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Influence of flavanone on the stabilization of ethylene-propylene elastomer

Summary — Antioxidating properties of flavanone were investigated with electroanalytical methods. Voltamperograms of flavanone oxidation on the Pt electrode reveal that along with increasing polarization rate the peak potential shifts slightly towards more positive potentials. The dependence of the peak current on the square root of the polarization rate is linear and the plot of the function passes through the origin of coordinates, which indicates no adsorption of the investigated substrate on the electrode and a diffusive control of the studied electrode reaction. To the ethylene-propylene elastomer (EPM) there were added 1.25 phr of flavanone and there was studied its impact on the stability of these blends subjected to thermal ageing and UV irradiation. The antioxidating efficiency of the investigated antioxidizer was established from changes in the deformation energy, crosslinking density and color of the EPM vulcanizates. Based on the results obtained, it was stated that flavanone performs its function well, providing good protection of the vulcanizates from oxidative processes.

Keywords: flavanone, antioxidants, elastomers, stability of elastomers.

WPŁYW FLAWANONU NA STABILNOŚĆ ELASTOMERU ETYLENOWO-PROPYLENOWEGO

Streszczenie — Metodami elektroanalitycznymi zbadano właściwości antyutleniające flawanonu (rys. 1—4, tabela 1). Woltamperogramy utleniania flawanonu na elektrodzie Pt wskazują, że wraz ze wzrostem szybkości polaryzacji potencjał piku przesuwa się nieznacznie w kierunku potencjałów bardziej dodatnich (rys. 2). Zależność prądu piku od pierwiastka z szybkości polaryzacji jest liniowa i przechodzi przez początek układu współrzędnych, co wskazuje na brak adsorpcji badanego substratu na elektrodzie i dyfuzyjną kontrolę badanej reakcji elektrodowej (rys. 3). Do elastomeru etylenowo-propylenowego (EPM) wprowadzano 1,25 phr flawanonu i badano jego wpływ na stabilność mieszanek EPM/flawanon poddawanych starzeniu termicznemu i działaniu promieniowania UV. Wydajność antyutleniającą badanego przeciwutleniacza sprawdzano określając zmiany energii deformacji, gęstości usieciowania oraz barwy wulkanizatów EPM. Na podstawie uzyskanych wyników stwierdzono, iż flawanon spełnia swoją funkcję, dobrze chroniąc wulkanizaty przed procesami oksydacyjnymi.

Słowa kluczowe: flawanon, przeciwutleniacze, elastomery, stabilność elastomerów.

Flavanoides are compounds naturally occurring in plants. Their presence has been confirmed in fruits, vegetables, leguminous plants as well as in numerous medical plants [1]. These compounds are often colored and play a significant role in plant physiology, showing the action of plant hormones and growth regulators, they are also energy carriers in the processes of photosynthesis of inhibitors and enzymatic precursors. Many flavanone containing plants are used in prophylaxis and therapy of various chronic diseases.

The basic structure of flavonoide molecules consists of two benzene rings (A and B), between which there is a heterocyclic ring of pyran or pyrone (C). The large variety of flavonoids stems from the fact that carbon atoms in A, B and C rings can undergo hydroxylation, methoxylation or glycosidation by means of mono- or oligosaccharides as well as acylation in various positions. Flavonoids show antioxidizing properties due to the presence of hydroxyl groups in their molecules [2]. The antioxidizing capability of these compounds depends on the number and position of hydroxyl groups [3].

Among flavonoids are flavonones that play a very important role. The basic flavonone skeleton is hydrogenated in relation to flavanone, *i.e.* it has no double bond between C_2 and C_3. The heterocyclic ring of flavanones (2,3-dihydro-2-phenylchromen-4-one) easily opens to convert them into chalcones (1,3-diphenyl-2-propen-1-one) according to equation [4, 5]:

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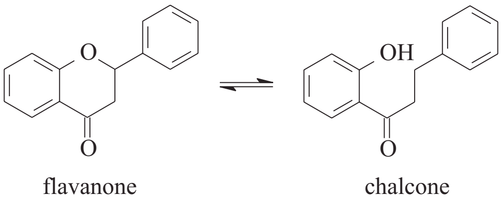


(1)

The electrochemical investigations of reduction and oxidation can be helpful in understanding how these compounds are metabolized by living organisms. It is also important to know the mechanism of these reactions in view of the identification of intermediate products that can be regarded as a significant aspect of these processes, especially their practical application [6].

Thanks to the development of electrochemical methods for the investigation of the mechanism of processes taking place at the electrode/solution interface, it became also possible to separate many processes into several subsequent stages. One can carry out electrochemical complex conversions connected with the addition or elimination of functional groups including the carbon skeleton reconstruction or the formation of heterocyclic systems [7].

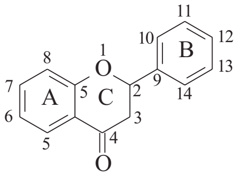
The stabilization and degradation of polymers continue to be a very important issue of the present industry [8]. The degradation of polymeric materials can take place under the influence of temperature (thermal degradation), radiation (photodegradation), mechanical stresses (mechanical degradation) or due to the action of microorganisms (biodegradation) [9]. The oxidation process of elastomers results in color change, luster loss, surface corrosion, deterioration in mechanical properties such as tensile strength and elongation at break [10—12]. From the available literature on polymer stabilization it follows that one should seek oxidative stabilizers such as substituted phenols [13]. Undoubtedly, flavanones belong to this group. The activity of an anti-ageing substance in a polymer depends on its scavenge to decompose peroxide- and hydroperoxide radicals as well as on their compatibility with the polymer [14]. At present commercial antioxidants for polymers include spherically masked amines, substituted phenols and phosphoric compounds. Most of them are carcinogenic compounds [15]. Therefore the derivatives of flavonoids seem to be an ecological alternative to the present stabilizers used in polymer processing.

The aim of this study was to investigate the antioxidizing capability of flavanone and to assess its effect on the stabilization of elastomers.

EXPERIMENTAL

Materials

Flavanone (2,3-dihydro-2-phenylchromen-4-one), which structure is presented as formula (I), was supplied by Sigma Aldrich Chemie GmbH.



(I)

As a supporting electrolyte solution of tetrabutylammonium perchlorate [$(C_4H_9)_4NClO_4$) from Fluka] in acetonitrile (CH_3CN, pure p.a. from POCh Gliwice, Poland) was used.

The ethylene-propylene elastomer (EPM, trade name Dutral CO-054) was delivered from Mentedison Ferrara (Italy). Dicumyl peroxide (DCP) from Fluka and 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT) from Sigma Aldrich Chemie GmbH were used as crosslinking agents.

Hexadecyltrimethylammonium bromide (CTAB) supplied by Sigma Aldrich Chemie GmbH was applied as a dispersing agent. Aerosil 380 silica from Degussa was used as a filler.

Preparation of elastomer blends

Two elastomer blends were prepared. EPM rubber was mixed with 2 phr of CTAB and a plasticized for 4 min. Next 30 phr of Aerosil 380 silica was added and to one of the blends additionally 1.25 phr of flavanone (antioxidant). Finally 2 phr of DCP together with 0.50 phr of TTT as a crosslinking agent and co-agent, respectively. All components were mixed at 40 °C for 10 min using a laboratory mixing mill with rolls of the following dimensions: length L = 330 mm, diameter D = 140 mm. The rotation speed of the front roll was V_p = 20 rpm, friction 1.1, the average temperature of rolls was about 40 °C.

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

Methods of testing

In order to assess the mechanism and kinetics of electrochemical oxidation of the compounds under investigation, the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods were used, employing an Autolab analytical unit (EcoChemie, The Netherlands). A three-electrode system was used for the measurements with platinum test and auxiliary electrodes. The potential of the tested electrode was measured versus a ferricinium/ferrocene reference electrode (Fc^+/Fc) which standard potential is defined as zero, independent of the solvent used. In our studies as a supporting electrolyte for flavanone 0.1 M solution of $(C_4H_9)_4NClO_4$ in CH_3CN was applied. Prior to measurements, all the solutions were deoxidised with argon. The measurements were carried out under argon atmosphere. The effect of polarisation rate on the electrooxidation of flavanone in an anhydrous medium was assessed.

The density of nodes in the spatial lattice of vulcanizates was determined with the method of equilibrium swelling according to standard PN/C-04236:1974. The vulcanizates were subjected to equilibrium swelling in toluene for 48 h at room temperature. The swollen samples were then weighed on a torsion balance and dried at the temperature of 60 °C to a constant weight and after 48 h they were reweighed. The crosslinking density (ν) was determined on the basis of Flory-Rehner's equation [16]:

$$\nu = -\frac{1}{V_o} \cdot \frac{\ln(1-V_r) + V_r + \mu V_r^2}{\left(V_r^{\frac{1}{3}} - \frac{V_r}{2}\right)} \tag{2}$$

where: V_r — *volume fraction of the elastomer in the swollen gel determined from equilibrium swelling (Q),* $\mu = 0.501 + 0.273\ V_r$ — *parameter elastomer-solvent interactions,* V_o — *molar volume of the solvent.*

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

Ageing characteristics were determined according to standard PN-C-04216:1982. Samples were subjected to the action of air at elevated temperature (353 K) for 7 days in a dryer with thermocirculation. UV ageing studies were performed with 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 °C, duration 8 h), night segment (no UV radiation, temperature 50 °C, duration 4 h). The ageing coefficient was calculated according to the relationship:

$$S = \frac{TS' \cdot Eb'}{TS \cdot Eb} \tag{3}$$

where: *TS, Eb — tensile strength and elongation at break before ageing process, respectively, TS', Eb' — corresponding values after ageing.*

The color of the vulcanizates obtained was measured using a CM-3600d spectrophotometer (Konica Minolta) with spectral range of 360—740 nm. Change of color dE^*ab was calculated from the equation:

$$\mathrm{d}E^*ab = \sqrt{\mathrm{d}L^{*2} + \mathrm{d}b^{*2}} + \mathrm{d}a^{*2} \tag{4}$$

where: *dL* — the brightness relationship between light and dark, da* — the relationship between green and red, db* — the relationship between blue and yellow, d — mean the difference of colors between the samples before and after ageing.*

RESULTS AND DISCUSSION

Electrochemical features of flavanone

The antioxidant activity of flavanone consists in inhibition of oxidation of polymers and other compounds, direct reaction with radicals (scavenging free radicals), dismutation of free radicals to compounds with much lower reactivity. Thus, it seems important to know electrochemical features of the investigated compound. The electrochemical behavior of flavanone was investigated using cyclic voltammetry.

The dependence of the current on the electrode potential characterizes the course of electrochemical reactions on the electrodes under investigation. Examples of the cyclic voltammogram and differential pulse voltammogram (that are characterized by a higher resolution) of flavanone electrooxidation are shown in Figure 1. The half-wave potential of the electrode reaction under investigation determined by cyclic voltammetry corresponds to the peak potential from pulse differential voltammetry

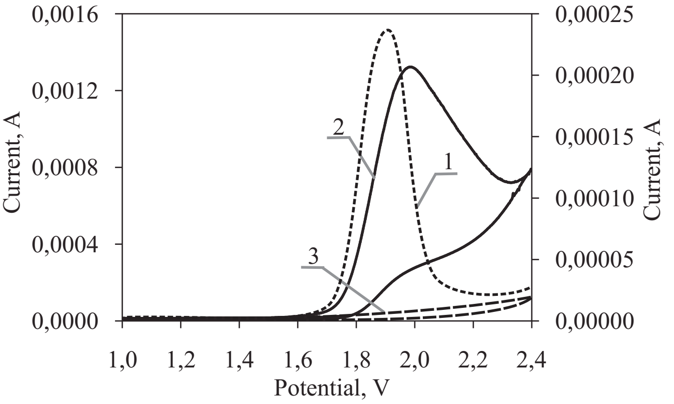


Fig. 1. Voltammograms of flavanone oxidation on the Pt electrode for 5 · 10^{-3} M flavanone solution in supporting electrolyte and polarization rate v = 0.01 V · s^{-1}: 1 — differential pulse curve (right axis), 2 — cyclic voltammogram (left axis); for comparison curve 3 — cyclic voltammogram of supporting electrolyte (left axis)

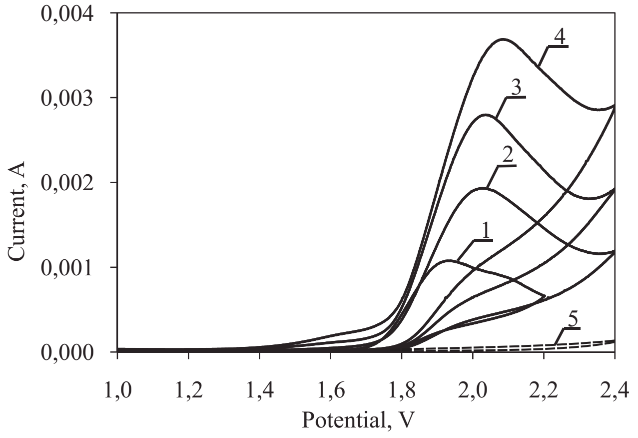


Fig. 2. Cyclic voltammograms of flavanone oxidation on the Pt electrode for 5 · 10^{-3} M flavanone solution in supporting electrolyte and for various polarization rates (v): 1 — 0.01 V · s^{-1}, 2 — 0.05 V · s^{-1}, 3 — 0.1 V · s^{-1}, 4 — 0.2 V · s^{-1}; for comparison curve 5 — supporting electrolyte (v = 0.01 V · s^{-1})

(Fig. 1, curves 1 and 2). From the measurements performed it follows that flavanone irreversibly oxidizes at least at the single electrode stage within the range of lower potentials than that of the electrolyte decomposition. Within the potential range under investigation where the electrooxidation peak of the compound on the Pt electrode is visible, the supporting electrolyte, besides charging the double electric layer, shows no peaks and is characterized by a small capacitive current (Fig. 1, curve 3).

The influence of the substrate concentration (*c*) and polarization rates (v) on the electrooxidation of flavanone was examined. Cyclic voltammograms of sample flavanone solution for various v values are shown in Fig. 2. The peak potential of electrooxidation (E_{pa}) shifted slightly towards more positive values with the increase of v. The dependencies of the peak current on the square root of the polarization rate for various concentrations of flavanone are presented in Figure 3. These dependencies are linear and the plots of the function pass through the origin of coordinates, which indicates a lack of adsorption of the substrate on the electrode and a diffusive control of the electrode reaction under investigation. This allows to analyze the currents generated due to the substrate diffusion on the electrode surface and to investigate the kinetics of this electrode reaction [17].

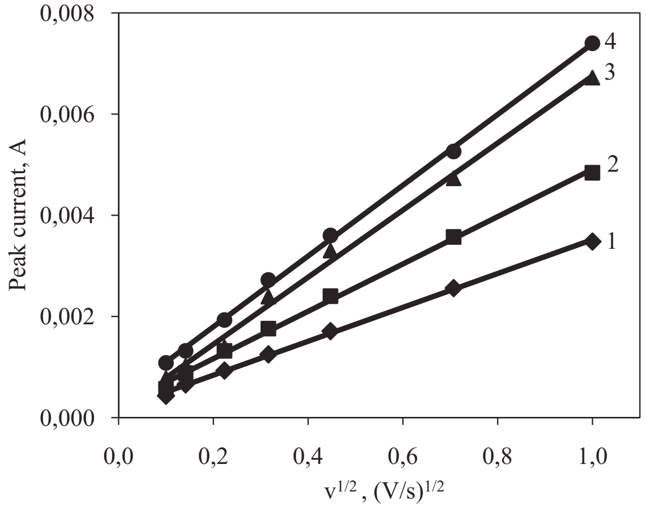


Fig. 3. Dependence of the peak current in flavanone oxidation at Pt on the square root of the polarization rate (v) for various flavanone solution concentrations (c): 1 — 2 · 10^{-3} M, 2 — 3 · 10^{-3} M, 3 — 4 · 10^{-3} M, 4 — 5 · 10^{-3} M

The cyclic voltammograms were used, as it was described in [18], to determine the peak potential (E_{pa}), half-peak potential ($E_{pa/2}$) and half-wave potential ($E_{1/2}$), as well as to calculate the anodic transfer coefficient (βn_β) and the heterogeneous rate constant (k_{bh}). Corresponding results for v = 0.01 V · s^{-1} and various flavanone concentrations are collected in Table 1. $E_{1/2}$ values were practically unchanged with increase of the antioxidant concentration amounting to about 1.91 V. While from Fig. 2 we can see that $E_{1/2}$ attain more and more positive values with increase of the polarization rate but for constant flavanone concentration. βn_β and k_{bh} values failed to change with the change in solution concentration and were equal to about 0.34, and 6.5 · 10^{-4} cm · s^{-1}, respectively.

Table 1. Values of peak potential (E_{pa}), half-peak potential ($E_{pa/2}$), anodic transfer coefficient (βn_β), half-wave potential ($E_{1/2}$), heterogeneous rate constant (k_{bh}) determined for the half-wave potential of the first electrode step in flavanone electrooxidation at platinum electrode for polarization rate v = 0.01 V · s^{-1}, and reagent diffusion coefficient $D = 2 \cdot 10^{-5}$ $cm^2 \cdot s^{-1}$

c mol/dm^3	E_{pa}, V	$E_{pa/2}$, V	βn_β	$E_{1/2}$, V	$k_{bh} \cdot 10^4$ cm · s^{-1}
$2 \cdot 10^{-3}$ M	1.99	1.86	0.31	1.92	6.49
$3 \cdot 10^{-3}$ M	1.96	1.84	0.34	1.89	6.29
$4 \cdot 10^{-3}$ M	1.98	1.86	0.34	1.91	6.61
$5 \cdot 10^{-3}$ M	1.94	1.82	0.34	1.90	6.52

The effect of flavanone concentration on the electrooxidation rate was assessed. The order of the electrode reaction was determined from the dependence of the logarithm of the oxidation current at a constant electrode potential on the logarithm of the flavanone concentration, shown in Figure 4.

The rate of the reaction under investigation depends on the flavanone concentration raised to an appropriate power. This power is an order of the electrode reaction under investigation and amounts to 1.0, being unchanged with changing electrode potential, which indicates a lack of change in the reaction mechanism within

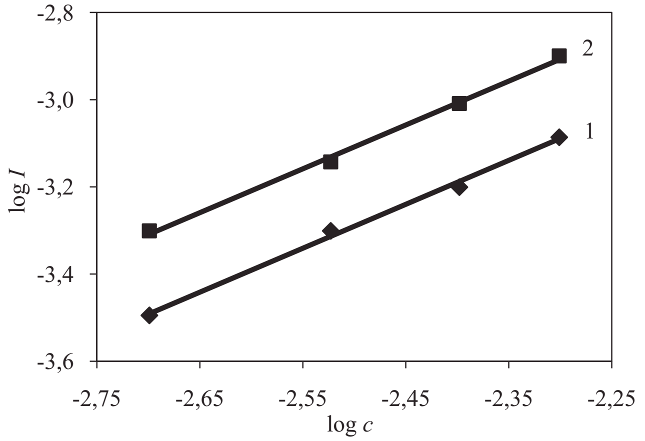


Fig. 4. Dependence of the logarithm of oxidation current (I) on the logarithm of flavanone concentration (c) for polarization rate v = 0.01 V · s^{-1} at a constant electrode potential (E) equal: 1 — 1.85 V, 2 — 1.90 V

this potential range. Results of the electrochemical investigation of flavanone prove its antioxidant activity.

Application of flavanone as an antioxidant in elastomers

The EPM vulcanizates without and with 1.25 phr additive of flavanone were subjected to thermal and UV ageing. Mechanical properties of these vulcanizates before and after ageing were investigated. Results are listed in Table 2.

Table 2. Mechanical properties of the EPM vulcanizates without and with flavanone subjected of thermal and UV ageing. *TS* — tensile strength, *Eb* — elongation at break, SE_{300} — stress at 300 % of elongation

Vulcanizates	Kind of degradation	SE_{300} MPa	*TS* MPa	*Eb*, %	*S*
EPM	before	3.94	22.8	736	—
	thermal	4.10	19.6	761	0.87
	UV	—	8.84	149	0.08
EPM/flavanone	before	3.90	22.50	702	—
	thermal	4.62	26.90	685	1.16
	UV	4.54	4.84	350	0.10

The addition of flavanone to the vulcanizate under investigation did not considerably affect its tensile strength (*TS*) and elongation at break (*Eb*). To the contrary, the flavanone containing vulcanizate subjected to thermal ageing was characterized by a higher *TS* than that before degradation, namely this value increased by 4.4 MPa (19.5 %), the value of stress at elongation of 300 % (SE_{300}) also increased by 0.72 MPa. In the case of EPM vulcanizate without antioxidant, one could observe decreased by 3.2 MPa (14 %) tensile strength and a slight increase in elongation at break up to 761 %. Comparing the coefficients of thermal ageing (*S*), it can be concluded that the EPM vulcanizate without the antioxidant undergoes thermal degradation to a larger extent ($S = 0.87$) than that protected with flavanone ($S = 1.16$).

After UV radiation ageing we observed a great decrease in *S* values to 0.08 and 0.10 for EPM vulcanizates without and with antioxidant, respectively. Considering the fact that the flavanone containing vulcanizate showed tensile strength decreased by 78.5 %, we can state that this antioxidant is not a good absorber of UV radiation. This fact indicates a very great change in the deformation energy under the influence of UV radiation.

Results of crosslinking density (*v*) investigations of prepared vulcanizates are presented in Table 3. Flavanone brings increase in *v* value of the vulcanizate: sample without flavanone shows $\nu = 1.11 \cdot 10^{-5}$ mol · cm^{-3}, while that containing flavanone $\nu = 4.00 \cdot 10^{-5}$ mol · cm^{-3}. The thermal ageing results in increasing of ν and decreasing equilibrium swelling (*Q*). In the case of the EPM vulcanizate, ν increases by 60 %, while that for the EPM/flavanone vulcanizate by 24 %. However a much greater increase in ν values was observed after the UV ageing, where the samples tested were affected by irradiation and temperature. The EPM vulcanizate after UV ageing was characterized by a very high value of $\nu = 22.18 \cdot 10^{-5}$ mol · cm^{-3}, while ν of the flavanone containing vulcanizate was increased as a result of irradiation by 75.5 % to $\nu = 7.02 \cdot 10^{-5}$ mol · cm^{-3}.

Table 3. Effect of flavanone on the equilibrium swelling (*Q*) and the crosslinking density (ν) of EPM vulcanizates (crosslinking density calculated on the basis of swelling in toluene)

Vulcanizates	Kind of degradation	*Q*	$\nu \cdot 10^5$ mol · cm^{-3}
EPM	before	5.92	1.11
	thermal	4.77	1.78
	UV	1.56	22.18
EPM/flavanone	before	3.33	4.00
	thermal	3.03	4.97
	UV	2.60	7.02

Table 4. Color parameters of EPM vulcanizates after ageing (description of symbols in the text)

Kind of degradation	d*L**	d*a**	d*b**	d*E*ab*
Before	—	—	—	—
Thermal	0.80	-0.14	5.50	5.56
UV	4.21	-0.00	-4.39	6.09

Table 5. Color parameters of EPM vulcanizates containing flavanone after ageing (description of symbols in the text)

Kind of degradation	d*L**	d*a**	d*b**	d*E*ab*
Before	—	—	—	—
Thermal	-0.55	3.17	5.18	6.10
UV	-0.32	0.92	3.12	3.26

The interpretation of the parameters of color change due to both the types of ageing performed, specified in Table 4 and 5 indicates that flavanone is a good stabilizer of vulcanizate color, protecting it against the UV radiation. Coefficient d*E*ab* indicating the change in color of the sample after UV ageing shows a considerably lower value (3.26) for the EPM/flavanone vulcanizate than for vulcanizate unprotected by the antioxidant (6.09). Thermal ageing gives a high value of d*E*ab* coefficient both for vulcanizate unprotected and protected by flavanone. It should be noticed that flavanones play the role of pigments in plants. Therefore when incorporated into a rubber blend they can also impart a color to it and change its original color under the influence of oxidizing processes during thermal ageing.

CONCLUSIONS

Flavanone shows very good antioxidizing properties what is proved by its high oxidation potential and low value of oxidation rate.

The addition of flavanone to the rubber blend brought about an improvement in the thermal stabilization of the EPM vulcanizate. Although flavanone appeared to be a very good thermal stabilizer, it showed no capability to absorb UV radiation. The weak protection against UV ageing can be connected with the mechanism of ageing as this radiation acts on the sample surface. For that reason, in order to protect the vulcanizate against UV radiation, the antioxidant should show a great mobility towards degradation areas.

Undoubtedly, the addition of flavanone contributed also to the increase in the crosslinking density of EPM rubber. The antioxidant under investigation appeared also to be a very good stabilizer of color, protecting the vulcanizate against changes in color under the influence of UV radiation.

The flavonoide derivatives seem to be proecological additives to elastomers acting as anti-ageing compounds. Therefore further studies on the antioxidizing capability of flavanones in polymers seem to be justified. Undoubtedly, one should pay a special attention to efforts that would improve the lability of these substances in polymers.

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