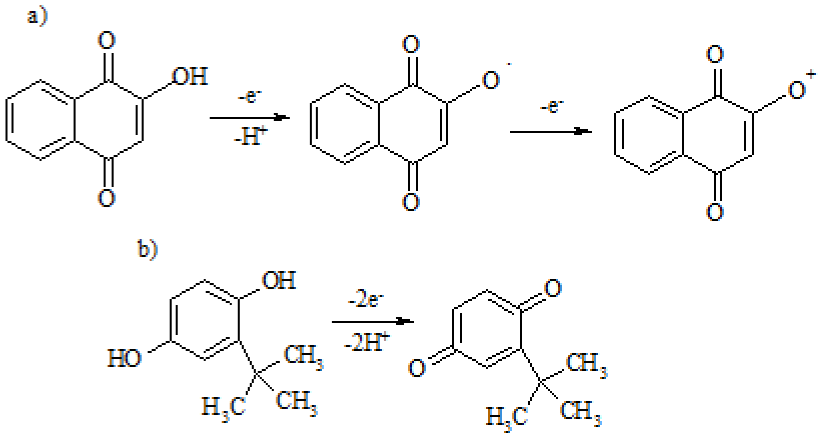


Figure 3. The HOMO molecular orbitals of the compounds: (A) – tert-butylhydroquinone, (B) – α–naphthoflavone, (C) – lawsone.

Table 1. Cyclic voltammetry and molecular orbital parameters for the compounds studied.

No.	Compound	E_p (V)	$E_{1/2}$ (V)	βn_β	D ($cm^2 s^{-1}$)	k_{bh} ($cm s^{-1}$)	E_{HOMO} (eV)
1	tert-butylhydroquinone	0.78	0.75	0.46	$6.86\cdot10^{-6}$	$4.22\cdot10^{-4}$	-8.764
2	α-naphthoflavone	1.62	1.55	0.28	$5.53\cdot10^{-6}$	$3.67\cdot10^{-4}$	-9.126
3	lawsone	2.36	2.31	0.36	$7.49\cdot10^{-6}$	$3.69\cdot10^{-4}$	-10.188

From the results given in Table 1 it follows that tert-butylhydroquinone is oxidized most easily and its $E_{1/2}$ is 0.75 V, while α-naphthoflavone and lawsone are oxidized with the greatest difficulty with $E_{1/2}$ equal 1.55 and 2.31 V, respectively. Tert-butylhydroquinone and α-naphthoflavone show the best anti-oxidizing properties within the potential range which was investigated. This is confirmed by the calculated E_{HOMO}, and totalled for tert-butylhydroquinone and α-naphthoflavone -8.764 and -9.126 eV, respectively, for lawsone -10.188 eV. The test compounds exhibit good antioxidant properties. On the basis of studies and literature data proposed mechanism anodic oxidation lawsone [48] and tert-butylhydroquinone (scheme 1).



Scheme 1. Proposed electrooxidation mechanism of a) lawsone and b) tert-butylhydroquinone.

One-electron electrooxidation lawsone takes place in two stages. In a first reaction step, the electrode is formed naphoxylene radical, in the second stage is formed naphtoxylene cation. Further electrooxidation may lead to a 1,2-naphthoquinone derivatives. In a parallel reaction of the naphthyloxy cations (or radicals) can couple producing polymeric materials. On the basis of studies it can be concluded that the tert-butylhydroquinone and naphthoquinone derivatives tested have high antioxidant properties. For this reason they may influence the improvement in the stabilization of polymeric materials.

3.2. FTIR (ATR) and thermogravimetry (TGA) analysis of investigated compounds

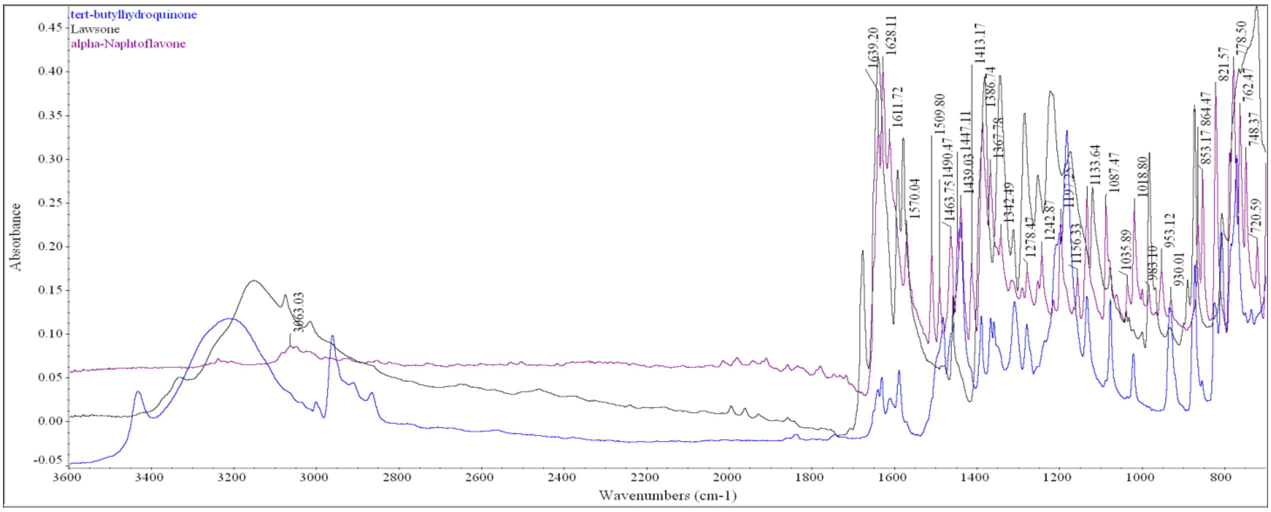


Figure 4. FTIR spectrum of tert-butylhydroquinone, α–naphthoflavone and lawsone.

Figure 4 is a typical FTIR spectrum of an tert-butylhydroquinone, α–naphthoflavone, lawsone. FTIR spectroscopy is a excellent tool of the structural analysis of antioxidants. FTIR spectrum of lawsone shows the band of phenolic O–H stretch between 3374 and 3523 cm^{-1}. The aromatic C=C stretching band is observed at 1424 cm^{-1}.The C=O stretching band is observed at 1592 and 1647 cm^{-1}. On the IR spectrum of *tert*-butylhydroquinone are present peaks at 3445 and 3279 cm^{-1} for -OH bonded with phenol. Band near 2963 cm^{-1} is assigned as unsaturated =CH. 1589, 1484 and 1442 cm^{-1} are characteristic for phenyl ring stretching and –C–OH. 808, 771 and 692 cm^{-1} band we reported for out of plane –CH and ring. The most intensive peak is C=O stretching and is observed at 1646 cm^{-1} in FTIR spectrum of α-naphtoflavone. Fundamental C=O bending mode was noticed at 606 cm^{-1}. The CC ring stretching vibrations was assigned to 1606 cm^{-1} for the flavone [49-50].

On the basis TGA was determined the thermal stability of the tested natural compounds. The comparison of the TGA curve for lawsone, *tert*-butylhydroquinone and *α*-naphtoflavone in air atmosphere, reveals that the substances show different thermal behaviors (Figure 5). The TG isothermal profile for *tert*-butylhydroquinone and *α*-naphtoflavone showed that this flavonoid presents one decomposition step, but the lawsone presented two decomposition stages as determined by TG analysis. The most thermally resistant is naphtoflavone, for them we noted t_{02} at 292 °C and t_{50} at 355 °C. Thermal decomposition of *tert*-butylhydroquinone and lawsone presented 2% weight loss at 189 and 187 °C. 50% weight loss of lawsone is noticed at 500 °C. Evaluation of thermal stability is very important for applications selected substances in polymers. Such additives must be stable in the temperature range of material processing.

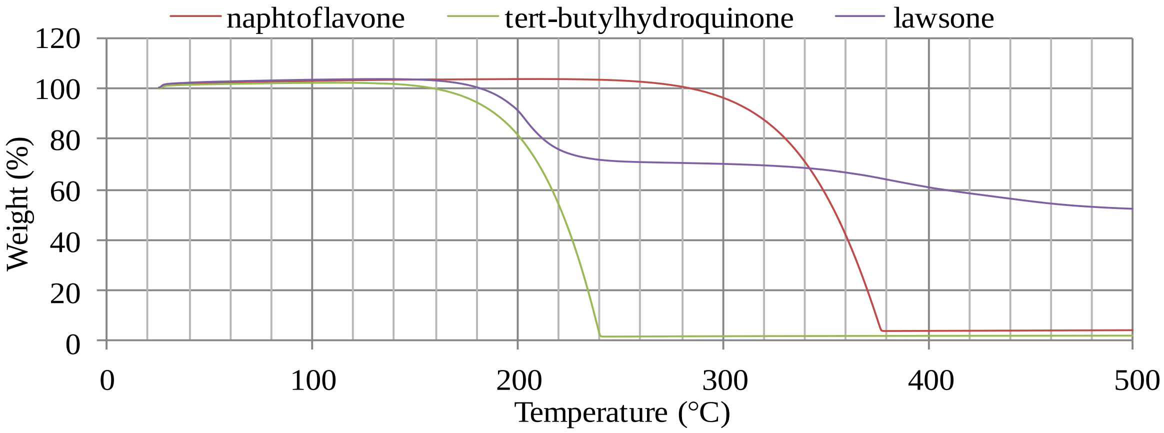


Figure 5. TGA curve of EPM vulcanizes containing natural antioxidants.

3.3. Effect of naphthoquinone derivatives on the stabilization of EPM copolymer

The naphthoquinone derivatives tested were used to improve the resistance of polymeric materials to ageing. Then the vulcanizates of ethylene-propylene copolymer containing natural ant-ageing substances were subjected to thermal and UV ageing followed by the determination of tensile strength. After UVA ageing an insignificant change in the mechanical properties of EPM and EPM/ tert-buthylnaphtoquinone was observed (Figure 6). Undoubtedly, the best protection against UV radiation is provided by lawsone, while *tert*-buthylnaphtoquinone constitutes quite a good protection against thermooxidation. Lawsone proved to be effective UV absorber to protect the composite against photodegradation (UVA). The addition of natural compounds significantly extended the oxidation induction time evaluated by using DSC method. OIT of EPM was 3.35 min and for the composite with lawson was longer than 18.15 min. tert-butylhydroquinone extended oxidation time of 11.85 min (Figure7).

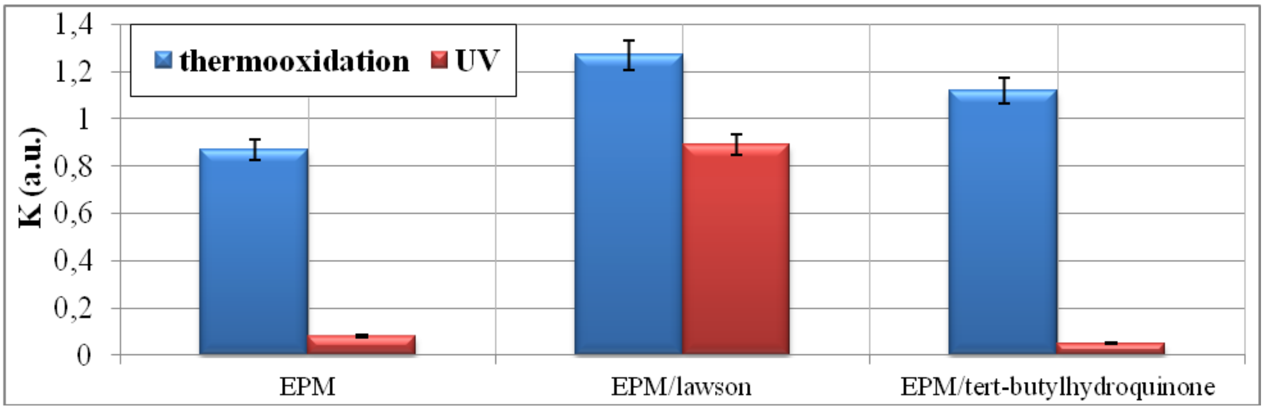


Figure 6. Ageing coefficient (K) of ethylene-propylene copolymer containing natural antioxidants.

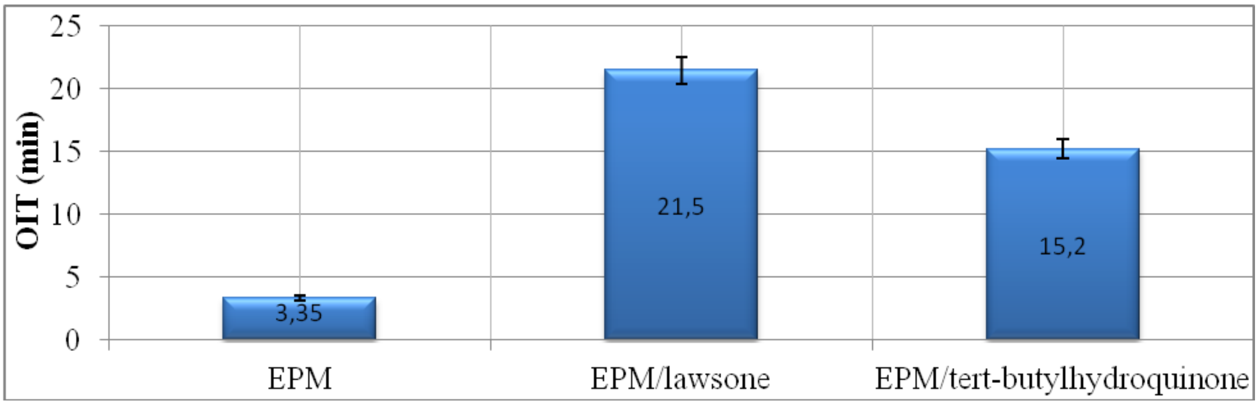


Figure 7. OIT (induction oxygen time and energy of oxidation) of EPM evaluated by using DSC method.

4. CONCLUSIONS

Tert-butylhydroquinone, α-naphthoflavone and lawsone improve the resistance of elastomers to ageing. The increase in the cross-link density under the influence of elevated temperature or UV radiation is the symptom of deterioration of usable properties. Be on the basis of electrochemical tests performed can be concluded that the best antioxidant properties owned tert-butylhydroquinone and α-naphthoflavone, and then lawsone. Based on the experimental results and quantum chemistry calculations, the electrooxidation mechanisms of tert-butylhydroquinone and lawsone were proposed. These compounds can be pro-ecological alternative antioxidants for polymers. Lawsone is a very good UV absorber and a thermal stabilizer. Tert-butylhydroquinone is best protected against the negative effects of a copolymer of thermooxidation. Both of the selected compounds are very attractive alternative to eliminate toxic additives from polymer technology.

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