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Natural Antioxidants as Multifunctional Additives for Polymeric Materials

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Abstract
The additional substances commonly used for polymeric materials mostly have a negative impact either on the natural environment or human health. Therefore, there is a need for replacing these compounds by more pro-ecological ones. In this paper, some natural antioxidants of plant origin, including xanthone, rutin hydrate, quercetin and a mixture of various polyphenols derived from green tea, were proposed as multifunctional as well as eco-friendly additional compounds for polymers. These substances were implemented by means of the impregnation process into ethylene-propylene copolymer (EPM) matrix. Some significant results of the research work are presented, including the mechanical properties and oxidation induction time (OIT) of the material tested. Moreover, ethylene-propylene copolymer (EPM) with antioxidants was investigated in terms of thermooxidative and UV ageing resistance. The impact of ageing processes on the material tested was analysed mainly by means of Fourier transform infrared spectroscopy (FT-IR) absorbance spectra and colour change assessment.

Key words: *flavonoids, natural stabilisers, ethylene-propylene copolymer.*

Introduction

Most of the existing polymeric materials consist not only of polymers but also of various additives which are responsible for improving their functional and processing properties. Unfortunately, the additional substances commonly utilised are not always environmentally friendly. Moreover, some of them are not even safe for human beings. Due to this fact, there has been an increasing interest in natural antioxidants of plant origin as pro-ecological additional substances for polymers. These substances have a great potential as natural stabilisers, pigments and ageing time indicators for elastomer as well as thermoplastics, which has been proven by many researches and printed publications [1-8].

It is an important fact that even a small amount of natural antioxidants is able to react with oxygen and its reactive species faster than a polymeric matrix. Therefore, most of these compounds are capable of inhibiting chain reactions which lead to sudden chemical degradation, and hence they can be applied as natural stabilisers [9]. Moreover, many substances of plant origin are characterised by a variety of colours and can be used as colorants for polymeric materials. Carotenoids are an example of natural antioxidants which have a real chance to become natural additives for polymers [10]. Some of them, especially carotenes, are known as popular food colouring agents, and sometimes they can also act as stabilisers. The most popular carotenes, such as β-carotene and lycopene, are sensitive to oxygen and UV radiation, thus many researches concerning the application of these substances as additives to polymers are still needed. Investigation results for lykopen's impact on polyolefins showed that these compounds can act as stabilisers, but only in the presence of a small amount of oxygen. However, in the case of a large concentration of reactive oxygen species, they cannot behave like antioxidants [11]. A very similar phenomenon was proved for β-carotene [12]. The material loses its colour under the action of oxygen, as shown when intros ducing carotenoid. Due to this fact, researchers noticed that these compounds can be applied not only as a natural dye but also as ageing time indicators for some kinds of polymers, like cyclic olefin copolymers, including thermoplastic copolymer of ethylene and norbornene (Topas E-140) [13]. Such a material with natural dye and ageing time indicator can be applied for intelligent packaging manufacturing. An analysis of the changing of packaging colour during ageing would facilitate quality assessment of packaging materials as well as the product in them, such as food.

Natural phenolic compounds are another group of antioxidants derived from plants. Phenolic acids, which are the simplest ones, such as ferulic acid, have already been applied as stabilisers in the food industry. Nevertheless, investigations concerning the application of these substances as polymer stabilisers are ongoing [14]. More complex phenolic compounds, such as flavonoids, are also attracting strong interest from scientists, because of their colouring and stabilising properties. The results of investigations show that these substances can be utilised as multifunctional additives for elastomers, polyolefins or other polymeric materials. Some flavonoids, especially the group of flavonols, are capable of protecting polypropylene from UV radiation and thermooxidative ageing, because they successfully prevent carbonyl moieties from forming [15]. The flavonoid impact on pro-ecological polymeric materials such as polylactide (PLA), polyhydroxybutyrate (PHB) [16], and polymers from the polyether group as well as on starch-based materials was also investigated [17]. Some results obtained proved that quercetin can protect selected biomaterials from photooxidative ageing [17]. Moreover, there are also some publications on issues of interest regarding the great stabilising properties of natural extracts derived from plants. These substances mostly consist of mixtures of various natural antioxidants, thus they have a large potential to become polymer stabilisers. Natural compounds derived from green and black tea are examples of substances with great stabilising properties [18-19]. These substances were used, for example, in polyolefins and epoxidised natural rubber matrix as anti-ageing additives [19-20] Furthermore, other natural antioxidants such a rosemary plant-derived compounds also have a large potential to become a stabiliser for polyolefins. These natural substances are characterised by

Table 1. Composition of basic blends of ethylene-propylene copolymer.

Composition	phr
Ethylene-propylene rubber (EPM)	100
Areosil 380 silica	30
Dicumyl peroxide (DCP)	4

more effective stabilising properties than commercial ones [21]. The increasing number of publications with significant results related to the application of natural antioxidants as pro-ecological additives for polymers encourages scientists to develop their researches and find new solutions in this topic.

Materials and methods

Reagents

The object of experimental work was ethylene-propylene rubber (EPM, Dutral CO-054, manufacturer: Montedison Ferara – Italy) cross-linked by dicumyl peroxide (DCP, from Fluka) and filled with Areosil 380 silica (from Degussa). Natural antioxidants, including: xanthone (from Sigma Aldrich, 97%), rutin hydrate (from Sigma Aldrich, 95%, HPLC), quercetin (from Sigma Aldrich, ≥95%, HPLC), and polyphenon 60 from green tea (from Sigma Aldrich, containing minimum 60% total catechins) were used as natural stabilisers.

Methods of experimental work

Sample preparation

First of all, a rubber blend was prepared by the reagent mixing process in accordance with ***Table 1***. The mixing process was performed in a laboratory mixing mill with rolls of length L = 450 mm and cross-section diameter D = 200 mm. The distance between rolls was about 1.5-3 mm. The rotation speed of the front roll (V_0) amounted to 16 rpm, the friction about 1-1.2, and the average temperature of the rolls was 25 °C.

Secondly, the ethylene-propylene copolymer blends prepared were vulcanised by means of an electrically heated hydraulic press. In this process every single piece of blend was placed between two steel vulcanisation moulds situated between the press shelves. Polytetrafluoroethylene (PTFE, Teflon®) films were applied as spacers to isolate the blends from the press plates and prevent adherence phenomena. The parameters of the vulcanisation process were as follows: time t = 30 min., temperature T = 160 °C, pressure p = 3 MPa.

The vulcanised flat samples were 120 mm long, 80 mm wide and 1 mm thick. The rectangular plates thus prepared were cut into 3 small pieces (40 x 80 x 1 mm) and then subjected to the impregnation process.

The last step of specimen preparation was impregnation. Vulcanised ethylene-propylene (EPM) copolymer was cut into pieces, which were next immersed in 0.5 l of every solution containing 4% of the selected antioxidant, such as xanthone, rutin hydrate, quercetin, and polyphenon 60 from green tea dissolved in ethanol. The impregnation process was performed in a 1.5 l beaker using a magnetic stirrer. The parameters of the impregnation process were as follows: time t = 4 h, temperature T = 50 °C, and the speed of mixing amounted to 700 rpm. After the impregnation, specimens were left to dry for 24 hours at room temperature. The samples prepared, described in ***Table 2***, were next tested.

Research methods

Ethylene-propylene copolymer with antioxidants was researched in terms of mechanical properties, such as stress at 300% elongation (SE_{300}), tensile strength (TS), and elongation at break (E_b). These tests were carried out in accordance with PN-82/C-04205 using a Zwick-Roel 1435 measuring instrument. Samples of the w-3 type with a width of 4 mm were prepared from every type of material containing the selected antioxidant. For every single sample the real thickness was measured at the three different locations, and the final value was calculated as an average for the three results obtained and used in this research. The measurement was carried out at an initial force of 0.1 N and at an elongation speed of 500 mm/min.

The oxidation induction time (OIT) was investigated on a Mettler Toledo DSC1 device using a STAR^e System equipped with a Gas Controller GC10. Samples of about 6-8 µg were placed in open aluminum crucibles and heated from room temperature to 220 °C at 20 °C/min in a nitrogen atmosphere. When the temperature reached 220 °C, the samples were left in this condition for 5 min, and after this time the gas was switched from nitrogen to air. The flow rate of air was about 60 ml/min. In this test, after consuming all the antioxidants, the samples were oxidised, which was visible as a deviation inform the baseline. The oxidation induction time (OIT) was estimated as the time between the moment of the gas switch and the appearance of the maximum exothermic peak related to the oxidation process.

Accelerated UV ageing was conducted in an UV 2000 Atlas chamber, using steel folders to place the ethylene-propylene copolymer (EPM) samples tested. The measurement lasted for 14 days and was divided into two alternately repeating segments with determined parameters. The first one, called the daily segment, was characterised by a UV radiation intensity of 0.7 W/m^2, temperature of 60 °C and duration of 8 h. The second one, called the night segment, consisted of no UV radiation, temperature of 50 °C and duration of 4 h.

The second type of ageing was thermo-oxidative, which was performed according to PN-82/c-04216 in a Binder dryer of the FD series with circulated air as well as at an elevated temperature of 100 °C. The ethylene-propylene copolymer (EPM) samples with antioxidants prepared were aged for 14 days. Before and after accelerated UV and thermo-oxidative ageing, optical characterisation and FT-IR analysis of the samples researched were performed to investigate changes in material properties.

Table 2. Description of samples prepared.

Name	Description
EPM	non-impregnated ethylene-propylene copolymer (reference sample)
EPM/EtOH	ethylene-propylene copolymer impregnated with ethanol (reference sample)
EPM/xanthone	ethylene-propylene copolymer impregnated with solution containing 4% xanthone dissolved in ethanol
EPM/rutin hydrate	ethylene-propylene copolymer impregnated with solution containing 4% rutin hydrate dissolved in ethanol
EPM/polyphenon 60	ethylene-propylene copolymer impregnated with solution containing 4% polyphenon 60 dissolved in ethanol
EPM/quercetin	ethylene-propylene copolymer impregnated with solution containing 4% quercetin dissolved in ethanol

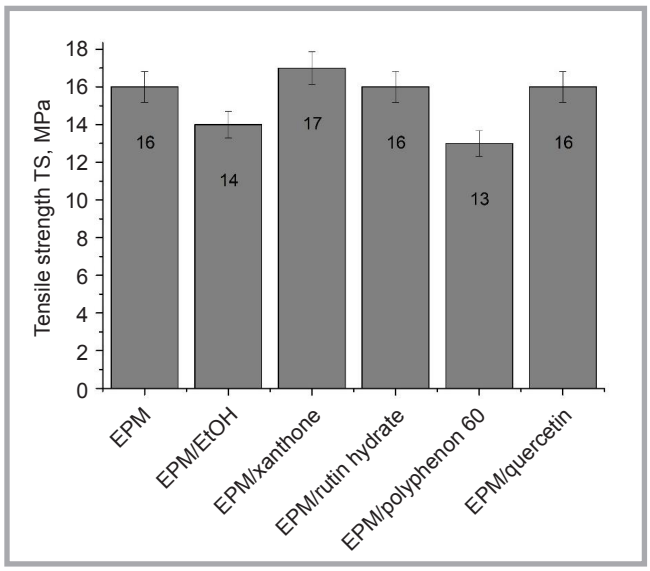

Figure 1. *Tensile strength (TS) values of non-impregnated and impregnated ethylene-propylene (EPM) vulcanizates.*

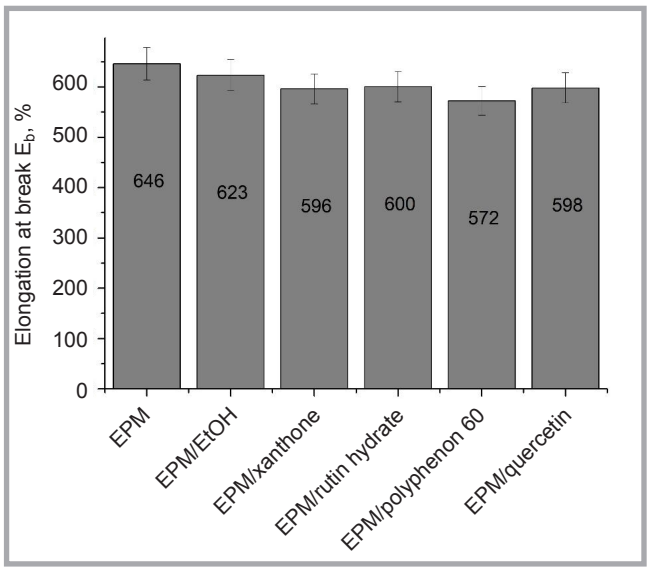

Figure 2. *Elongation at break (E_b) values of non-impregnated and impregnated EPM vulanizates.*

Fourier transform infrared spectroscopy (FT-IR) absorbance spectra were recorded in the range of 4000-400 cm^{-1} using a Thermo Scientific Nicolet 6700 FT-IR spectrometer with diamond Smart Orbit ATR sampling equipment. In this research structural changes of the materials tested which occurred as a result of ageing processes were investigated.

Optical characterisation of aged and unaged samples was performed by means of colour measurement. The colour of ethylene-propylene (EPM) samples containing selected antioxidants was measured in accordance with PN-EN ISO 105 – J01 using a UV-VIS CM-36001 spectrophotometer from Konica Minolta. This device measures the signal reflected from the surface of the sample and converts it into a colour impression that is perceived by the human eye. The results were described with the CIE-Lab system (L – lightness, a – red-green, b – yellow-blue). Moreover, colour difference (ΔE), whiteness index (W_i), chroma (C_{ab}) and hue angle (h_{ab}) values were calculated according to ***Equations (1)–(3)*** and ***(4)*** below. The values Δa, Δb and ΔL used in these equations were calculated as the difference in a, b and L parameters between the impregnated and non-impregnated materials as well as between the aged and unaged materials. These parameters are useful for estimating polymer colour change after impregnation as well as after the ageing process [22].

$$\Delta E = \sqrt{(\Delta a)^2 + (\Delta b)^2 + (\Delta L)^2} \quad (1)$$

$$W_i = 100 - \sqrt{a^2 + b^2 + (100 - L)^2} \quad (2)$$

$$C_{ab} = \sqrt{a^2 + b^2} \quad (3)$$

Results and discussion

Mechanical properties analysis

Research of mechanical properties of the samples was carried out in order to determine the impact of the impregnation process on the values of ethylene-propylene copolymer, such as stress at 300% elongation (SE_{300}), tensile strength (TS) and elongation at break (E_b). Results of the research are presented in tables or bar charts. The values of stress at 300% elongation (SE_{300}) are shown in ***Table 3***.

In the case of EPM material's stress at 300% elongation (SE_{300}), the impact of the impregnation process on this property is visible only in the presence of xanthone. The value of this property for ethylene-propylene copolymer (EPM) impregnated with xanthone is the highest, amounting to 2.74 MPa. The impact of the impregnation process on the stress at 300% elongation (SE_{300}) in the case of the other impregnated ethylene-propylene vulcanizates is not significant. The results are almost the same in the range of 2.43-2.44 MPa and are very similar to those of the reference sample (SE_{300} = 2.47 MPa) (***Figure 1***).

The tensile strength (TS) result of the ethylene-propylene (EPM) reference sample amounts to 16 MPa. Impregnated ethylene-propylene vulcanizates are characterised by very similar results of this property. The impregnation process with pure ethanol as well as with a solution of polyphenon 60 in ethanol caused about a 12-19% decrease in the tensile strength (TS) value. The highest value of tensile strength (TS) is visible in the case of ethylene-propylene (EPM) copolymer

$$h_{ab} \begin{cases} arctg\left(\frac{b}{a}\right), \text{ when } a > 0 \cap b > 0 \\ 180° + arctg\left(\frac{b}{a}\right), \text{ when } (a < 0 \cap b > 0) \cup (a < 0 \cap b < 0) \\ 360° + arctg\left(\frac{b}{a}\right), \text{ when } a > 0 \cap b < 0 \end{cases} \quad (4)$$

Equations (4)

Table 3. *EPM material's values of stress at 300% elongation (SE_{300}).*

Sample	SE_{300}, MPa
EPM	2.47
EPM/EtOH	2.43
EPM/xanthone	2.74
EPM/rutin hydrate	2.44
EPM/polyphenon 60	2.44
EPM/quercetin	2.43

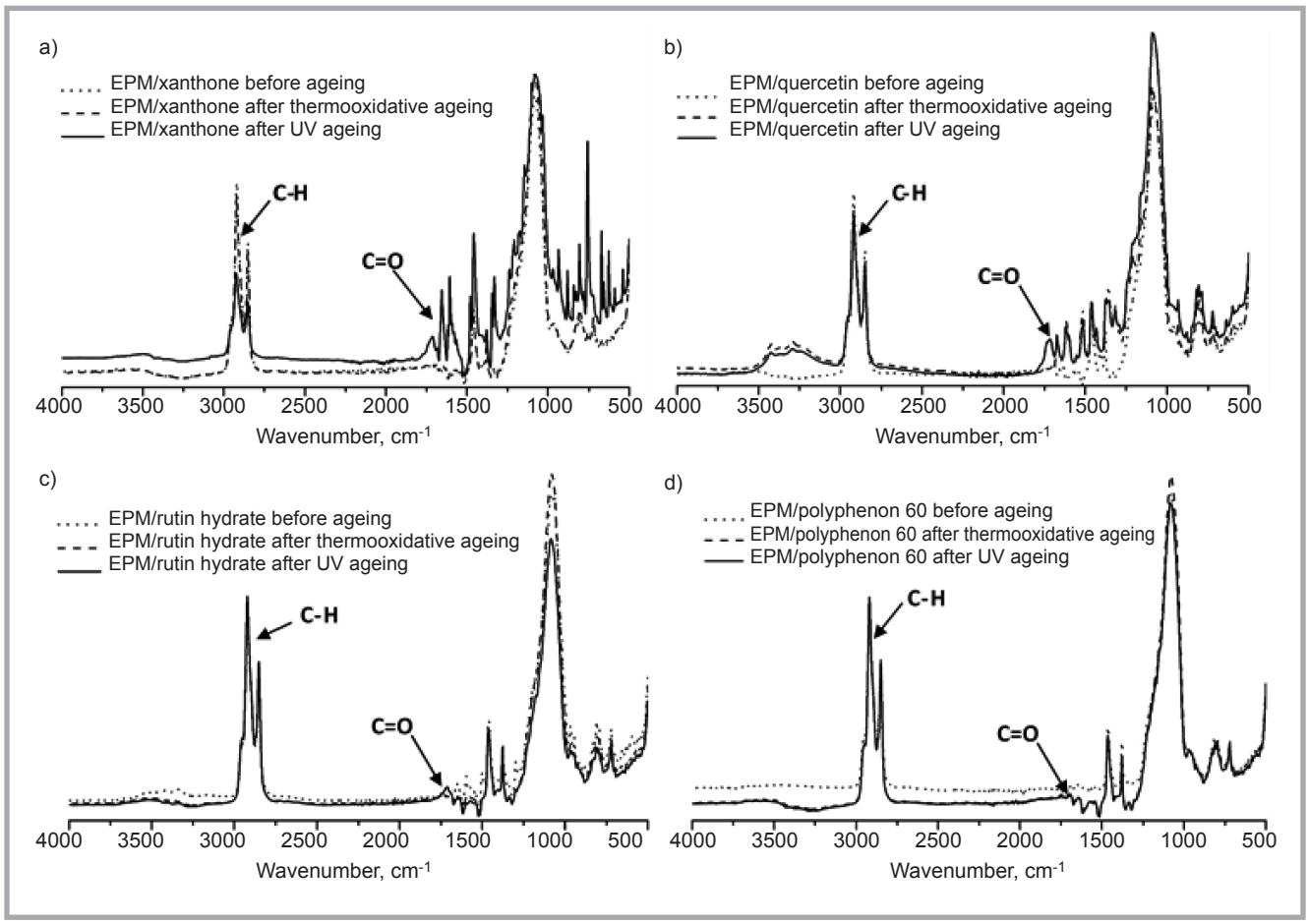

Figure 3. *FT-IR spectra before and after ageing of ethylene-propylene copolymer impregnated with selected antioxidants: a) xanthone, b) quercetin, c) rutin, d) polyphenon 60.*

with xanthone, which amounts to 17 MPa (***Figure 2***).

The reference sample has the highest value of the elongation at break (E_b) parameter, which equals 646%. The impregnation process of ethylene-propylene copolymer with pure ethanol (EPM/EtOH) caused a slight decrease in this property, while impregnation with ethanol with antioxidants led to a visible fall in the elongation at break (E_b) parameter.

Oxygen induction time (OIT) parameter

In ***Table 4***, the oxygen induction time (OIT) of ethylene-propylene copolymer as well as energy oxidation values are shown. The OIT parameter is related to oxygen resistance. Thus, this property is also responsible for the material's exploitation time. The higher the value of this parameter, the longer the material can be used in oxygen conditions.

According to the results of the Oxidation Induction Time (OIT) parameter, shown in ***Table 4***, the impregnated ethylene-propylene copolymer samples have about a 10-70% longer oxidation time in comparison to the non-impregnated ones. The natural antioxidants incorporated into the ethylene-propylene matrix by means of impregnation acted as stabilisers and extended the oxidation time as well as the exploitation time. The sample of ethylene-propylene copo-

Table 4. *Comparison of Oxidation Induction Time (OIT) results of ethylene-propylene samples.*

Sample	EPM	EPM/xanthone	EPM/rutin hydrate	EPM/polyphenon 60	EPM/quercetin
OIT value, min.	10.08	13.25	14.62	10.98	16.83
Energy of oxidation, J/g	3164	4702	5248	4110	4619

Table 5. *Chemical groups assigned to the wavenumbers of FT-IR.*

Wavenumber, m^{-1}	Chemical group
2850; 2920	C-H aliphatic
808; 1080; 1376; 1452	C-C aliphatic
1700	C=O
1050	C-O

Table 6. *Results of carbonyl index for every ethylene-propylene copolymer sample after the thermooxidative and UV ageing process.*

	Carbonyl index	
	After thermooxidative ageing	After UV ageing
EPM	0.25	0.37
EPM/xanthone	0.11	0.82
EPM/rutin hydrate	0.08	0.13
EPM/polyphenon 60	0.10	0.10
EPM/quercetin	0.20	0.32

lymer impregnated with quercetin has the highest Oxidation Induction Time (OIT) parameter, which amounts to 16.83 min. The highest value of this parameter is also related to the best resistance to the oxidation process. Quercetin reveals slightly better antioxidant properties than rutin hydrate or xanthone. This compound is also characterised by an average value of oxidation energy in comparison to the other antioxidants. The oxidation energy value of ethylene-propylene copolymer impregnated with quercetin amounts to 4619 J/g. It can be noticed, that the ethylene-propylene samples with higher as well as lower energy tested have a lower value of the Oxidation Induction Time (OIT) parameter

Analysis of Fourier transform infrared spectroscopy (FT-IR) absorbance spectra

In the case of ethylene-propylene copolymer samples stabilised by the natural antioxidants analysed in this research, it was thought that it would be interesting to see the difference between spectra obtained before and after various aging processes. It is especially important in terms of the 1700 cm^{-1} wavenumber, which corresponds to carbonyl moieties as its intensity ratio. Moreover, the carbonyl index was calculated on the basis of carbonyl and aliphatic moiety absorbance. This index reveals the impact of UV and the thermooxidative ageing process on ethylene-propylene copolymer impregnated with the natural antioxidants.

The moieties analysed are presented in ***Table 5***. These chemical groups can be easily investigated because they are assigned to the wavenumbers. The FT-IR spectra with carbonyl as well as alkyl groups belonging to samples tested before and after thermooxidative and UV ageing are presented in ***Figure 3***.

According to the FT-IR spectra and carbonyl index results, almost all antioxidants used are good thermal or UV stabilisers. In the case of UV ageing, only xanthone has a significantly higher carbonyl index in comparison to the reference sample. This substance can be utilised only as a thermal stabiliser. The most efficient stabilisation in terms of thermooxidative ageing was provided by rutin hydrate, which also turned out to be a good UV stabiliser. Ethylene-propylene copolymer impregnated with this compound has the lowest carbonyl index, which amounts to 0.08. Also, polyphenon 60 has good stabilisation properties, proven by a low carbonyl index of 0.1 for every ageing process investigated.

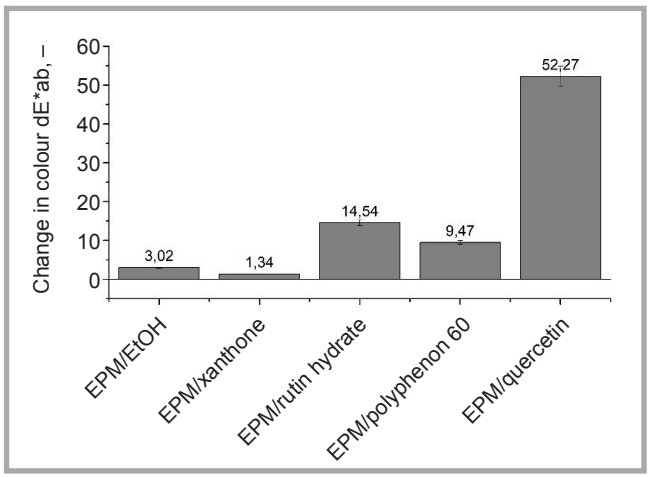

Figure 4. *Colour difference (ΔE) between non-impregnated and impregnated ethylene-propylene copolymer (EPM).*

Optical characterisation of samples researched

Colour measurement enabled to assess the difference between non-impregnated and impregnated ethylene-propylene copolymer samples as well as between aged and non-aged vulcanisers. Colour difference (ΔE), whiteness index (W_i), chroma (C_{ab}) and hue angle (h_{ab}) results are presented in the figures below. It can be assumed that a colour difference (ΔE) above 5 means that the colour of sample tested and the reference one are significantly different.

According to ***Figure 4*** the highest values of colour change with regard to the sample reference are noted for ethylene-propylene copolymer impregnated with quercetin (EPM/quercetin), amounting to 52.27. Moreover, rutin hydrate and polyphenon 60 also have colour difference results above 5, which means that they are able to significantly change the colour of the material, acting as colorants. Therefore, these natural substances can be utilised to dye materials, such as ethylene-propylene copolymer.

According to ***Figure 5.a***. the highest results of colour change after thermooxidative ageing are noted for ethylene-propylene copolymer impregnated with polyphenon 60 and quercetin. In the case of ethylene-propylene copolymer with polyphenon 60 (EPM/polyphenon 60), the value of chroma after thermooxidative aging is significantly higher, which can be seen in ***Figure 5.c***. This parameter as well as the hue allow to differentiate EPM/polyphenon 60 materials before and after ageing. As can be noticed in ***Figure 5.b***, ethylene-propylene copolymer impregnated with quercetin (EPM/quercetin) became darker after thermooxidative ageing. Quercetin and polyphenon 60 can be used as thermooxidative ageing process indicators.

In the case of UV ageing, as can be noticed in ***Figure 5.a***, the highest values of colour difference are noted for materials with xanthone and quercetin. According to ***Figure 5.b***, ethylene-propylene copolymer impregnated with xanthone (EPM/xanthone) after UV ageing is characterised by a significantly higher value of chroma. The whiteness index and hue of this sample are definitely lower, which is visible in ***Figure 5.b*** and ***5.d***. Selected antioxidants, such as xanthone and quercetin, can be utilised as UV ageing indicators, because of their noticeable changes in colour during the ageing process.

Conclusions

Summarising, natural antioxidants of plant origin have the potential to become pro-ecological and multifunctional additives for polymers, including elastomers like ethylene-propylene copolymer. These compounds can be incorporated into the polymeric matrix by means of the impregnation process. Most of the antioxidants selected do not change the mechanical properties of the polymers significantly, such as the tensile strength (TS), but they can cause a slight decrease in stress at 300% elongation (SE_{300}) and in the elongation at break (E_b). The exception was xanthone, which caused a slight improvement in these properties. Moreover, these natural substances, especially quercetin,

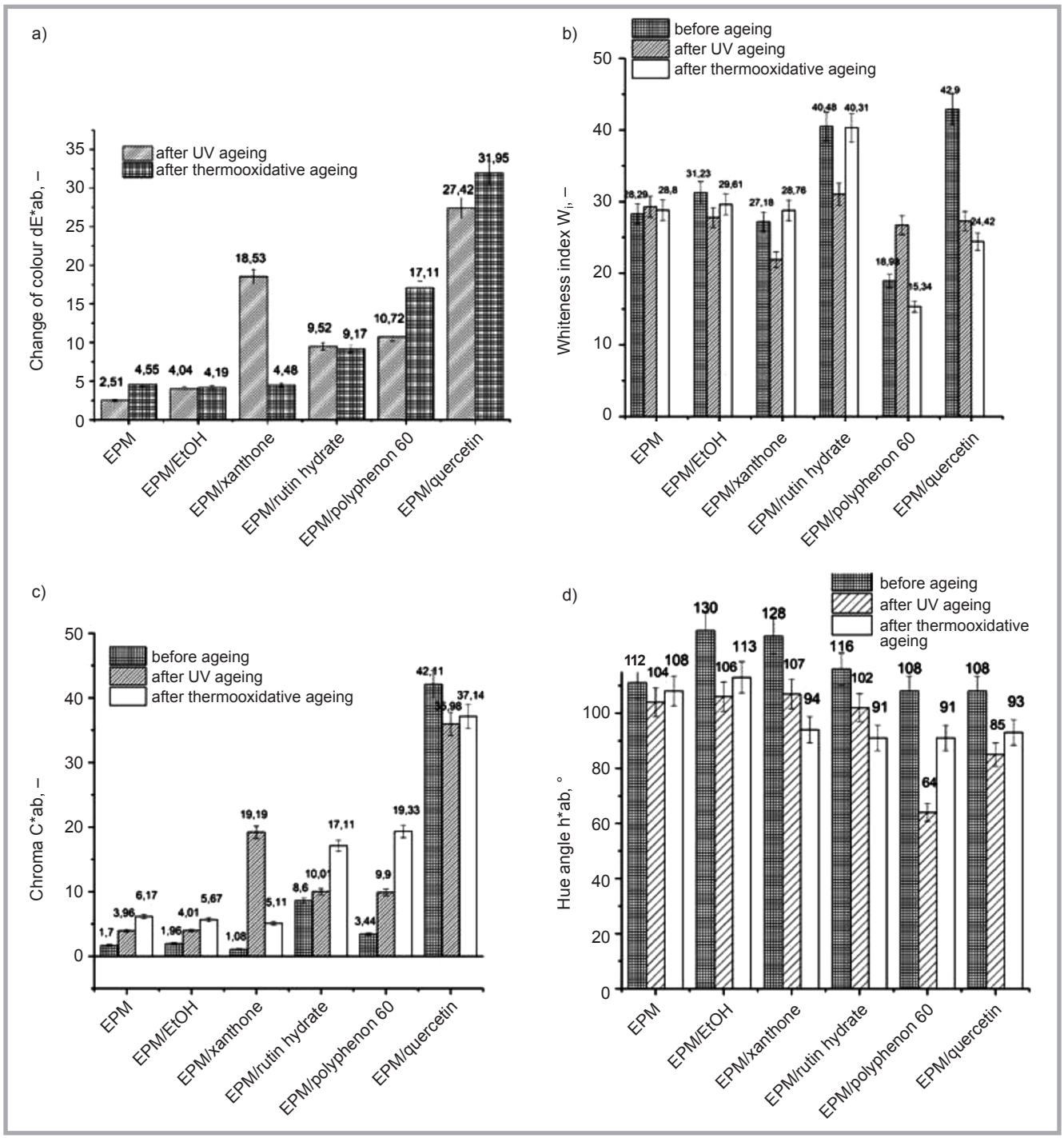

Figure 5. *Influence of the ageing process on a) change in colour (dE*ab), b) whiteness index (W_i), c) chroma (C*ab) and d) hue angle (h*ab).*

are able to stabilise ethylene-propylene copolymer (EPM) by means of extending the oxidation time. As was proven during the FT-IR spectra analysis and by the carbonyl index calculated, some of the antioxidants selected, including rutin hydrate and polyphenon 60, perform well in polymer stabilisation during thermooxidative and UV ageing. Furthermore, natural compounds such as quercetin and rutin hydrate can colour the polymeric matrix. Thus, these substances derived from plants can be used as natural colorants. Some of the antioxidants tested, including quercetin, xanthone and polyphenon 60, are also able to change their colour during the ageing process and can be used as ageing indicators. The results presented confirm that the antioxidants selected have potential to replace conventional stabilisers in the polymer industry. These substances of plant origin are safer for human health and more environmentally friendly than the more common antioxidants, such as amine-based ones, which are unfavourable because of their toxicity. Moreover, some of them, like quercetin and rutin hydrate, are able to be used as natural colorants for polymers, including ethylene-propylene copolymer. Furthermore, the ethylene-propylene copolymer materials prepared containing colour-changing natural antioxidants, like quercetin, xanthone and polyphenon 60, can be applied for the production of intelligent packaging materials with controlled degradation time.

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