

Ageing of elastomeric composites with natural antioxidant

A. Masek*, M. Zaborski* and M. Lipińska*

*Technical University of Lodz, Institute of Polymer and Dye Technology, Stefanowskiego 12/16 Lodz 90-924, Poland, anna.masek@p.lodz.pl

ABSTRACT

The stabilization of polymeric materials is of paramount importance, first of all, from the point of view of the dynamically growing polymer industry. Polymer ageing due to oxidation is common and poses serious problems as the absorption even of a low quantity of oxygen can cause irreversible and very damaging changes in the physical and mechanical properties of polymers. The degradation, ageing and stabilization of polymers constitute a large area of interest for both industry and science intending to obtain new, stable polymeric materials.

Polymeric goods during their use are exposed to the action of factors and agents from external environment. The structure and properties of materials change along with time. However, these changes depend on both the material structure and type of environmental impacts. The action of external elements on polymers results in the release of low-molecular compounds such as initiators, solvents, stabilizers and products of their decomposition. Therefore, one should aim at using pro-ecological or environmentally friendly additives to polymers.

In our studies, we propose the use of natural proecological substances, such as flavonoids, to protect elastomers against ageing. Flavonoids are natural vegetable dyes synthesized from phenylalanine. From the literature it follows that flavonoids are very good reducing agents, so they can react with the reactive forms as free radicals as well as they can form complexes with transition metals, which are responsible for ageing [1-5].

Based on changes in deformation energy, cross-link density and color resulting from UV, climatic and ozone ageing processes, we assess the susceptibility of composites to degradation under the influence of specified environmental elements. The susceptibility of composites to the decomposition by microorganisms is assessed by means of microbiological tests. From our first investigations it follows that flavonoids very well fulfill the function of elastomer oxidation inhibitors, protecting composites against adverse environmental conditions.

Keywords: elastomer, antioxidant, ageing of polymer, weathering, polymer.

1 EXPERIMENTAL

The object of study was ethylene-propylene rubber (EPM). Dicumyl peroxide, DCP (from Fluka) was used as cross-linking agent, 1,3,5-Triallyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (Sigma Aldrich Chemie GmbH) as co-agent of cross-linking 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 flavonoid derivatives: *chalcone* (Fluka 95%), hesperidin methyl chalcone amounting 1,5 phr (parts per hundred parts of rubber).

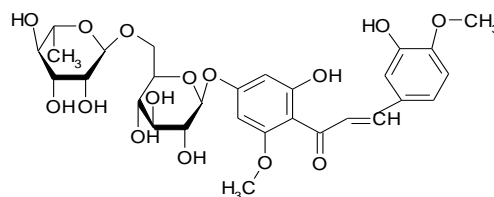


Fig. 1. Structure of hesperidin methyl chalcone.

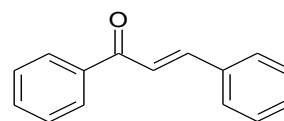


Fig. 2. Structure of *trans*-chalcone.

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 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.

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°C , duration 8h), night segment (no UV radiation, temperature 50°C , duration 4 h). Weathering was performed by WOM Ci 4000 apparatus of Atlas. The measurements 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 244min, humidity 80%, spray on), night segment (no UV radiation, temperature 50°C , duration 120min, humidity 70%).

The ageing coefficient was calculated according to the relationship: $S = [\text{TS}' \cdot \text{EB}'] / [\text{TS} \cdot \text{EB}]$, 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 $\Delta E \Delta L$ 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.

2 RESULT AND DISCUSSION

Natural antioxidants of the flavonoid group decrease the cross-link density of EPM rubber, but they exert no effect on the mechanical properties of EPM vulcanizates. The tensile strength of vulcanizates before ageing ranged from 17 to 21.9 MPa at elongations of 580-831%. The greatest decrease in strength was observed after UV ageing of a reference vulcanizate sample and a sample containing HALS stabilizer. The best antioxidant for ethylene-propylene rubber was chalcone-hesperidin. The coefficients of both UV and climatic ageings were close to 1, indicating an insignificant degree of degradation. The most adversely affected in ageing was the reference sample of vulcanizate containing no antioxidant, which showed the greatest decrease in mechanical properties. On the other hand, the commercial stabilizer, HALS, insignificantly protected EPM against UV and climatic ageing. Chmiassorb only proved true as thermal stabilizer (Table 1).

Table 1: Mechanical properties of EPM vulcanizates with flavonoids.

Vulcanizates	Kind of ageing	TS	E _B	S
		[MPa]	[%]	-
EPM	-	19,90	782	-
	UV	4,7	330	0,10
	Weathering	12,9	590	0,49
	Thermo-oxidation	9,9	480	0,31
EPM/Chimassorb944 (Hals)	-	17,8	831	-
	UV	9,9	171	0,12
	Weathering	8,8	185	0,11
	Thermo-oxidation	17,4	790	0,93
EPM/hesperidin-methyl chalcone	-	21,2	580	-
	UV	18,4	530	0,80
	Weathering	19,8	611	0,98
	Thermo-oxidation	21,8	616	1,09
EPM/trans-chalcone	-	21,9	589	-
	UV	10,0	395	0,31
	Weathering	5,05	279	0,11
	Thermo-oxidation	13,2	772	0,79

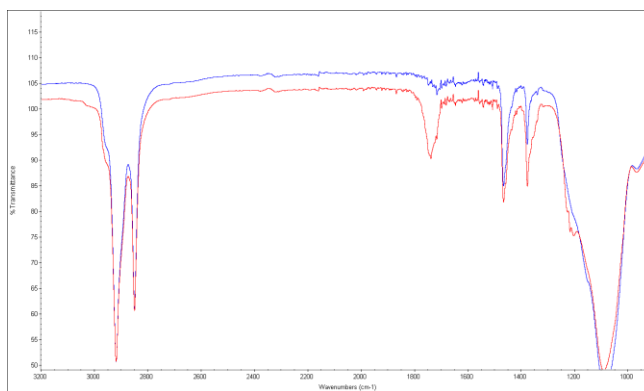


Figure 1: FT-IR spectrum of EPM vulcanizates before and after ageing.

The extent of sample degradation was assessed on the basis of the intensity of band corresponding to carbonyl groups. IR spectrum (Fig. 1) shows clear bands corresponding to carbonyl groups formed during oxidation, at 1700 cm^{-1} after UV ageing for a reference sample and a low intensity at 1700 cm^{-1} for a sample containing hesperidin methyl chalcone, testifying to a slight degradation.

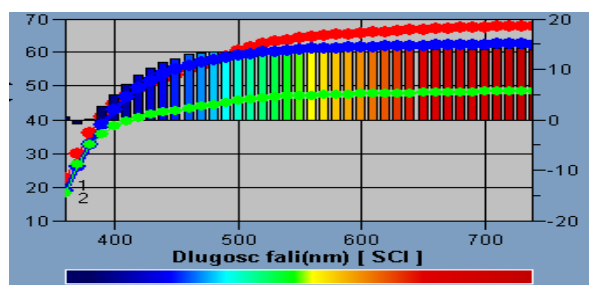
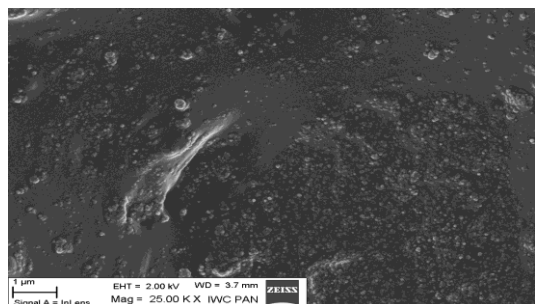
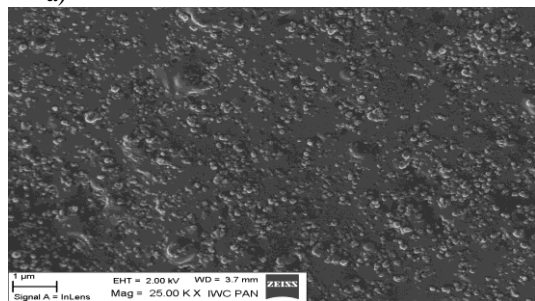


Fig.3. Reflectance of wavelength for EPM vulcanizates with chalcone-hesperidin before and after UV ageing.

As flavonoids play a double role of antioxidants and pigments, their addition considerably influences the color of EPM vulcanizates. Under the influence of ageing, the structure of flavonoids changes showing color alterations that can be controlled by means of a spectrophotometric measurement. Figure 2 shows changes in the color of EPM vulcanizate after UV and climatic ageing processes testifying to a progressive degradation of the vulcanizate.



a)



b)

Fig.3. SEM of EPM vulcanizates with the hesperidin-chalcone (a-b).

The SEM photo (Fig.3) of the EPM vulcanizate fracture shows an uniform dispersion of filler in the rubber. Silica forms its own network in the elastomer.

We also determined the oxygen induction time (OIT) by means of DSC, which indicated a considerably prolonged duration of the oxidation of EPM rubber containing flavonoids compared to a reference sample. The addition of chalcone-hesperidin prolonged the sample oxidation by 21.6 min. and the oxidation energy was also lower. The addition of chimassorb 944 increased the time of EPM

oxidation only by 5.81 min., but it considerably decreased the oxidation energy of EPM.

Table 2: OIT of EPM vulcanizates.

Vulcanizates	Energy of oxidation [J/g]	OIT [min]
EPM	4848	2,88
EPM/chimassorb944	2207	8,69
EPM/hesperidin methyl chelcone	3771	24,48

Thermogravimetric measurements of flavonoid derivatives were also carried out, which allowed us to confirm the thermal stability of these compounds during polymer processing. Some samples were subjected to microbiological tests, which have confirmed that some flavonoids increase the vulcanizate susceptibility to biodegradation.

All in all, it appears that the use of natural antioxidants instead of amine derivatives is an interesting and attractive solution. For economic reasons, we propose to search for natural antioxidants extractable from the food industry wastes, which would considerably reduce the cost of using this type of additives.

REFERENCES

- [1] Masek A., Zaborski M., Chrześcijanska E., Kosmalka A., *Comptes Rendus Chimie*, 15, 331-33, 2011.
- [2] Masek A., Zaborski M., Chrześcijanska E., *Food Chemistry*, 121, 669-704, 2011.
- [3] Boersma A., Cangialosi D., Picken S., *Journal of Polymer Degradation and Stability*, 79, 427-438, 2003.
- [4] Ismail M. N., Abd El Ghaffar M. A., Shaffei K. A., Mohamed N. A., *Polymer Degradation and Stability* 63, 377-383, 1999.
- [5] Albertsson A. Ch., Karlsson S., *Journal Applied Polymer Science* 35, 1289-1302, 1998.

Acknowledgement

This study was supported by Ministry of Science of Higher Education (N R05 0006 06/2009).