INFLUENCE OF FLAVONOIDS AND AMINOACIDS ON THE STABILIZATION OF POLYMERS

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Abstract

The aim of our studies is to assess the effect of flavonoid derivatives and other natural substances as well as amino acids on the stabilization of elastomeric materials. It seems that natural antioxidants with oxygen in the structure, such as phenol derivatives, can be extracted from the industrial wastes plants, and are more appropriate solutions. The natural antioxidants which were added to ethylene-octene elastomer. Vulcanizates were then subjected to numerous ageing: weathering, thermo-oxidation ageing and thermal-shock as a function of the aging time. The efficiency of used anti-ageing agents was checked on the base of the changes after the degradation in deformation energy, cross-link density, color and values of carbonyl index (FT-IR), OIT of the vulcanizates. Therefore polyphenols and aminoacid are considered to be the best stabilisers for rubbers against to oxidation processes.

1. Introduction

Synthetic polymers play an important role in contemporary world. Their use brings enormous benefits in the packaging industry as well as in agriculture and the building industry. However, once their working life is terminated, the resultant wastes pose problems with their utilization. An alternative solution was found in the form of synthetic polymers based on renewable raw materials. Both natural and synthetic polymers are characterized by a high resistance to ageing if they contain highly effective antioxidants. A polymer is resistant to the action of various degrading factors until the stabilizer incorporated is removed or spent.

Antioxidants used in polymers include organic substances such as aliphatic and aromatic amines, polyphenols, benzofuranes or phosphates, vitamins E and C. The studies described in the literature mainly concern the improvements made to the structure of the antiageing compounds used, especially the modification of amine structure with steric hindrance of the HALS type that are now most popular.

Contemporary antioxidants should be characterized by a high and thorough protection against the synergic action of various degrading factors, such as moisture, temperature or solar radiation, preferably with as low concentration as possible and at the lowest prices of polymer processing and antioxidant preparation. It seems that one should search for new natural antioxidants such as the derivative of flavonoids and naphthochinones that have been not used yet in the technology of elastomers.

The properties of flavonoids have been extensively examined, among others, in terms of their antioxidant capacity and classified according to the donor mechanism of oxidation chain fission. Nowadays flavonoid derivatives show stronger antiageing properties than those of all the other natural antioxidants. An additional advantage is their antibacterial effect, more and

more frequently reported in the literature. This property of flavonoids can be appropriately used, e.g. in designing materials with specific properties.

Beside a patent of Goodyear company[5], concerning most flavonoid derivatives as antioxidants for tires, there is a lack of other information about parameters such as concentration, volatility or solubility and behavior of flavonoids in polymers, their effect of eleastomer cross-linking or filler activity. Hence one should extent the knowledge on the use of flavonoids in elastomers [1-6].

In the literature, one can find reports on the antioxidant capacity of some derivatives of amino acids, but they exclusively concern their use in biological systems. Thus, it seems that the amino acids proposed as compounds inhibiting the oxidation of polymeric materials are both innovative and environmentally friendly solution.

So far, it has been impossible to design a „material with ideal properties", i.e. such a one, whose properties are invariable with time, and after its exploitation life, the material would be decomposed to bioproducts such as CO_2, biomass and water, preferably being completely compostable.

2. Materials and testing methods

➢ The object of study was ethylene-octene rubber (Engage 8150, manufacturer DuPont Dow Elastomer).

Composition	M1	M2	M3	M4
	(phr)	(phr)	(phr)	(phr)
Engage	100	100	100	100
DCP	2,00	2,00	2,00	2,00
CTAB	2,00	2,00	2,00	2,00
A380	30	30	30	30
Naringin		1,5		
Flavone			1,5	
Quercetin				1,5

Table 1. Composition of EPM elastomer blends containing flavonoide derivatives.

Mentedison Ferrara – Italy). Dicumyl peroxide, DCP (from Fluka) was used as cross-linking agent, 1, and hexadecyltrimethylammonium bromide, CTBA (Sigma Aldrich Chemie GmbH) as dispersing agent. Areosil 380 silica (from Degussa) was used as filler.

The anti-ageing substances used included the following flavonoide derivatives: Naringin (Fluka 95%), Flavone (Aldrich 98%), Quercetin (Fluka 98%).

3. Measurement methods

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°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°C, under a pressure of 15 MPa for 30 min.

The density of nodes in the spatial lattice of vulcanizates was determined by the method of equilibrium swelling according to standard PN-74/C-04236. 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 in a dryer at a temperature of 60°C to a constant weight and after 48 h they were reweighed. The cross-linking density was determined on the basis of Flory-Rehner's equation:

$$\vartheta_e = -\frac{1}{V_0} * \frac{\ln(1-V_r)+V_r+\mu V_r^2}{(V_r^{\frac{1}{3}}-\frac{V_r}{2})}$$

(1)

for the elastomer-solvent interactions amounting to $\mu = 0{,}501 + 0{,}273\ V_r$, where V_r is the volume fraction of the elastomer in the swollen gel.

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 60^0 C, duration 8h), night segment (no UV radiation, temperature 50^{0}C, duration 4 h). The ageing coefficient was calculated according to the relationship: S= [TS'*EB']/[TS*EB], where TS – tensile strength, EB – elongation at break, TS', EB' – corresponding values after ageing. The color of the vulcanizates obtained was measured by means of a CM-3600d spectrophotometer. The radiation source consisted of four impulse xenon tubes. The spectral range of the apparatus was 360-740 nm, where change of color ΔE was calculated by the equation:

$$\Delta E = \sqrt[2]{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

(2)

ΔL represents the brightness relationship between light and dark, Δa represents the relationship between green and red and Δb represents the relationship between blue and yellow and symbol Δ implies the difference of colours between the samples before and after ageing.

The spectra of vulcanizates were taken by means of a Bio-Rad IR spectrophotometer. The carbonyl index was calculated on the basis of the ratio of the dependence of band at a wavelength of ~1700 cm^{-1} (carbonyl group) to the intensity of band at ~2800 cm^{-1} (–CH group).

OIT

The OIT (oxygen induction time) test were performed on a Mettler Toledo DSC instrument. Samples of 4 mg were heated from room temperature up to the test temperature, 220°C, with 20°C /min under nitrogen atmosphere. After 5 min at 220°C, 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 oxidize producing a deviation in the baseline. The OIT was measured as the time between the gas switch and an intersection with a tangent from the maximum derivate after

oxidation has started. Two analyzes on each sample were performed to ensure the accuracy of the result.

4. Result and discussion

Some flavonoids affect the cross-link density of Engage rubber vulcanizates. It seems that flavonoids can be the coagents of ethylene-propylene rubber cross-linking. The greatest influence on the cross-link density was exerted by flavone, increasing the concentration of lattice nodes by $2.17*10^{-4}$ mol/cm^3. After climatic ageing, it was observed that ve of the reference vulcanizate was increased up to $6.53*10^{-4}$ mol/cm^3, so further cross-linking occurred. On the other hand, in the case of Engage vulcanizates containing flavonoids, the cross-link density was decreased under the influence of climatic factors.

No significant effect of flavonoids on the mechanical properties of vulcanizates was observed. Before ageing, the tensile strength of the Engage rubber vulcanizates ranged from 20.70 to 23.60 MPa at an elongation of 397-524%.

Vulcanizates	$v_{(t)}*10^5$, Before ageing	$v_{(t)}*10^5$, After wethering
Engage	3,20	6,53
Engage /naringin	3,66	3,60
Engage /flavone	5,37	3,71
Engage /quercetin	4,03	3,73

Table 2. Effect of flavonoids on the cross-linking density of Engage vulcanizates, $v_{(t)}$ – crosslinking density calculated on the basis of swelling in toluene.

Vulcanizates	SE$_{300}$, (MPa)	TS, (MPa)	Eb, (%)
Engage	5,86	22,90	524
Engage /naringin	8,31	21,80	449
Engage /flavone	9,83	20,70	397
Engage /quercetin	7,53	23,60	433

Table 3. Effect of flavonoids on the tensile strength of Engage vulcanizates. TS – tensile strength,

Eb – elongation at break.

Vulcanizates	SE_{300}, (MPa)	TS, (MPa)	Eb, (%)	TS_{A}/TS_{BA}	Eb_{A}/Eb_{BA}	$(TS*Eb)_{A}/(TS*Eb)_{BA}$
		After wetahreing				
Engage	2,70	3,51	383	0,15	0,73	0,11
Engage /naringin	6,80	18,80	466	0,86	1,04	0,90
Engage /flavone	-	8,14	282	0,39	0,71	0,28
Engage /quercetin	6,73	17,70	434	0,75	1,00	0,75

Table 3. Effect of flavonoids on the tensile strength of Engage vulcanizates. TS – tensile strength, Eb– elongation at break.

After climatic ageing, the greatest decrease in mechanical properties was observed in the reference vulcanizate unprotected with antioxidants. The ageing coefficient of this sample was equal to 0.11, which indicates a high degree of degradation. It was the flavonoids used that appeared to be very good antiageing compounds for ethylene-caprylene. Undoubtedly, the vulcanizates were best protected against the adverse action by naringin and quercetin. The smallest protection against ageing was provided by flavone. The tensile strength of the vulcanizate with this flavonoid after ageing was decreased by 12.56 MPa. The ageing coefficients of the vulcanizates containing flavonoids amounted to 0.90, 0.75 and 0.28 for naringin, quercetin and flavone, respectively. That different influence of flavonoids on the stabilization of rubber is closely connected with the structure of antioxidant molecule. The greatest effect on the activity of antioxidant is exerted by the number and position of its hydroxyl groups. Flavone is characterized by the simplest molecular structure and therefore it shows the lowest antioxidant capacity compared to that of naringin or quercetin possessing developed structures and active OH groups.

The use of natural antioxidant can replace the stabilizers of amine group or phosphoric derivatives applied so far. Polyphenols can be obtained, e.g. by extraction of waste materials from the food industry, which will makes it possible both to utilize these waste and considerably decrease the cost of using this type of compounds.

Conclusion

Undoubtedly, the flavonoid derivatives used protect the vulcanizates of ethylene-propylene rubber against climatic ageing. Naringin and quercetin have appeared to be the best antiageing compounds. We hopefully believe that the natural antiageing compounds proposed by us will find their use in industry replacing the amine derivatives applied so

References:
[1] Cheng-YU Wang F. Polymer analysis by pyrolysis gas chromatography. Journal of chromatography A. 891, PP. 325–336 (2000).
[2] Allen Norman S., Barcelona A., Edge M., Wilkinson A., Galan Merchan C., Ruiz Santa Quiteria V. Aspects of the thermal and photostabilisation of high styrene–butadiene copolymer (SBC). Polymer Degradradation and Stability 91, pp. 1395-1416 (2006).
[3] Vineis P., Pirastu R. Aromatic amines and *cancer*. Cancer Causes Control 8, pp. 346-355 (1997).
[4] Sander A., Linseisen J., Rohrmann S. Intake of heterocyclic aromatic amines. Cancer Causes Control. 22, pp. 109–114 (2011).

[5] Boersma A. Predicting the efficiency of antioxidants in polymers . Polymer Degradation and Stability 91, pp. 472-478 (2006).
[6] Ismail M. N., Abd El Ghaffar M. A., Shaffei K. A., Mohamed N. A. Some novel polyamines as antioxidants for SBR vulcanizates. Polymer Degradradation and Stability 63, pp. 377-383 (1999)

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