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Research article

Eugenol and cloves as plant-origin stabilizers in epoxidized natural rubber compositions

Malgorzata Latos-Brozio[*], *Agata Dumka, Anna Masek*

Institute of Polymer and Dye Technology, Department of Chemistry, Lodz University of Technology, Lodz, Poland, Stefanowskiego 16, 90-537 Lodz, Poland

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Abstract. In polymer materials technology, replacing synthetic stabilizers with natural antioxidants is a current and developing issue. Cloves have antimicrobial and antioxidant properties, which is why they are often used in medicine and in gastronomy. Eugenol – the main component of clove oil, is also a strong antioxidant. The aim of the study was to analyze and compare the anti-aging effects of eugenol and cloves in epoxidized natural rubber (ENR) compositions. The 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonate (ABTS), 2,2-diphenyl-1-picrylhydrazyl (DPPH), ferric reducing antioxidant power (FRAP) and CUPric reducing antioxidant capacity (CUPRAC) tests showed the ability of plant materials to reduce free radicals, as well as iron and copper ions. ENR compositions with additives were characterized by a longer oxidation induction time (OIT). The samples after solar aging showed better resistance to elevated temperature and solar radiation, as evidenced by aging coefficients (*K*) calculated on the basis of mechanical properties and carbonyl indexes of samples with eugenol and cloves. Cloves and eugenol can be successfully used as natural stabilizers in elastomeric materials.

Keywords: *eugenol, cloves, stabilizers, epoxidized natural rubber (ENR), solar aging*

1. Introduction

In recent years, polymers produced from renewable and plant-based sources have gained a lot of attention. Due to the substitution of petroleum products with other substances, as well as environmental protection, the production of innovative polymeric materials from renewable organic raw materials is of academic and commercial interest [1]. Materials made on the basis of natural polymers and plant additives are becoming more and more popular.

Natural rubber (NR) is a renewable material, which combines excellent mechanical and dynamic properties. The main component of NR is cis-1,4-polyisoprene [2]. It was found that the molecular weight of natural rubber has a significant impact on the technological, thermomechanical, dynamic and mechanical properties of vulcanizates. According to Hayeemasae *et al.* [3], the molecular weight of natural rubber seems to be an important factor related to the mechanical properties and strengthening behavior of vulcanizates. The higher molecular weight of the rubber provided greater maximum torque and torque differential as well as better resistance to degradation during processing. As the molecular weight increased, an improvement in rubber stability at elevated temperatures was observed [3]. Materials based on natural rubber have always been and are still in use in a variety of applications, mostly in the form of filled vulcanizates [4, 5]. The chemical modification of NR by epoxidizing natural rubber latex produces a special rubber called epoxidized natural rubber (ENR). ENR rubber has improved properties depending on the degree of epoxidation, as well as increased polarity compared to natural rubber [5, 6].

[*]Corresponding author, e-mail: malgorzata.latos@p.lodz.pl

To obtain elastomeric materials with the expected properties, rubbers are mixed with many additives, including fillers and stabilizers. The introduction of silica as a filler into rubber mixtures is intended to improve the mechanical properties of materials, in particular, the resistance to tearing, cutting, chipping, and cracking. Epoxy moieties in the ENR backbone allow for a chemical reaction with the silanol groups on the silica, thus forming a permanent chemical bond between rubber and silica [4]. In elastomer technology, there is also interest in replacing synthetic stabilizing compounds with natural antioxidants [7]. Synthetic antioxidants based on phenols and amines and 2,2,4-trimethyl-1,2-dihydroquinoline are the most common antioxidants used in the rubber industry. However, due to some environmental problems during their production, attempts are made to replace them with natural alternatives [8].

The aim of the study is the analysis and comparison of the stabilizing effect of eugenol and cloves in epoxidized natural rubber with silica compositions. Cloves and eugenol were selected for the study due to their antioxidant properties described in the scientific literature [9, 10]. Commercial cloves (*Syzygium aromaticum L.*, family *Myrtaceae*) are dried and unexpanded flower buds, which contain a variety of bioactive compounds, such as sesquiterpenes and triterpenoids [11]. Cloves are commonly used as a spice or in many food and pharmaceutical applications. Thanks to its anti-fungal, anti-allergic, anticancer and anti-mutagenic properties, essential oil from the buds of *S. aromaticum* is widely used in medicine, especially in dental care. The main bioactive compound of clove oil – eugenol (4-allyl-2-methoxyphenol) showed strong antimicrobial and antioxidant properties. As a food additive, eugenol has been classified by the food and drug administration (FDA) as a substance generally regarded as safe [12], which gives it the potential to be used also in packaging materials for contact with food.

The data in the literature indicate attempts to use essential clove oil in polymeric materials. Sayed *et al.* [13] produced biofilms based on polyvinyl alcohol (PVA) physically cross-linked with various weight ratios of alkaline cellulose and clove oil. Biofilms have shown a remarkable effect against various pathogens and have been dedicated as a candidate for packaging applications. Other literature reports show the possibility of creating active and biodegradable packaging materials containing clove oil based on bacterial cellulose/poly(3-hydroxybutyrate) (BC/PHB) [14], as well as poly(lactide)/poly(butylene adipate-co-terephthalate) (PLA/PBAT) [15]. Clove oil has also been added to chitosan-based films [16]. Mayer *et al.* [17] proposed the synthesis of polymeric antioxidants using eugenol, which provided excellent processing stability for polypropylene (PP). In addition, a eugenol methacrylate monomer was synthesized that showed the potential to copolymerize with a wide range of different acrylate or vinyl monomers. The antioxidant and antimicrobial properties exhibited by these copolymers open up the prospect of using these materials in various application areas, including the food and biomedical sectors [18].

There is a lack of data in the literature on attempts to use unprocessed cloves in elastomeric materials. Replacing clove oil directly with cloves can reduce the cost of the final polymer product. In addition, there are no publications on the use of eugenol as an antioxidant for elastomers. The scientific novelty of the research is the use of eugenol and cloves in elastomeric materials as antioxidant and anti-aging substances, as well as protecting ENR-based materials against adverse solar aging, elevated temperature and ultraviolet radiation (UV).

2. Experimental

2.1. Materials

The objects of the tests were samples of epoxidized natural rubber with the addition of cloves or eugenol. The following ingredients were used to prepare the elastomeric compositions: epoxy natural rubber with an epoxidation rate of 50% (ENR 50) (Muang Mai Gutherie, Phuket, Thailand); fumed silica Aerosil A380 (Evonik Industries AG, Essen, Germany) – hydrophilic colloidal silica with a specific surface area of 380 m^2/g, used as a filler; DCP-bis(α,α-dimethylbenzyl) peroxide (Merck Schuchard OHG, Hohenbrunn, Germany), acting as an organic crosslinker; natural eugenol ≥98% (Sigma Aldrich, Beijing, China) – an organic compound from the group of phenols, an antioxidant, the main component of clove oil, giving it a characteristic, intense smell; cloves – a popular spice in the form of dried undeveloped flower buds obtained from Madagascar (Kamis, Wolka Kosowska, Poland). The cloves were milled in a ball mill prior to incorporation into the elastomers. The particle size of ground cloves was measured based on optical microscope LAB 40M

(OPTA-TECH Sp. z o.o., Warsaw, Poland) photos and was 5–1200 µm (determined using microscope software MultiScan 8.0 (CSS, Warsaw, Poland)). The particles of ground cloves were characterized by various shapes and a wide range of sizes. Figure 1 shows photos of ground cloves (Figure 1a – camera photo, Figure 1b – photo from an optical microscope with exemplary determined lengths of clove particles), as well as camera photos of ENR samples with eugenol and cloves before and after aging (Figure 1c) and microscopic photos of ENR samples with cloves (Figure 1d), which showed inclusions of various sizes of the natural additive. Table 1 lists the compositions of the polymer compositions.

The weighed components of the elastomeric mixtures were combined using a laboratory rolling mill (parameters: roller length L = 450 mm; roller diameter D = 200 mm; width of the gap between the rollers 1.5–3 mm; rotational speed of the front roller V_p = 16 rpm; friction 1–1.2; average roller temperature

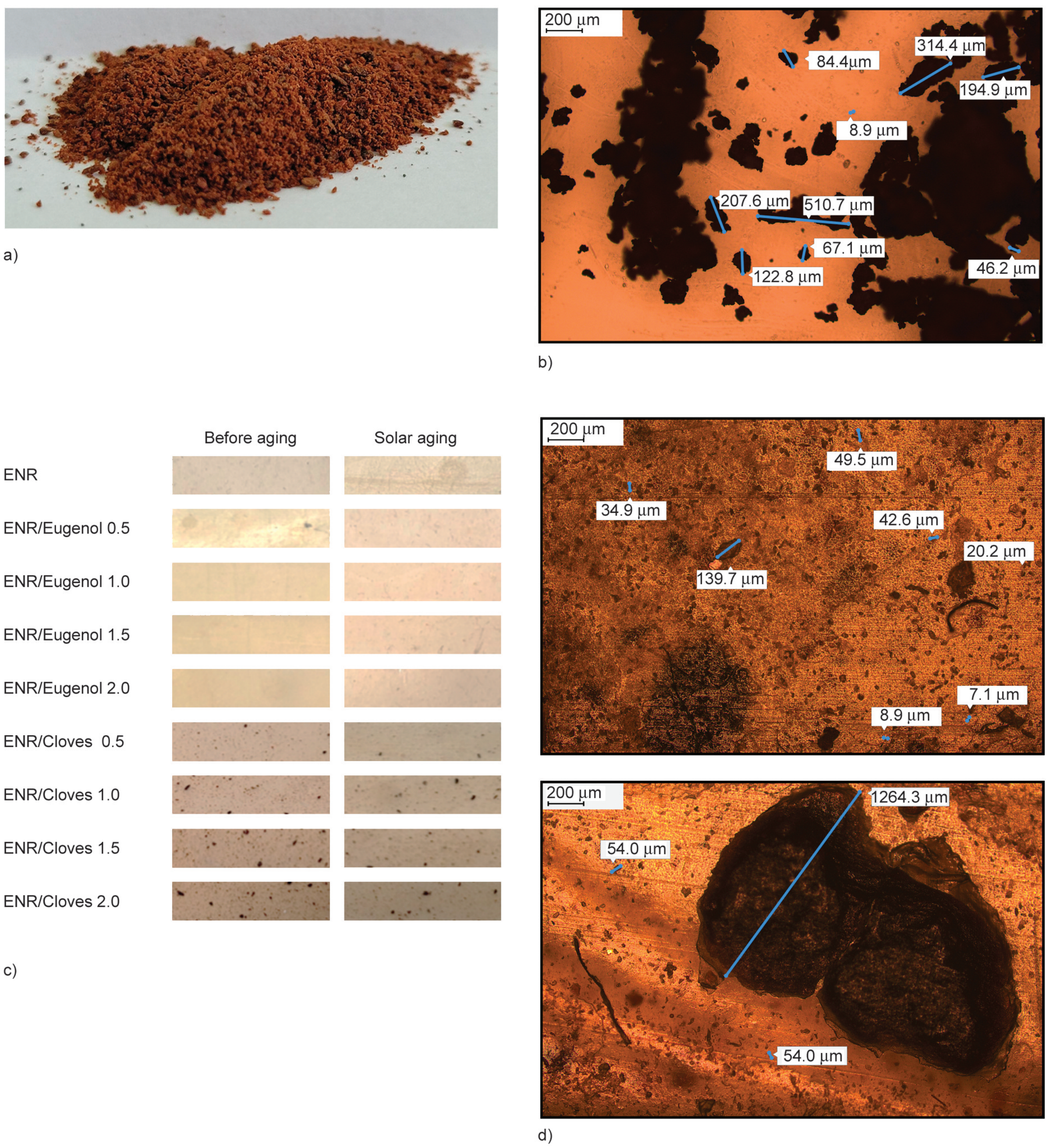

Figure 1. Photos of ground cloves: a) photo from a camera, b) photo from an optical microscope with 100× magnification. Photos of ENR samples: c) photos of samples from a camera before and after solar aging, d) photos of ENR/clove samples from an optical microscope with 100× magnification. Blue arrows mark the lengths of clove particles in the photos (5–1200 µm).

Table 1. The composition of epoxy natural rubber with eugenol and cloves. The composition of prepared samples is given in parts per hundred rubber [phr].

Sample	ENR	Aerosil A380	DCP	Eugenol	Cloves
ENR	100	10	0.5	–	–
ENR/Eugenol 0.5	100	10	0.5	0.5	–
ENR/Eugenol 1.0	100	10	0.5	1.0	–
ENR/Eugenol 1.5	100	10	0.5	1.5	–
ENR/Eugenol 2.0	100	10	0.5	2.0	–
ENR/Cloves 0.5	100	10	0.5	–	0.5
ENR/Cloves 1.0	100	10	0.5	–	1.0
ENR/Cloves 1.5	100	10	0.5	–	1.5
ENR/Cloves 2.0	100	10	0.5	–	2.0

about 25 °C; mixing time approx. 10 min). The next step was the process of vulcanization of rubber mixtures performed using an electrically heated hydraulic press. The parameters of the vulcanization process were as follows: vulcanization time 1h; vulcanization temperature 160 °C; pressure on the press shelves 3 MPa.

2.2. Methods

Ability to reduce free radicals and transition metal ions

The antioxidant activity of cloves and eugenol, understood as the ability to reduce free radicals, was determined by methods using $ABTS^{+•}$ (2,2′-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid) cation radicals (Sigma Aldrich, Saint Louis, USA) and $DPPH^{•}$ (1,1-diphenyl-2-picrylhydrazyl) radicals (Sigma Aldrich, Taufkirchen, Germany). The degree of reduction of $ABTS^{+•}$ or $DPPH^{•}$ radicals was calculated using the Equation (1):

$ABTS^{+•}$ or $DPPH^{•}$ radical reduction degree =

$$= \frac{A_0 - A_1}{A_0} \cdot 100 \qquad (1)$$

where A_0 is the absorbance of the reference sample without plant additive and A_1 is the absorbance of the sample with cloves and eugenol.

The ability of cloves and eugenol to reduce iron ions (test FRAP – ferric reducing antioxidant power; $Fe^{3+} \rightarrow Fe^{2+}$) and copper ions (test CUPRAC – CUPric reducing antioxidant capacity; $Cu2^{+} \rightarrow Cu^{1+}$) was tested. The quantitative ability of cloves and eugenol to reduce transition metal ions was calculated by comparing the change in absorption (ΔA) of the tested sample with the ΔA value determined for standard solutions without plant substances. The obtained ΔA value was directly proportional to the concentration of the antioxidant substance.

For the antioxidant tests ABTS, DPPH, FRAP, and CUPRAC, ethanolic dispersion of cloves and solutions of eugenol were prepared at a concentration of 0.05–0.5 mg/ml. Ground cloves and eugenol were weighed in appropriate amounts put into volumetric flasks, and then covered with ethanol (96%). The detailed methodology of the determinations of ABTS, DPPH, FRAP, and CUPRAC was described by the authors in previous publications [19, 20]. The measurements were repeated three times for each sample and averaged.

Solar aging: For controlled solar aging, the Atlas SC 340 MHG Solar Simulator (AMETEK Inc., Berwyn, IL, USA) equipped with a 2500 W MHG lamp was utilized. The rare earth halogen lamp provided a unique range of solar radiation (ultraviolet, vis, infrared radiation). The irradiance was 1200 W/m^2 at 100% lamp power. Aging at a temperature of 60 °C and humidity of 70% lasted 100 h.

Oxidation induction time (OIT) experiment

The determination of the resistance of the samples to oxidation was performed using the DSC1 differential scanning calorimeter (Mettler-Toledo Sp.zoo., Warsaw, Poland). The elastomer compositions were heated in an inert gas atmosphere to a temperature of 220 °C. After the required measurement conditions were achieved and a stabilization period (5 min at 220 °C, argon), the inert gas was switched to air, and the measurement of oxidation induction time was started. The OIT measurement of ENR samples with cloves and eugenol was performed at 220 °C. The final time (endset) of the oxidation peak was given as the test result.

Determination of the aging coefficient (K)

Based on changes in static mechanical properties of the samples after solar aging, the aging coefficients K were determined. Mechanical properties such as tensile strength (T_S) and elongation at break (E_b) of the elastomer compositions were tested with a Zwick-Roell 1435 device (Zwick Roell Polska Sp.zoo. Sp.k., Wroclaw, Poland). The test parameters were as follows: tensile speed 500 mm/min, initial force 0.1 N. For the experiment, six samples in the shape of a 'dumbbell' with a thickness of about 1 mm and a width of 4 mm were prepared. Using the Equation (2), the aging coefficients K were calculated:

$$K = \frac{(T_S \cdot E_b)_{\text{after solar aging}}}{(T_S \cdot E_b)_{\text{before solar aging}}} \tag{2}$$

where T_S [MPa] – tensile strength, E_b [%] – elongation at break.

Carbonyl index (CI)

Fourier transform infrared (FTIR) spectra were recorded in the 4000–400 cm^{-1} range with a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with diamond Smart Orbit attenuated total reflectance (ATR) sampling accessory (Thermo Fisher Scientific, Waltham, USA). Measurements were made for unaged materials and samples after solar aging at three different points on the materials, and the result was given as an average. Based on the FTIR spectrum, a carbonyl index (CI) which informs about the amount of C=O carbonyl groups formed during the aging process of elastomer compositions was calculated for sample after solar aging according to the Equation (3):

$$\text{Carbonyl index} = \frac{I_{C=O}}{I_{C-H}} \tag{3}$$

where $I_{C=O}$ – intensity of the peak that corresponds to the C=O groups (~1700 cm^{-1}), and I_{C-H} – intensity of the peak that represents the –CH groups (~2800 cm^{-1}).

Change of color after solar aging

The material's colors were described by the CIE-Lab system using a UV-VIS CM-36001 spectrophotometer (Konica Minolta Sensing, Osaka, Japan). Measurements were taken at three different points on the samples and the result was given as an average. The values of color difference (ΔE) were calculated according to the Equations (4):

$$\Delta E = \sqrt{(\Delta a)^2 + (\Delta b)^2 + (\Delta L)^2} \tag{4}$$

where L – lightness, a – red-green, b – yellow-blue. Statistically, it is assumed that: $0 < \Delta E < 1$ – no difference in colors; $1 < \Delta E < 2$ – the difference is noticed only by an experienced observer; $2 < \Delta E < 3.5$ – the difference is also noticed by an inexperienced observer; $3.5 < \Delta E < 5$ – the observer notices a clear difference in colors; $5 < \Delta E$ – the observer perceives the colors as completely different.

3. Results and discussion

The first step was to determine the antioxidant activity of cloves and eugenol. Figure 2 presents the ability of plant materials to reduce free radicals (Figure 2a and Figure 2b) and the ability to reduce transition metal ions (Figure 2c and Figure 2d). Both ethanol dispersions of cloves and solutions of eugenol (at concentrations of 0.05–0.5 mg/ml) exhibited good ability to reduce ABTS and DPPH radicals as well as iron and copper ions. A dispersion of cloves and a solution of eugenol at a concentration of 0.5 mg/ml showed a significant reduction in ABTS radicals of approximately 96%. Cloves were characterized by higher antioxidant activity than eugenol. The greater antioxidant activity of cloves than eugenol was associated with the presence of many active substances in clove buds. According to the data from the literature, the essential oil of cloves of the clove buds contained mainly eugenol (about 65%), and β-caryophyllene (about 14%), eugenol acetate (about 14%), and also in an amount of approximately 1% compounds α-humulene, α-cubene, β-cedrene and caryophyllene oxide [21]. Moreover, clove powder extract was shown to have fourteen phenolic compounds in its phenolic profile, classified into phenolic acids of hydroxybenzoic (catechol and gallic, protocatechuic, and syringic acids) and hydroxycinnamic (caffeic, *p*-coumaric, *trans*-cinnamic, and *trans*-ferulic acids) acids, flavonoids (namely flava-3-nols [(+)-catechin]), flavonols (quercetin, isorhamnetin, and rutin trihydrate), flavones (apigenin 7 glucoside), and stilbenes (resveratrol) [22]. Due to their significant antioxidant properties, both eugenol and cloves can be successfully used as antioxidants in elastomeric materials.

After confirming the antioxidant activity and the ability of cloves and eugenol to reduce transition metal ions that can catalyze aging processes, natural

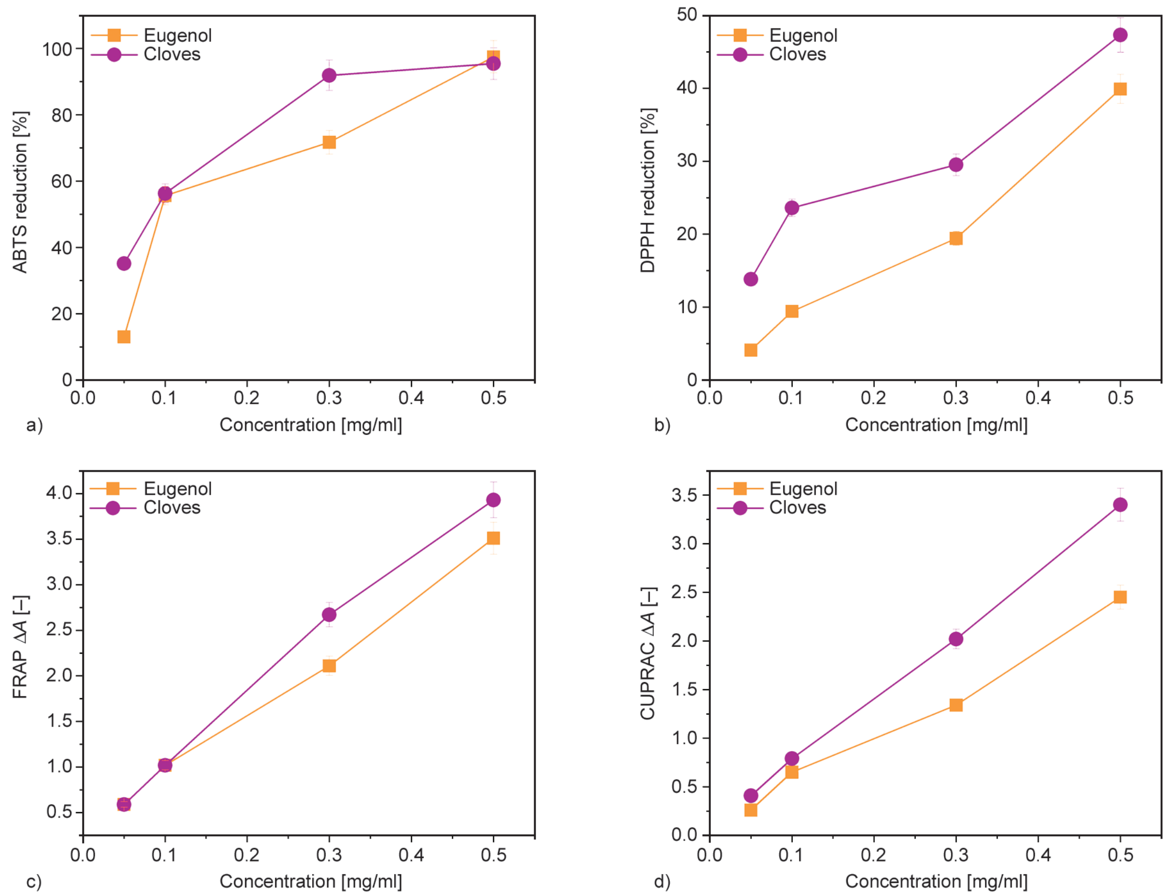

Figure 2. a) Reduction of free radicals ABTS and b) DPPH; c) ability to reduce iron ions FRAP and d) copper ions CUPRAC measured for eugenol and cloves.

substances were introduced into the elastomeric material. The study of elastomers began with the determination of the oxidation induction times of the samples. Figure 3 presents the oxidation induction times (endset – the end of the oxidation peak) of the samples. The ENR reference sample had an OIT of 9.3 min. Compositions with the addition of eugenol

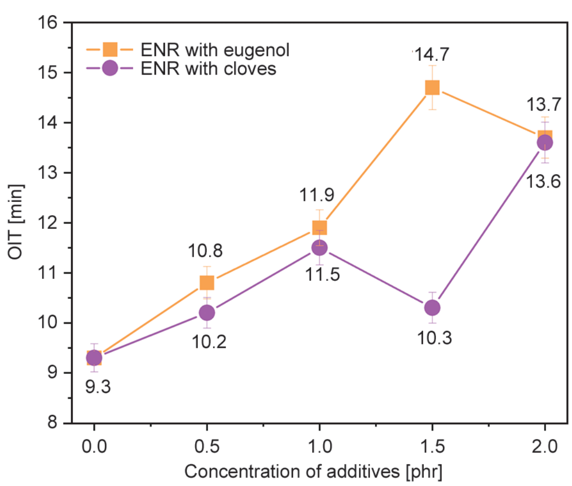

Figure 3. Oxidation induction time (OIT) of ENR composition with eugenol and cloves.

and cloves were characterized by a longer OIT time and, thus, better resistance to oxidation. The best resistance to oxidation was shown by samples containing eugenol in the amount of 1.5 and 2.0 phr and cloves in the amount of 2 phr. Longer OIT times of samples containing higher concentrations of eugenol and cloves may correspond to a higher content of active compounds, which correlated with the determined antioxidant activity.

Subsequent tests were performed on elastomer samples before and after solar aging. Based on the change in the mechanical properties of the samples after aging, the aging coefficients K were determined (Figure 4). Figure 4a summarizes the results of elongation at break for compositions before and after solar aging, and Figure 4b shows the tensile strength of unaged and aged materials. The introduction of eugenol and cloves into the ENR matrix resulted in a decrease in the tensile strength of the samples. The elongation at break of the materials was reduced by the addition of 1–2 phr of cloves. The samples obtained, especially those containing cloves, were characterized by inhomogeneity (Figure 1c and Figure 1d).

To improve the homogeneity of the materials and their mechanical properties, the method of sample preparation could be optimized. The ground cloves can be divided into fractions with a specific grain size (sieve analysis). It would then be worth preparing an elastomer masterbatch with the clove fraction and other ingredients. In the final step, the masterbatch would be combined with the crosslinking substance on the rolling mill. The dispersion of ground cloves in the ENR samples is shown in Figure 1c and Figure 1d. Inclusions of additives and local aggregates were visible in transparent samples. In addition, the plant material itself, by nature, usually does not have fully reproducible composition and properties in a given series of materials. Plant additives, especially cloves, could disturb the continuity of the polymer matrix and affect the cross-linking process, which resulted in a decrease in mechanical properties. Solar aging caused a significant deterioration of the mechanical properties of the materials. The greatest decrease in T_S and E_b values was found for the reference ENR and for the ENR sample containing 0.05 phr of eugenol. The decrease in the value of the mechanical properties of the samples corresponds to the degradation processes taking place in the materials. Based on the mechanical properties, the aging coefficients K of the samples were calculated (Figure 4). When the K value is close to 0, the sample is susceptible to degradation. On the other hand, a K value close to 1 indicates the resistance of the material to degradation caused by solar aging. The reference ENR sample had the lowest aging coefficient (K = 0.23 [–]). Elastomeric compositions with the addition of eugenol and cloves were characterized by higher K coefficients and, thus, better resistance to solar aging. Aging coefficients K of samples with eugenol ranged from 0.29 to 0.44 [–], with the highest values being achieved for materials containing 1 and 1.5 phr of eugenol. The compositions with cloves were characterized by greater resistance to solar aging, as indicated by the aging coefficients K in the range of 0.53–0.60 phr. The better resistance to aging of samples with cloves may be related to the high amount of active compounds in this plant material, as well as the higher antioxidant activity of cloves in comparison to eugenol.

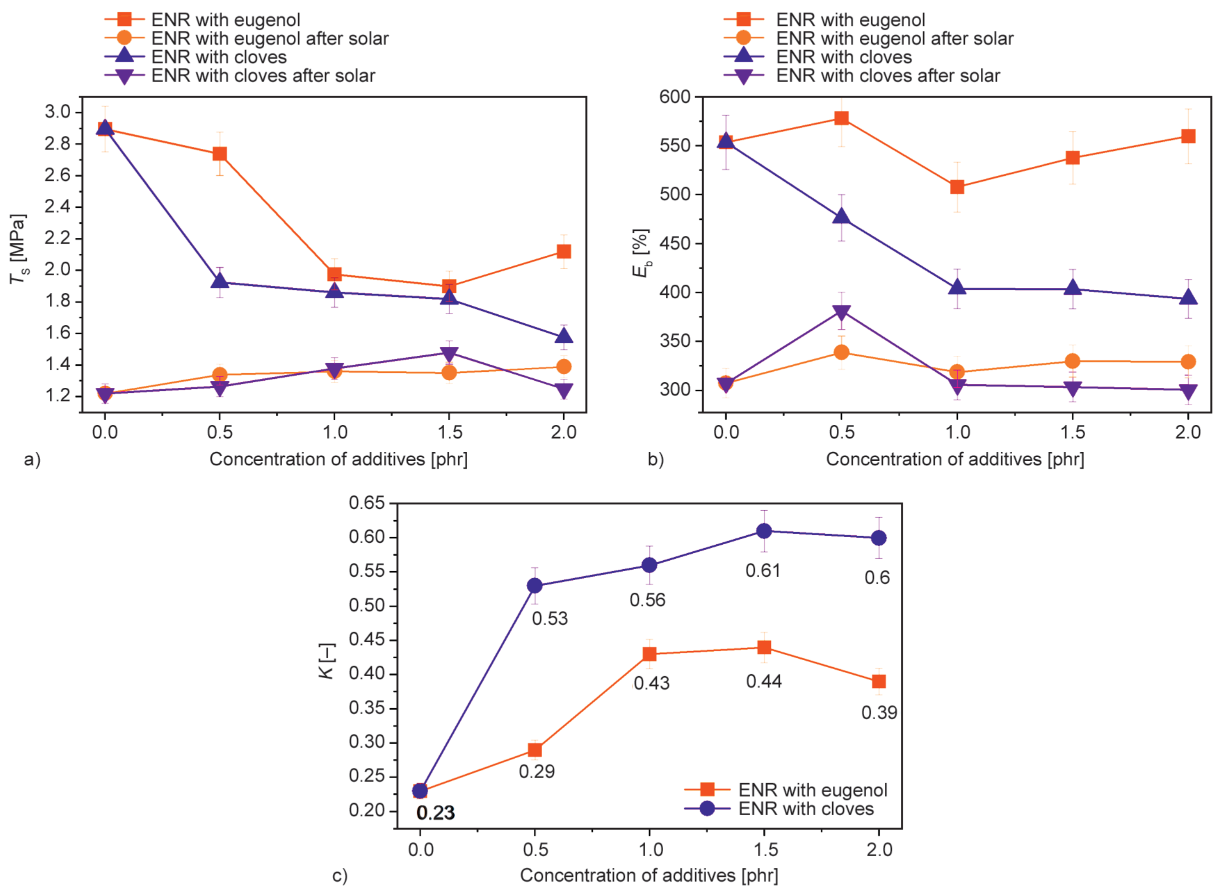

Figure 4. Mechanical properties: a) tensile strength (T_S) and b) elongation at break (E_b) before and after solar aging; c) aging coefficients K of materials.

The next step was to determine the carbonyl indexes after solar aging (Figure 5 and Figure 6). The FTIR spectra (Figure 5) showed bands characteristic of ENR rubber, including a broad band at approximately 3400 cm^{-1} corresponding to OH (hydroxyl) stretching, CH_2 stretching at 2961 cm^{-1}, C=C stretching at 1666 cm^{-1}, CH_2 stretching at 1451 cm^{-1}, CH_3 deformation at 1378 cm^{-1}, COC (epoxy ring) at 870 cm^{-1} and CH olefin wagging at 832 cm^{-1}. Additionally, bands typical of CO (ester) stretching were identified at 1092 and 1064 cm^{-1} [23]. After solar aging, the intensity of the bands at approximately 3430 cm^{-1} increased (identified as OH stretching), which suggested the formation of OH groups related to side reactions during ENR chain cleavage [23]. The bands around 3430 cm^{-1} and around 3350 cm^{-1} can be assigned to the related alcohols and hydroperoxides, respectively [24]. The appearance of absorption bands at approximately 1700 cm^{-1}, identified as C=O (carbonyl) groups of aldehyde and ketone, was characteristic of the formation of chain scissions [23]. Moreover, changes in the intensity of the bands were observed in the area at 1100–1020 cm^{-1} and at approximately 870 cm^{-1} related to the CO and COC functional groups, respectively.

The *CI* indices (Figure 6) were calculated based on FTIR spectra (Figure 5). Higher values of carbonyl indexes indicated greater structural changes in materials related to the appearance of functional groups on the surface of the samples, which are characteristic of the degradation process of elastomeric compositions. ENR vulcanizates with plant additives had lower values of the carbonyl index than those of the reference sample, which indicated that there were minor changes in the structure of the materials caused by the destructive effect of solar aging. This can indicate a good inhibition of the oxidation of materials by the antioxidants used. The lowest carbonyl indices were found for ENR samples that contained the lowest concentrations of eugenol and cloves. This suggests that the smallest structural changes and, thus, the smallest degradation took place in the samples with the lowest antioxidant content. In materials containing higher amounts of cloves, bioadditive

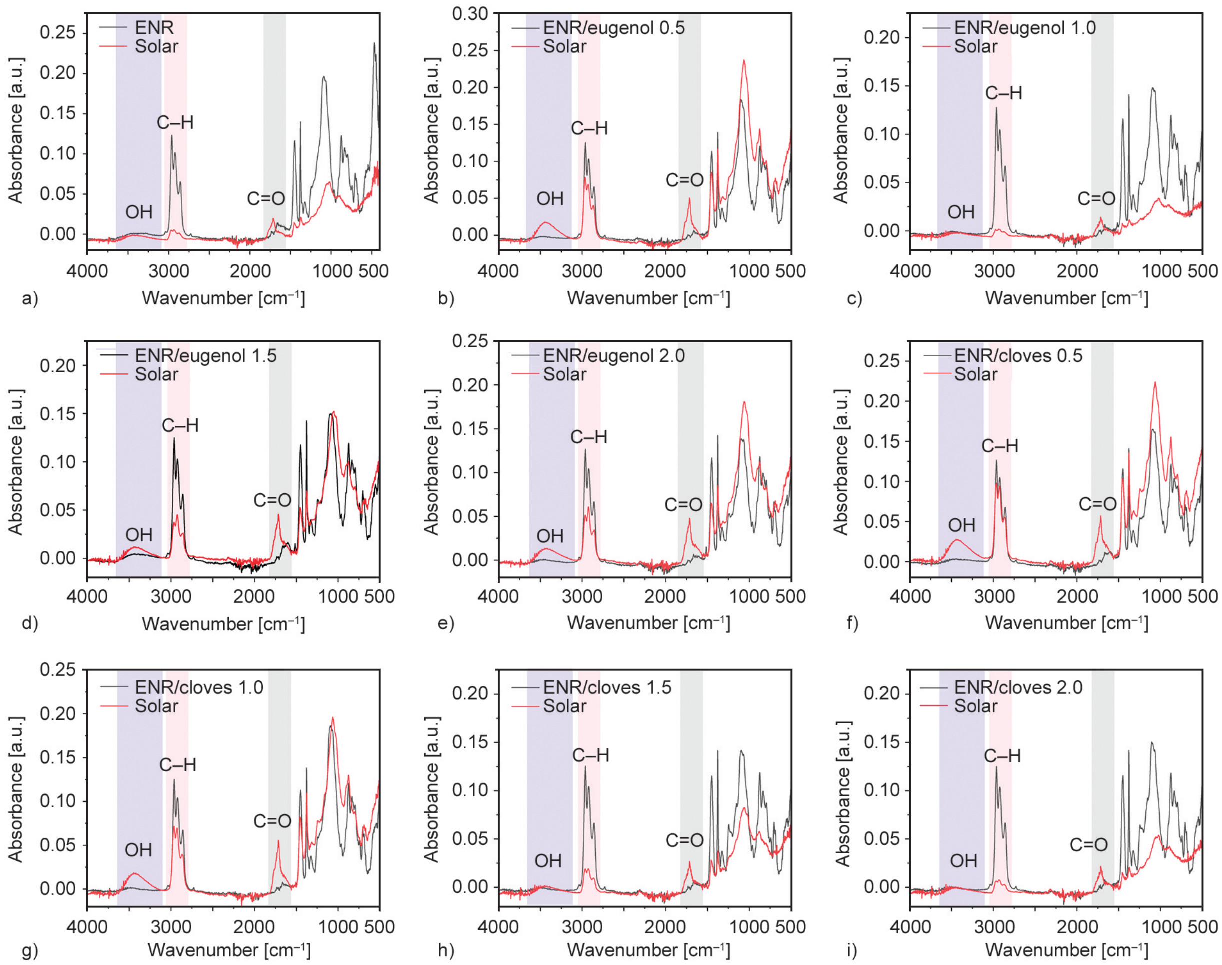

Figure 5. FTIR spectra of ENR (a), ENR with eugenol (b–e) and ENR with cloves (f–i) before and after solar aging.

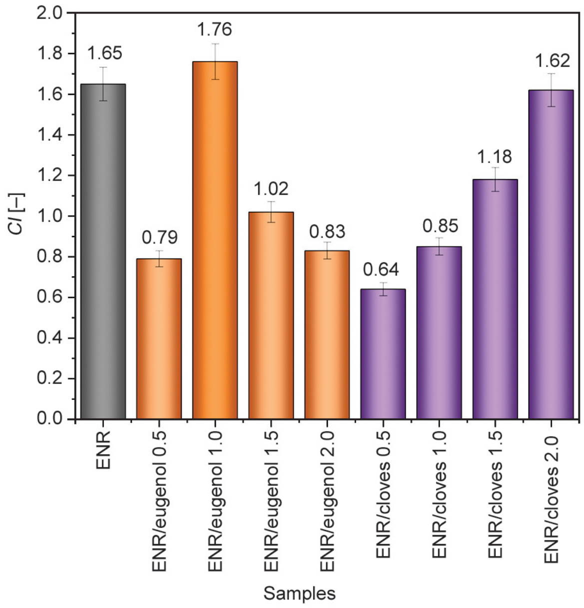

Figure 6. Carbonyl index (*CI*) of samples after solar aging.

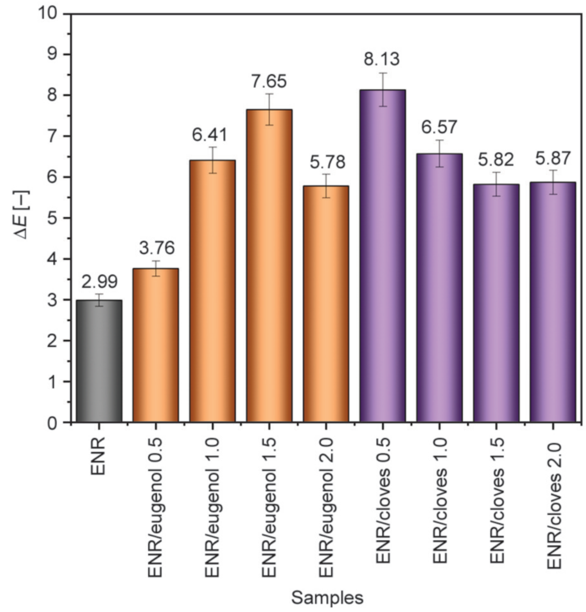

Figure 7. Change of color (ΔE) of ENR samples with eugenol and cloves during solar aging.

degradation processes could be dominant, which was recorded in the FTIR spectra (Figure 5), which may explain the higher *CI* of samples with higher additive content. Clove powder has its own carbonyl content, and if it is added to the ENR composition at a higher concentration, the total carbonyl content of the polymer may increase. However, a larger amount of cloves added to the elastomer provided the addition of a larger amount of antioxidants (including eugenol and polyphenolic compounds), which could protect the material to a greater extent compared to samples containing less phytoactive. Moreover, oxidation of the cloves in the elastomer composition during aging could have protected the polymer from degradation. Unlike samples with cloves, materials with eugenol do not show a clear trend in *CI* results. The highest *CI* value for ENR/eugenol 1.0 and the higher *CI* of the ENR/eugenol 1.5 sample than ENR/eugenol 2.0 may be related to the fact that the FTIR analysis was based on the examination of the sample surfaces at several points in the materials, which had imperfect sample homogeneity. The surface inhomogeneity of the ENR/eugenol compositions suggested by the *CI* results could be improved by optimizing the material production process and immobilizing liquid eugenol on the filler to limit the migration of the additive to the surface of the sample.

The last study was the analysis of the color of the samples after solar aging (Figure 7). The smallest color change was recorded for the reference ENR without plant additives (ΔE =2.99 [–]), which meant that the color difference was noticed by the average observer. The reference sample after solar aging had a clearly cracked and damaged surface (Figure 1c and Figure 1d). The compositions containing cloves and eugenol were characterized by a distinct color change after aging (color change coefficient 5 <ΔE). The greater color change in the samples may be due to the oxidation of natural compounds. The oxidation reaction of plant additives often causes a change in their color, which can also be seen in polymeric materials characterized by high transparency. An interesting phenomenon was observed for materials containing cloves. The sample with the lowest clove concentration had the greatest color change, and with increasing concentration of the additive, the color change of the samples was smaller (Figure 1c and Figure 1d). This result may be related to the stabilizing effect of cloves in higher concentrations, which corresponds to the antioxidant activity of the plant material.

As polymers age, they decompose under the influence of the sum of all chemical and physical factors that affect the material. In the case of solar aging, photodegradation (due to solar radiation), thermodegradation associated with increased temperature, and thermooxidation (due to the presence of air) occur. When enough energy is supplied to the polymer macromolecule (in the form of heat, ionizing and electromagnetic radiation, and mechanical stress) exceeding the critical binding energy (bond dissociation energy), the bonds in the polymer macromolecule can dissociate into free radicals. Free radical decomposition of the polymer leads to its degradation. In the ENR composition with cloves and eugenol, natural additives acted as elastomer stabilizers. In the studies described in this work, both eugenol and cloves showed the ability to reduce ABTS and DPPH free radicals and transition metal ions (Figure 2). Moreover, the antioxidant properties of eugenol and cloves have been examined and confirmed in the literature. The main phenolic compound of clove oil – eugenol and clove oil showed strong antioxidant and radical scavenging activity [25, 26]. Generally, for polyphenolic compounds of plant origin, the principle of antioxidant activity is based on the availability of electrons that neutralize free radicals. Additionally, antioxidant activity is related to the number and nature of the hydroxylation pattern in the aromatic ring. It is generally assumed that the ability to act as a hydrogen donor and inhibit oxidation increases by increasing the number of hydroxyl groups in the phenol ring [25]. In ENR samples, eugenol and polyphenols contained in cloves (phenolic acids including hydroxybenzoic and hydroxycinnamic acids, flavonoids, flavonols, flavones and stilbenes) could limit and delay solar aging of materials by acting as free radical scavengers, reacting with free radicals generated during polymer decomposition. Moreover, these natural compounds *RO*• and peroxyl *ROO*• radicals, prevented and delayed the oxidation reactions of ENR. Figure 8 shows a schematic mechanism of ENR stabilization with eugenol and cloves.

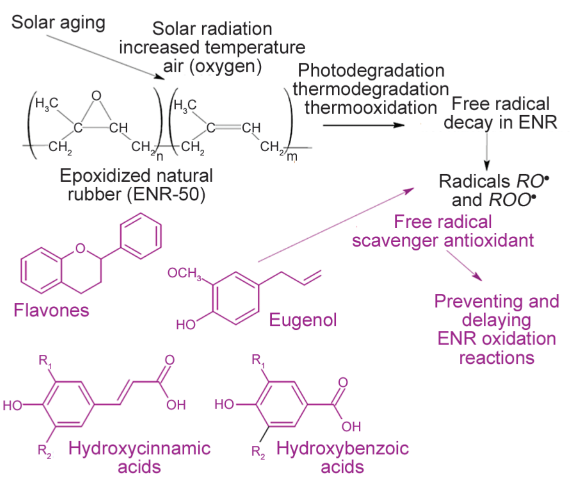

Figure 8. Schematic mechanism of ENR stabilization with eugenol and cloves (containing phenolic compounds, including flavonoids, hydroxycinnamic acids and hydroxybenzoic acids) during solar aging.

4. Conclusions

Cloves and eugenol showed significant antioxidant potential. However, due to the complex composition of active substances, cloves showed a better ability to reduce ABTS and DPPH free radicals, as well as a greater ability to reduce iron and copper transition metal ions. Elastomeric compositions based on ENR with the addition of eugenol and cloves were characterized by better resistance to oxidation, which was suggested by longer OIT oxidation induction times of the samples. Higher solar aging coefficients *K* showed that the addition of cloves and eugenol increased the resistance of the materials to this type of aging. Furthermore, materials containing eugenol and cloves showed less structural changes after solar aging, which corresponded to lower carbonyl index *CI* of compositions with plant additives.

The introduction of cloves and eugenol to ENR-based elastomeric materials resulted in a decrease in the mechanical properties of the samples, which could have been the result of the imperfect homogeneity of the products. On the other hand, high mechanical strength is not always expected from polymeric materials. Taking into account the favorable resistance to oxidation and solar aging, the produced samples can potentially be used as flexible packaging materials.

The research results presented in the paper show that both cloves and eugenol can be successfully used in elastomeric compositions as natural stabilizers protecting polymers against elevated temperature and solar radiation.

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