

Research article

A novel approach to the production of polymer products with enhanced antimicrobial effect and high UV aging resistance

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Abstract. Herein, a novel approach was developed for the introduction of stabilizing compounds into polymers through a pre-impregnation process prior to processing, which is expected to improve their dispersion and, consequently, increase their efficacy. Ethylene-norbornene copolymer (EN) pellets were impregnated with quercetin or rutin in ethanol or a mixture of solvents (ethanol-dioxane (3:1)) for 24 h. Then, EN-based samples containing impregnated pellets were manufactured using a laboratory extruder. The research demonstrated that the materials containing impregnated pellets exhibited improved thermo-oxidation resistance, higher antibacterial effect (the number of dead cells increased from 8 to 59%), and satisfactory photostability. This may be a direct result of their better dispersion degree and their more gradual, controlled release from the EN during operation. If we compare the stabilizing effect of both polyphenols, quercetin was more efficient, which may be attributed to the presence of hydroxyl group at the C3 position in the C ring, which could increase the reactivity of the catechol structure of the B ring. The proposed approach effectively solves the issues that arise during the commonly used processing techniques and may facilitate the broader utilization of natural stabilizers in the polymer industry.

Keywords: bioadditive, cyclic olefin copolymer, impregnation, ultraviolet aging, stabilization

1. Introduction

At the industrial level, the most frequently used substances to stabilize polymer products are those of petroleum origin (*e.g.*, butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), bisphenol A (BPA), or Irganox 1010) [1]. Nevertheless, a few years ago, concerns were raised regarding the potential impact of these additives on human health and the natural environment. A number of scientific studies have demonstrated the migration phenomenon of synthetic stabilizers and their degraded toxic and carcinogenic products, which can be released from polymer products under various operational conditions. For

instance, at elevated temperatures, the diffusion of stabilizing compounds increases, which can result in their higher migration rate from polymers [2]. Lundbäck *et al.* [3] stabilized polyethylene (PE) with 0.1 wt% Santonox R and the produced samples were aged at different temperatures (75–95 °C) in anaerobic and aerobic environments. The authors confirmed that the antioxidant was released into the surrounding medium in a gradual manner as temperature and aging time increased. The migration phenomenon of Irganox 1010 and Irgafos 168 from polyolefins was also documented by Marcato *et al.* [4]. It is important to note that this effect is not

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always convenient in certain applications, such as in baby care products, children's toys, or food packaging areas [5, 6].

In light of the unfavorable consequences associated with the utilization of synthetic stabilizers and the progressively stringent regulations concerning the impact of polymer products on the natural environment, antioxidants of natural origin have emerged as a subject of growing scientific interest in recent years [7]. These compounds can be extracted from plant resources and are distinguished by their relatively low toxicity, as well as their antioxidant, antibacterial, anti-inflammatory, and anticancer features [8–13]. Thus, their use has become a viable strategy to protect the polymer during processing (against thermo-oxidation) and during its lifespan (against thermo- and photooxidation), additionally providing new desired functionalities (e.g., antibacterial effect) and reducing the polymer's environmental footprint. For instance, Zia *et al.* [14] manufactured low-density polyethylene (LDPE) films containing 5 wt% of curcumin. The incorporation of this flavonoid resulted in enhanced thermal stability of the LDPE and, at the same time, improved its water vapor barrier properties. Moreover, these biocomposites demonstrated a notable antioxidant effect against lipid oxidation. In another study, Martínez *et al.* [15] examined the antioxidant and antimicrobial properties of a range of natural extracts, including rosemary, citric, acerola, garlic, paprika, beet, oregano, arugula, lettuce, celery, spinach, watercress, and chard. All of the tested extracts exhibited antibacterial activity against *Clostridium perfringens* and antioxidants properties, with rosemary, oregano, and citric extracts having the greatest ability to inhibit oxidation processes.

Nonetheless, the majority of polyphenols display poor solubility characteristics, which constrains their utility in numerous fields, including medicine and the food industry. Moreover, in the polymer field, the poor compatibility/solubility of the additive within the polymer matrix may be the underlying cause of its migration phenomenon, which consequently affects the overall performance [16, 17]. For example, Ambrogi *et al.* [18] studied the impact of the water extract derived from the bark of French maritime pine (Pycnogenol®) as a potential stabilizing compound for polypropylene (PP). The authors observed that the pronounced heterogeneity of the resulting

sample could potentially affect the mechanical properties of the material subjected to thermal aging (70°C). Similarly, Tátraaljai *et al.* [19] reported that although quercetin, which is among the most potent polyphenols and demonstrates superior antioxidant characteristics, also exhibits some limitations, including poor homogeneity within the polyethylene matrix. This issue was addressed by combining quercetin with a secondary antioxidant (Sandostab P-EPQ). The resulting interaction enhanced the dispersion and efficacy of quercetin. Furthermore, in addition to the conventional blending of flavonoids with a polymer matrix in an extruder, laboratory mixers, *etc.*, some scientists have proposed as an alternative the use of a method of impregnating the manufactured polymer samples with stabilizing substances. Latos-Brozio and Masek [20] employed the solvent impregnation method to stabilize polylactide (PLA) and polyhydroxyalkanoate (PHA) with polyphenols derived from *Cistus Linnaeus* and *Juglans regia Linnaeus* Walnut Green Husk. Nevertheless, the calculated impregnation efficiency with both extracts was only around 10%. In other studies concerning the impregnation of polymer products with antioxidants, a heterogeneous distribution of these compounds was observed when polyethylene terephthalate/polypropylene (PET/PP) films were impregnated with olive leaf extract or foamed polycaprolactone was impregnated with quercetin [21, 22].

Therefore, the aim of this work was to employ the pre-impregnation process before processing as an innovative approach to introduce stabilizing compounds into polymers, which is expected to improve their dispersion and, consequently, increase their efficacy. The impact of this process on the release of antioxidants (quercetin, rutin) from the polymer, their antibacterial activity, thermal resistance and their effect during long-term exposure to ultraviolet radiation, was studied. Ethylene-norbornene copolymer (Topas E-140) was applied as the polymer matrix in this study, which is an ideal model material for studying the anti-aging effect of various stabilizers due to its high transparency and lack of the need for cross-linking agents that could disturb the interpretation of the obtained results. The proposed approach can effectively solve the issues of commonly used processing methods and may lead to a more widespread use of natural stabilizers in the polymer industry.

2. Experimental

2.1. Materials

Ethylene-norbornene copolymer (TOPAS E-140) from Topas Advanced Polymers GmbH (Raunheim, Germany) was used as a polymer matrix. Quercetin hydrate ($\geq 95\%$) and rutin hydrate ($\geq 94\%$) from Sigma-Aldrich Chemie GmbH (Steinheim, Germany) were applied as stabilizing compounds. The chemical structures of the stabilizers and the polymer matrix used are shown in Figure 1. Ethanol (96%) and 1,4-dioxane (p.a.) from Chempur Sp. z o.o. (Piekary Śląskie, Poland) were used as solvents in the impregnation process.

2.2. Impregnation of ethylene-norbornene copolymer (EN) pellets

EN polymer pellets were impregnated with quercetin and rutin, as shown in Figure 2a. 100 g of polymer pellets were placed in a round bottom flask to which 3 g of antioxidant was added, and the whole was poured with 200 ml of ethanol or a mixture of solvents (150 ml of ethanol and 50 ml of dioxane). The second approach, involving the use of two solvents, was to test whether the dioxane content, in which the EN polymer has a greater tendency to swell than in ethanol, would lead to a more effective impregnation process. The impregnation was carried out for 24 h using a mechanical stirrer (150 rpm), and the flask was placed in a heating mantle (40 °C). After this time, the flask with the impregnated pellets was placed in a rotary evaporator to remove the solvent. The temperature in the water bath was 40 °C, and the process was performed at an initial pressure of 175 mbar. Table 1 shows a simple comparison of the

prepared materials and the calculated impregnation efficiency values, which were determined from the mass changes of the components.

2.3. Processing of EN-based samples

EN-based samples containing impregnated pellets (5 wt% of QUE(IM-ET), QUE(IM-ET/DI), or RUT(IM-ET)) were manufactured using a laboratory extruder from Zamak Maercator Sp. z o.o. (Skawina, Poland) equipped with a single-screw (diameter of 25 mm, L/D ratio of 24) (Figure 2b). The processing temperature was 150 °C, and the samples were extruded at a rotational speed of 40 rpm. Moreover, for comparative purposes, a material with the addition of rutin, which was traditionally introduced during extrusion in the powder form, was produced. The prepared EN-based samples were cooled at room temperature. EN-QUE(IM-ET), EN-QUE(IM-ET/DI), and EN-RUT(IM-ET) are samples containing impregnated polymer pellets, while EN-RUT(NON-IM) is material with the addition of antioxidant in powder form.

2.4. Accelerated ultraviolet (UV) aging tests

The produced samples were subjected to long-term exposure (300, 600, and 900 h) to UVA radiation and elevated temperature in a special chamber (UV 2000) from Atlas Material Testing Technology LLC (Mount Prospect, IL, USA) according to the PN-EN ISO 4892-3:2006 standard. The aging process included alternating repeated cycles: day cycle – temperature 60 °C, radiation intensity 0.77 W/m² ($\lambda = 340$ nm), duration of 8 h and night cycle – temperature 50 °C, no radiation, duration of 4 h.

Table 1. Composition and efficiency of the impregnated EN pellets.

Sample	EN [g]	Quercetin [g]	Rutin [g]	Ethanol [ml]	Dioxane [ml]	Impregnation efficiency [%]
QUE(IM-ET)	100.014	3.000	0	200	0	45.6
QUE(IM-ET/DI)	100.122	3.004	0	150	50	47.5
QUE(RUT-ET)	100.003	0	3.000	200	0	53.5

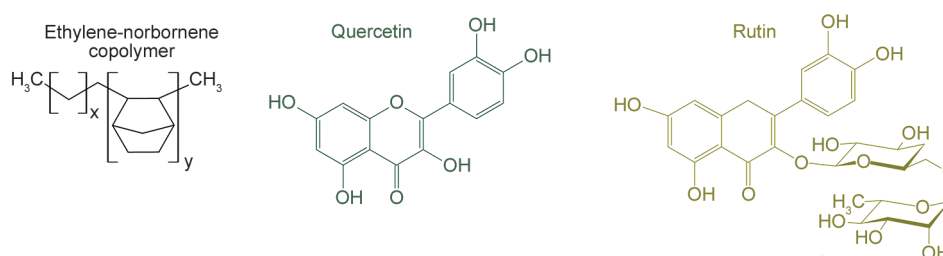


Figure 1. Chemical formulas of the components used in this study.

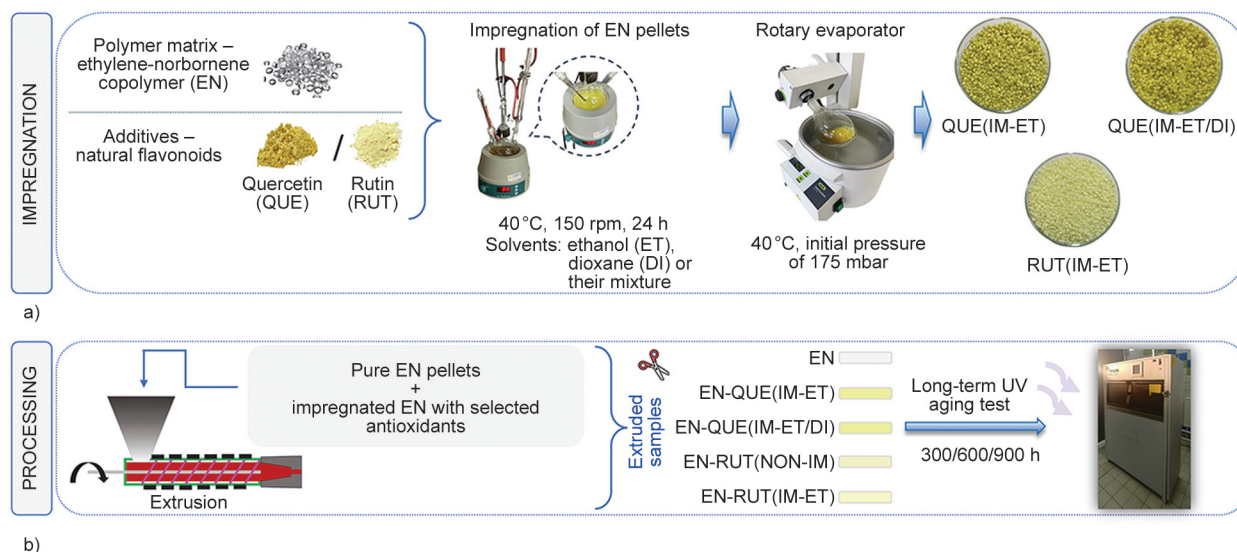


Figure 2. Impregnation process of EN polymer pellets with natural antioxidants (a), and the processing stage of EN-based samples (b).

2.5. Characterization techniques

2.5.1. Thermogravimetric analysis (TGA)

The thermal stability of the prepared samples was assessed using a Mettler Toledo TGA/DSC1 device (Mettler Toledo GmbH, Greifensee, Switzerland). The tests were carried out in the temperature range of 25–600 °C at a heating rate of 20 °C/min in a synthetic air atmosphere (gas flow – 60 cm³/min).

2.5.2. Oxidative-induction time (OIT) determination

One of the most frequently employed techniques for evaluating the stability and efficacy of a stabilizing system for a polymer is the determination of the OIT parameter. This test was conducted using a differential scanning calorimeter (DSC1) from Mettler Toledo GmbH (Greifensee, Switzerland) and a STARE system (Version 10, 2010) according to the ISO 11357-6: 2018 standard [23]. The measurements were carried out in an air atmosphere (air flow rate: 50 ml/min) at a temperature of 240 °C for a period of 60 min.

2.5.3. Microbial colonization assessment

Flow cytometry was employed to evaluate microbial colonization. A suspension of *E. coli* bacteria with a volume of 20 µl was applied to the surface of the tested EN-based materials. The prepared samples were then incubated at 37 °C for 60 min. Subsequently, the bacterial suspension was removed from the sample surface and subjected to a staining procedure in accordance with the ‘Viability/Cytotoxicity Assay Kit for Bacteria Live and Dead Cells’ test

from ImmuniQ (Żory, Poland). Following incubation with fluorescent reagents, the results were read using an Accuri C6 flow cytometer, and the % content of live and dead bacteria in the suspension was then analyzed using BD CSampler software. Moreover, the test was standardized using two control materials: a positive control (+) (dead microbial cells treated with 98% ethanol) and a negative control (–) (unmodified suspension of microorganisms). For each tested sample, three test repetitions were conducted.

2.5.4. Migration of flavonoids from the EN polymer

The migration of flavonoids, introduced in the impregnated pellets and powder forms into the EN polymer, was tested in accordance with the EN 13130 standard. The release of these compounds was examined in an ethanol model solution at a temperature of 25 °C. Samples measuring 2.1×2.1 cm were immersed in 10 ml of ethanol and incubated at 25 °C for 28 days. To ascertain the release of the flavonoids over time, 2 ml of these solutions in contact with the tested materials were collected at 2, 4, 7, 14, and 28 day intervals. The solutions were analyzed using a UV-Vis spectrophotometer (Evolution 220) from Thermo Fisher Scientific Inc. (Waltham, MA, USA) in the wavelength range of 190–1100 nm, with pure ethanol serving as the blank. Furthermore, standard solutions of quercetin and rutin (of known concentration) were prepared, allowing for the calculation of the concentrations of the migrating compounds.

First, the molar absorption coefficients were calculated according to the Equation (1). Subsequently, the concentrations of migrating flavonoids into the model fluids were determined using the transformed version of Equation (1):

$$\varepsilon = \frac{A}{c \cdot l} \quad (1)$$

where ε – molar absorption coefficient [$\text{dm}^3/(\text{mol} \cdot \text{cm})$], A – absorbance of the standard solution at a specific wavelength [–], c – concentration of the standard solution [mol/dm^3], l – cuvette thickness [1 cm].

2.5.5. Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra were recorded using a Nicolet 6700 spectrometer from Thermo Fisher Scientific Inc. (Waltham, MA, USA). It was equipped with a smart orbit attenuated total reflectance (ATR) diamond crystal sampling tool. Absorbance measurements were performed in the range of $4000\text{--}400\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} (64 scans). Subsequently, the carbonyl index values were calculated in accordance with the Equation (2):

$$CI = \frac{A_{\text{C=O}} (\sim 1720\text{ cm}^{-1})}{A_{\text{C-H}} (\sim 2920\text{ cm}^{-1})} \quad (2)$$

where CI – carbonyl index [–], $A_{\text{C=O}}$ – absorbance intensity of the carbonyl group peak [–], $A_{\text{C-H}}$ – absorbance intensity of the methylene group peak [–].

2.5.6. Color change measurements

The color change of EN-based samples subjected to UV aging tests was measured using a UV-Vis spectrophotometer (CM-3600d) from Konica Minolta Sensing (Osaka, Japan). This test was conducted in compliance with the PN-EN ISO 105-J01 standard. The color difference (ΔE) was calculated in accordance with Equation (3), wherein the coordinates a^* , b^* , and L^* represent the values in the CIE-Lab color space:

$$\Delta E = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2} \quad (3)$$

2.5.7. Mechanical properties

Tensile strength (TS) and elongation at break (Eb) were examined using a Zwick Roell Z005 device (Zwick GmbH, Ulm, Germany). The measurements were carried out on the ‘dumbbell’-shaped specimens

(type 2) with a thickness of 1 mm and a width of 4 mm, in accordance with the PN-ISO 37:1998 standard. The specimens were prepared from the extruded samples using a Zwick Roell cutting press with a standardized blade. Six measurements were performed for each material. The stretching speed was 500 mm/min, and the initial force was 0.1 N. Based on the TS and Eb results, the aging factor (A_f) values were calculated using Equation (4):

$$A_f = \frac{(TS \cdot Eb)_{\text{after aging}}}{(TS \cdot Eb)_{\text{before aging}}} \quad (4)$$

3. Results and discussion

3.1. Thermal stability of the EN-based

materials containing natural stabilizers

The thermal stability of polymers is often enhanced through the incorporation of antioxidants. Herein, the impact of quercetin and rutin, introduced into the EN polymer in the impregnated pellets and powder form, on its thermal stability was investigated. The obtained results are presented in [Figure 3](#) and [Table 2](#).

It was observed that all of the proposed stabilizing systems resulted in an increased thermal resistance of the EN polymer. The initial temperature of thermal decomposition ($T_{5\%}$) for the pure EN was 403°C . In contrast, for the remaining samples, this value was higher by $5\text{--}27^\circ\text{C}$. The greatest improvement in thermal resistance was observed for the EN-RUT(IM-ET) and EN-QUE(IM-ET) samples, exhibiting $T_{5\%}$ values of 430 and 426°C , respectively. Furthermore, it is noteworthy that the EN demonstrated enhanced thermal stability due to the incorporation of quercetin and rutin, particularly in the form of impregnated pellets where ethanol was utilized as a solvent. The observed enhancement in the resistance of EN to elevated temperatures resulting from the incorporation of specific polyphenols can be directly ascribed to the chemical structure of these compounds, particularly the abundance of hydroxyl (OH) groups, which are capable of scavenging free radicals within the EN fragments. Moreover, it is important to highlight that the higher thermal stability observed in the EN-RUT(IM-ET) material containing impregnated pellets, in comparison to the EN-RUT(NON-IM) sample, may be attributed to the controlled and gradual release of rutin from the polymer matrix, which is a consequence of the pre-impregnation process prior to processing. In the

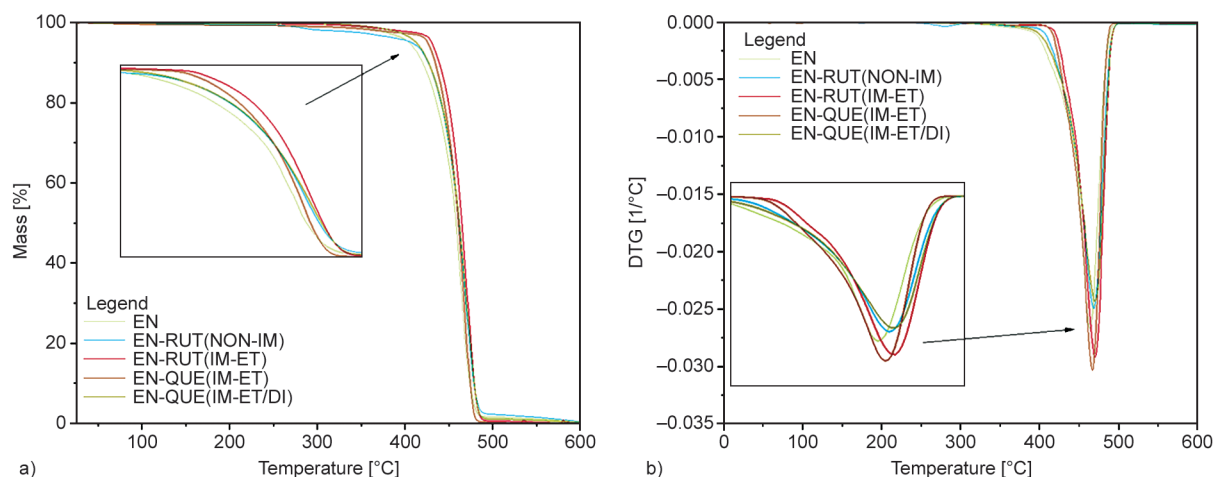


Figure 3. Thermogravimetric analysis (TGA) (a) and derivative thermogravimetry (DTG) curves (b) of the tested samples.

Table 2. Mass loss temperatures (determined on the basis of TGA curves), where $T_{x\%}$ is a temperature at which the mass change is $x\%$ (5, 20, 50 or 90%), and the temperatures at which the rate of weight loss was maximum ($T_{d,max}$) settled by the peak on the DTG curves.

Sample	$T_{5\%}$ [°C]	$T_{20\%}$ [°C]	$T_{50\%}$ [°C]	$T_{90\%}$ [°C]	$T_{d,max}$ [°C]
EN	403	435	457	472	463.0
EN-QUE(IM-ET)	426	444	460	474	466.0
EN-QUE(IM-ET/DI)	412	441	462	478	470.5
EN-RUT(NON-IM)	408	441	460	477	467.5
EN-RUT(IM-ET)	430	448	465	478	470.5

remaining stages of thermal decomposition ($T_{20\%}$, $T_{50\%}$ and $T_{90\%}$), the tendency for the received values was analogous to that for a mass loss of 5%.

In addition, in recent years, a lot of research has been carried out on natural stabilizing substances due to the negative impact of synthetic stabilizers on both human health and the environment. In our previous work [24], the influence of synthetic stabilizers Ri-anox 626, 1726 and 3114 on the thermal stability of EN polymer was investigated, for which the $T_{5\%}$ values were 421, 423 and 408 °C, respectively. Therefore, comparing these values with the results obtained in this publication, it is evident that the pre-impregnation approach allows for obtaining natural stabilizing systems that are characterized by even higher thermal stability compared to the commonly used synthetic stabilizers.

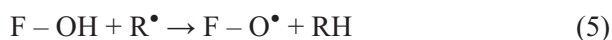
The second test conducted to evaluate the resistance of the manufactured EN-based materials to the thermo-oxidation process was the determination of oxidative induction time (OIT). The obtained results are presented in Table 3. As with the TGA analysis, it was observed that the application of all additives resulted in a delay to the thermo-oxidative degradation of the ethylene-norbornene copolymer. The oxidation of

the pure EN polymer commenced at 1.41 min and concluded at 5.93 min. Conversely, the incorporation of quercetin in the form of impregnated pellets (ethanol utilized as a solvent) permitted an almost 12 fold postponement in the commencement of this process (16.55 min), and the sample underwent complete oxidation after 24.40 min. In comparison to the results obtained with EN-QUE(IM-ET), the effectiveness of the pre-impregnation process using a mixture of solvents (ethanol and dioxane) was found to be slightly lower. Furthermore, the OIT results for materials with the addition of rutin revealed enhanced thermo-oxidative resistance for the EN-RUT(IM-ET) sample, which contained impregnated pellets. In this case, the oxidation onset and endset were observed to be 11.25 and 16.11 min, respectively. As posited by Koontz *et al.* [25], the antioxidant activity is anticipated to be greater as it is more uniformly dispersed into the polymer. Thus, based on this analysis, it can be inferred that the proposed method of introducing polyphenols allows for more optimal antioxidant dispersion in the polymer matrix with its more gradual release and, consequently, for enhanced stability of the polymeric material in a thermo-oxidizing environment.

Table 3. OIT values determined by DSC method.

Sample	Oxidation peak parameters		
	Onset [min]	Maximum [min]	Endset [min]
0EN	1.41	2.28	5.93
EN-QUE(IM-ET)	16.55	19.80	24.40
EN-QUE(IM-ET/DI)	12.52	13.83	17.13
EN-RUT(NON-IM)	9.60	10.05	14.52
EN-RUT(IM-ET)	11.25	12.60	16.11

The stabilizing effect of quercetin and rutin on ethylene-norbornene copolymer may be attributed to their chemical structure and the presence of active OH groups in the phenolic rings, which effectively delayed the thermo-oxidative degradation process. These substituents possess the capacity to react with free radicals generated during exposure to oxygen and elevated temperatures, thereby impeding further degradation through the following reaction mechanism – Equation (5) [26]:



Furthermore, the higher thermo-oxidative stability of materials containing quercetin may be attributed to its lower molecular weight and higher diffusion coefficient in comparison to the rutin molecule. This leads to enhanced chain mobility and heightened reactivity in free radical scavenging, as observed in the case of samples with the addition of quercetin. However, the somewhat reduced mobility of rutin constrains its capacity to interact with macroradicals and peroxides generated within the polymeric chains, thereby limiting its efficacy in mitigating thermo-oxidation.

3.2. Microbial colonization assessment for the EN-based samples

Bacterial infections have a profound impact on public health. They are an indirect cause of infectious diseases, and their resistance to antibiotics represents a significant global threat to food security and public health [27, 28]. The development of novel antibacterial materials for use in biomedicine, food packaging, and the textile industry has become a crucial area of research. As evidenced in the literature, the most commonly used particles with antibacterial properties include Ag, TiO₂, Cu, and ZnO [29]. In this study, the effect of quercetin and rutin incorporated into the EN polymer on its antibacterial activity against a gram-negative *Escherichia coli* bacteria

was analyzed. The results of the microbial colonization assessment are presented in Figure 4. Following the treatment of EN-based surfaces with a suspension of *E. coli* bacteria, the number of dead cells was observed to range from 8 to 59%, while for the reference EN, it was only 11%. The analysis of the impact of the additives utilized revealed a markedly diminished antibacterial efficacy in materials containing rutin. However, the application of rutin in the form of impregnated pellets resulted in an increase in the percentage of dead cells, from 8 to 14%, in comparison to the sample with rutin in conventional powder form. Conversely, the materials with the addition of quercetin demonstrated the highest antibacterial activity, with the EN-QUE(IM-ET/DI) exhibiting the greatest efficacy, where a mixture of ethanol and dioxane was used during pre-impregnation process (the amount of dead microbial cells was 59%).

In recent years, many researchers have directed their attention towards the development of novel substituents for antibiotics that are already in clinical use. Natural flavonoids have garnered particular interest due to their notable antibacterial activity against a multitude of pathogenic microorganisms [30–32]. Xie *et al.* [33] reported that the efficiency of flavonoids as antibacterial agents may depend on their chemical structure. For instance, the presence of hydroxyl (OH) groups on aromatic rings or hydrophobic components, such as oxygen-containing heterocyclic moieties and alkyl chains, can enhance their antibacterial capacity. The antibacterial mechanism of these compounds may include the inhibition of nucleic acid synthesis, biofilm formation, energy metabolism, cytoplasmic membrane damage, alteration of membrane permeability, and the weakening of pathogenicity [34]. Conversely, Yuan *et al.* [35] posited that the antimicrobial effect provided by flavonoids may be related to their lipid-water partition constituents or polarities.

Herein, in the case of samples containing quercetin, which demonstrated the highest antibacterial activity, it can be postulated that the functional groups of this polyphenol may interact with *E. coli* cells, thereby disturbing their function and morphology. The deterioration of the permeability of bacterial cell walls impedes the balanced exchange of contents between cells and the environment, affecting protein synthesis, inhibiting nucleic acid synthesis, and reducing enzyme activities, which ultimately results in the death of these bacteria [36].

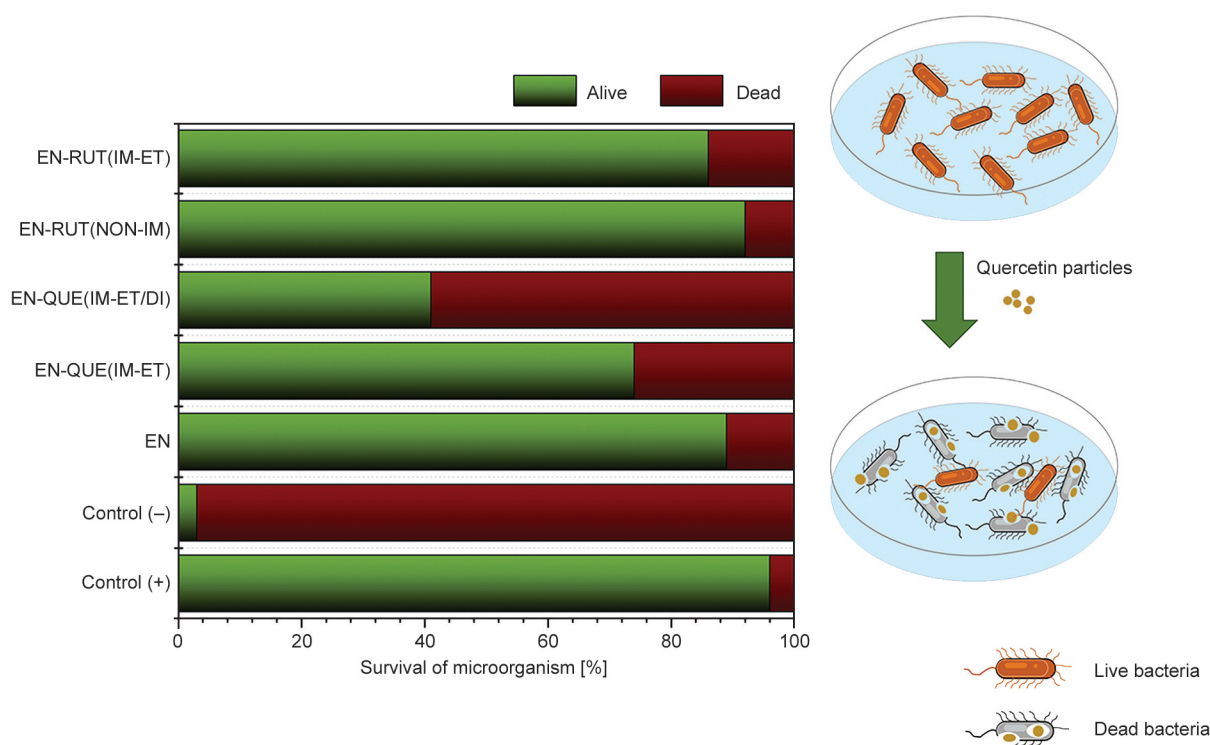


Figure 4. Microbial colonization results for the EN-based materials.

3.3. Migration of flavonoids from the polymer matrix

Currently, all polymer products are formulated with a range of additives that serve to enhance their functionality. Nevertheless, the potential of these compounds to contaminate food, water, or soil has been widely documented in the literature [37, 38]. Several studies have demonstrated the quantification of migrated stabilizers from a variety of polymers, with the majority of these research focusing on PP and LDPE [39–41]

In this study, the release of quercetin and rutin from the EN polymer, in the form of either powder or impregnated pellets, was examined by placing the samples in ethanol, which is a suitable simulant for fatty foods. The concentrations of substances migrating to the surrounding environment were calculated based on the UV-Vis spectra obtained for standard solutions of quercetin and rutin with a known concentration. The obtained results are shown in Figure 5. It is evident that the migration of the antioxidant introduced into the EN in traditional powder form was significantly greater compared to samples for which the pre-impregnation process was applied. The concentration of released rutin in the EN-RUT(NON-IM) material after two days of incubation was 0.09 mmol/l, and after 28 days, it reached approximately 0.12 mmol/l. In contrast, the quantity

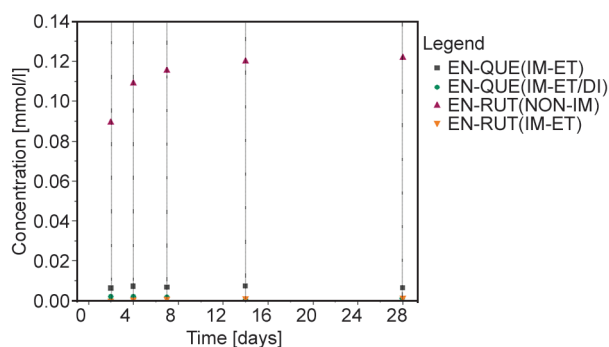


Figure 5. Migration of flavonoids from the EN within a period of 28 days.

of migrating compounds in the other tested samples remained below 0.01 mmol/l throughout the study period. It may be inferred from these findings that the proposed pre-impregnation method, prior to processing, results in a more controlled release of active substances, which may be of particular significance in terms of further enhancing the stabilizing effect of these materials during their service life. The development of stabilizers with high effectiveness and anti-migration performance has attracted the attention of numerous researchers. According to Li *et al.* [42] this can be accomplished in three ways: by immobilizing the antioxidant on inorganic compounds, by increasing the molecular weight of the antioxidant through grafting or polymerization, and by intercalation-mediated assembly. However, the strategy

proposed in this work, which involves pre-impregnating antioxidants on polymer granules prior to processing, also yielded comparable anti-migration outcomes. The technique employed is straightforward and cost-effective. Furthermore, it is important to note that the produced materials comply with the requirements set forth in EU Regulation No. 10/2011 (on plastic materials and articles intended to come into contact with food) [43].

3.4. Effect of the proposed pre-impregnation process with flavonoids prior to processing on the aging behavior of the EN polymer

For the substantiation of the validity of the proposed approach to introducing flavonoids into the polymer via the pre-impregnation process, the produced samples were subjected to accelerated aging tests in an ultraviolet chamber for 300, 600, and 900 h. The conducted research enabled the determination of whether, as a consequence of enhanced dispersion and more controlled release of the stabilizer from the polymer matrix, the stabilizing impact of these compounds would be augmented.

3.4.1. Determination of surface changes as a result of accelerated UV aging tests

The photooxidation of polymers is a process that provokes both chain scission and cross-linking reactions, which can result in a significant decline in their original performance. Initially, FTIR spectroscopy was employed to evaluate the impact of flavonoids in the form of impregnated pellets or powder on the surface oxidation of the EN polymer during its exposure to radiation and elevated temperature. This

method enabled the identification of alterations in chemical structure that occurred throughout the entire UV aging period. Figure 6a presents the FTIR spectrum for the reference EN polymer, both in its original state and following exposure to UV radiation. In the case of the unaged EN, four characteristic absorption peaks were identified, with the maxima occurring at 2916, 2847, 1459, and 715 cm^{-1} . These peaks were assigned to the given chemical moieties in Table 4. Upon analysis of the spectra obtained following accelerated photoaging tests, the formation of new absorption bands at a wavelength of 1706 cm^{-1} and a second, much broader band with a maximum at 1171 cm^{-1} was observed. These bands are characteristic photodegradation products of polyolefins. Figure 6b provides a detailed illustration of the absorption band within the wavelength range of 1900–1500 cm^{-1} . It is evident that the exposure of the EN to UV light results in the formation of double bonds ($\text{C}=\text{C}$), ketone ($\text{C}=\text{O}$) and ester ($\text{COO}-$) groups. Furthermore, the second band with a maximum at 1171 cm^{-1} also corresponds to the formation

Table 4. Tabularized values of wavenumbers attributed to the specific chemical moieties.

Wavenumber [cm^{-1}]	Chemical group	References
3600–3000	Hydroxyl (OH) group	[44]
2916	C–H stretching (asymmetric)	[45]
2847	C–H stretching (symmetric)	[45]
1732	Ester and/or aldehyde group	[46]
1709	Ketone ($\text{C}=\text{O}$) group	[47]
1550–1650	$\text{C}=\text{C}$ double bonds	[48]
1459	C–H bending	[48]
1171	C–O stretching	[46]
715	C–H rocking	[48]

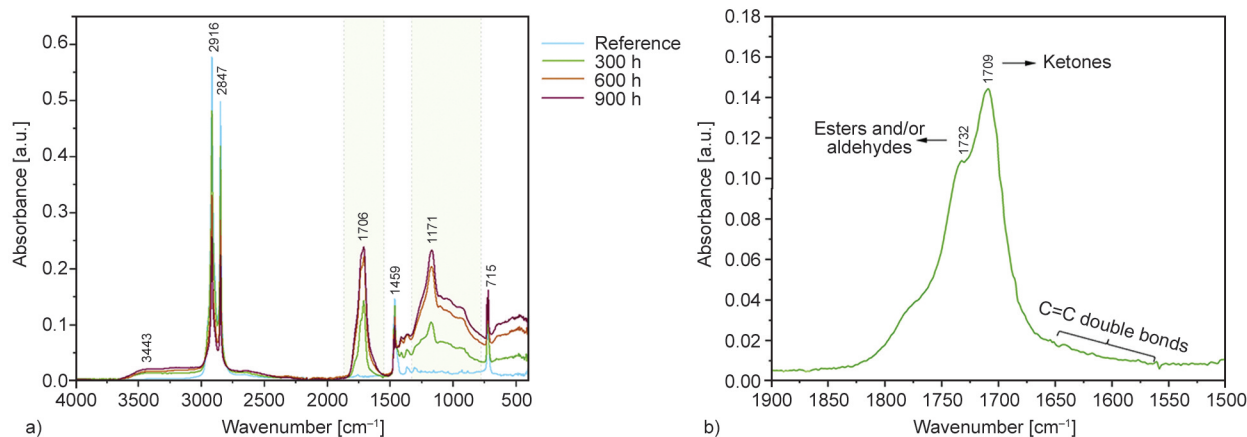


Figure 6. FTIR spectra recorded for the reference EN polymer before and after its long-term exposure to radiation (a), FTIR spectrum in the range of 1900–1500 cm^{-1} showing the formation of characteristic photo-oxidation products (b).

of carbonyl groups (C=O stretching). Additionally, a slight increase in absorbance intensity due to photoaging was observed at wavelengths in the range of $3600\text{--}3000\text{ cm}^{-1}$, which can be attributed to the formation of hydroxyl groups. It is important to note that the absorbance of these individual groups increases in proportion to the length of exposure to the specified environmental factors.

The photoaging process of a polymer is typically initiated through the absorption of ultraviolet (UV) energy by its unsaturated bonds. This results in the breaking of carbon-hydrogen (C–H) bonds in the polymer's skeleton and the formation of free radicals. However, the EN polymer lacks any unsaturated bonds in its chemical structure. In such cases, the process may be initiated by the presence of impurities, catalyst residues, carbonyl groups, and so forth, which were introduced during synthesis, processing, or storage.

The FTIR spectra recorded for the remaining EN-based samples are presented in Figure 7. The photooxidation process yielded comparable results, with the formation of carbonyl and hydroxyl products but in diminished quantities. This outcome substantiates the efficacy of the natural stabilizers employed in mitigating the adverse effects of photoaging. Nevertheless, to provide a quantitative demonstration of the progress of photodegradation, carbonyl index (*CI*) values were calculated based on Equation (2). The obtained results are shown in Figure 8. It is evident that the calculated *CI* values increase in proportion to the aging duration. The highest *CI* values were observed for the reference EN (0.30, 0.67, and 0.93 after 300, 600, and 900 h of UV aging, respectively). Upon analysis of the *CI* values following 300 h of exposure to UV light, it became visible that all samples containing quercetin or rutin exhibited significantly enhanced resistance to the specified

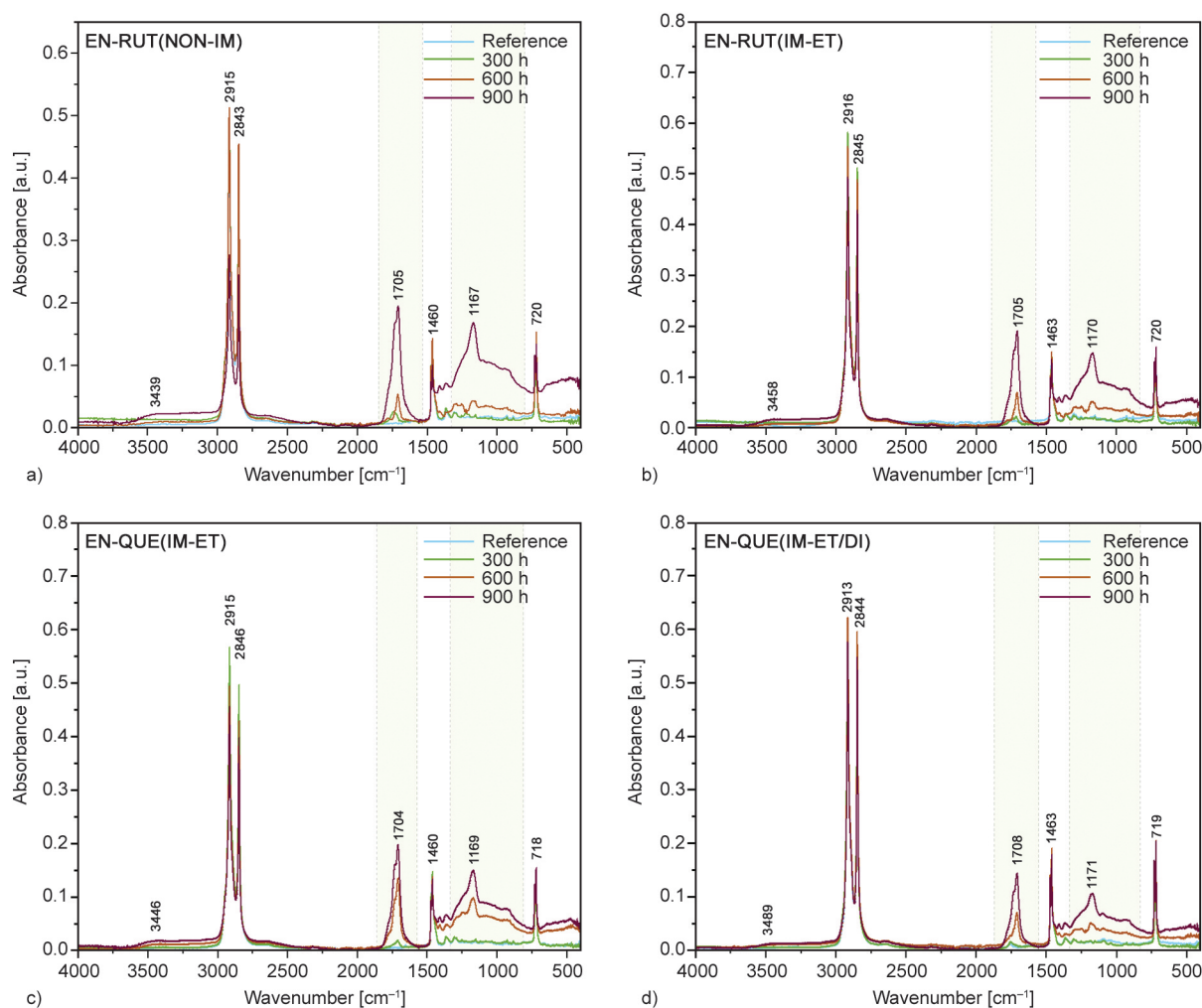


Figure 7. FTIR spectra recorded for the EN polymer containing flavonoids in the form of impregnated pellets or powder. a) EN-RUT(NON-IM), b) EN-RUT(IM-ET), c) EN-QUE(IM-ET), d) EN-QUE(IM-ET/DI).

conditions when compared to the pure EN (CI approximately 0.05). Nevertheless, in subsequent stages of photodegradation, the discrepancies in CI values became more pronounced. It was observed that the material exhibiting the least susceptibility to UV radiation was EN-QUE(IM-ET/DI) ($CI = 0.25$ after 900 h of aging). The greater resistance to UV aging of the EN-QUE(IM-ET/DI) sample compared to EN-QUE(IM-ET) may be attributed to the higher tendency of the EN to swell in dioxane. This may result in a greater quantity of flavonoids being absorbed in the EN granules. Furthermore, it permits a gradual and controlled release of these active substances from the polymer when subjected to UV radiation.

Moreover, the higher antioxidant activity of materials with the addition of quercetin compared to samples containing rutin may be directly related to their different chemical structure. Aliaga and Lissi [49] reported that quercetin exhibits greater reactivity than rutin. This is related to the presence of additional reactive centers and an extra hydroxyl group in the C ring, which is responsible for its excellent antioxidant effect. These observations are consistent with our results. Moreover, it is noteworthy that the CI value after 900 h of UV aging for EN-RUT(IM-ET) is twice as low as for EN-RUT(NON-IM). This indicates that the proposed method of introducing stabilizing substances into the polymer through the pre-impregnation process allows for their more controllable release and long-term antioxidant activity.

It should also be emphasized that the produced materials exhibit similar photostability compared to those with the addition of synthetic stabilizers. In our

previous work [24], the CI values after 300 h of photoaging for the EN polymer containing Rianox 1726 and Rianox 3114 were 0.14 and 0.19, respectively. In this study, the determined CI values for the samples with the addition of natural stabilizers were lower than 0.10 after 300 h of exposure to UVA radiation. This confirms that natural stabilizers, which are much safer and less toxic, can successfully replace synthetic stabilizers in polymer products.

The formation of carbonyl products and conjugated double bonds in the polymer skeleton as a consequence of photooxidation is frequently accompanied by a change in color or yellowing of the polymer product. In this research, the change in coloration (ΔE) was calculated according to Equation (3) based on the determined color parameters (L^* , a^* , b^*). The results obtained are presented in Figure 9.

As illustrated in Figure 9, all tested samples exhibited a change in color as a result of exposure to UV radiation. In the case of the reference EN, which was originally transparent, it became significantly yellow after 900 h of photoaging, resulting in a ΔE value of 14.6. As documented in the literature, this is a common phenomenon when diverse oxygen-containing species, conjugated polyenes, and ring-opening reaction products are generated [50]. However, the color change observed in materials containing quercetin ranged from light to dark yellow. This is a typical phenomenon observed in phenolic antioxidants, which, upon oxidation, form colored quinone complexes. On the other hand, a comparison of the ΔE values for samples with the addition of rutin reveals that the material containing this substance in the form of impregnated

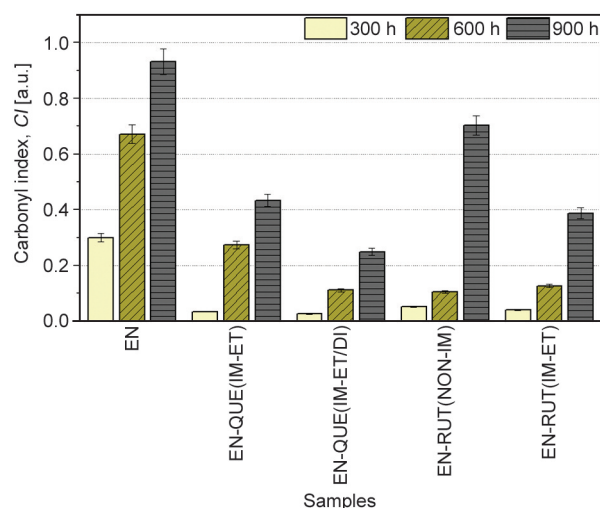


Figure 8. Carbonyl index values determined for the EN-based samples after 300, 600 and 900 h of UV aging.

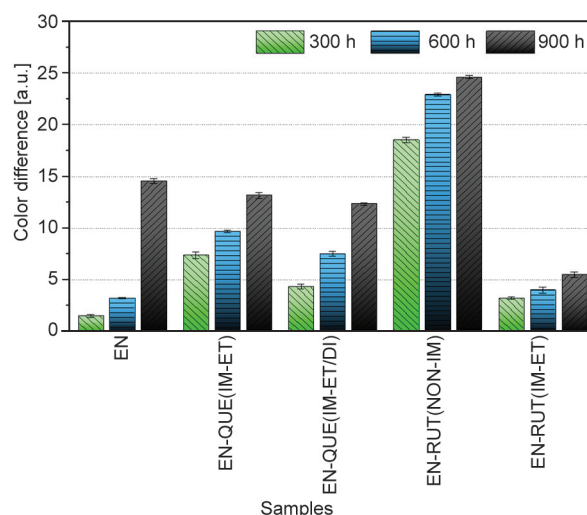


Figure 9. Changes in coloration of the tested materials as a result of their exposure to long-term radiation.

pellets exhibited a markedly reduced color change. The EN-RUT(NON-IM) demonstrated a notable susceptibility to UV light, resulting in ΔE values exceeding 20 after 600 and 900 h of photoaging. This may be attributed to the observation that the EN-RUT(NON-IM) exhibited a comparatively reduced degree of dispersion. The higher surface roughness resulted in a larger specific surface area, which demonstrated an enhanced capacity to absorb UV light rays.

3.4.2. Changes in the mechanical properties of EN-based materials as a result of UV aging tests

The last analysis conducted on the EN-based samples was the determination of mechanical properties,

which served to reinforce the conclusions drawn from the surface tests. The obtained results are presented in Figure 10. The incorporation of natural flavonoids in the form of impregnated pellets did not result in a notable impact on the tensile strength and elongation at break of the EN polymer. The TS value for all unaged samples tested was within the range of 34 MPa, and Eb was approximately 850%. However, as the photoaging process proceeded, a notable decline in mechanical properties was observed, particularly in the case of the pure EN, for which the TS after 300 hours of exposure to UV radiation was only 9.2 ± 0.4 MPa and Eb was $241 \pm 21\%$. Conversely, the reduction in mechanical properties observed in materials upon the addition of quercetin or rutin was

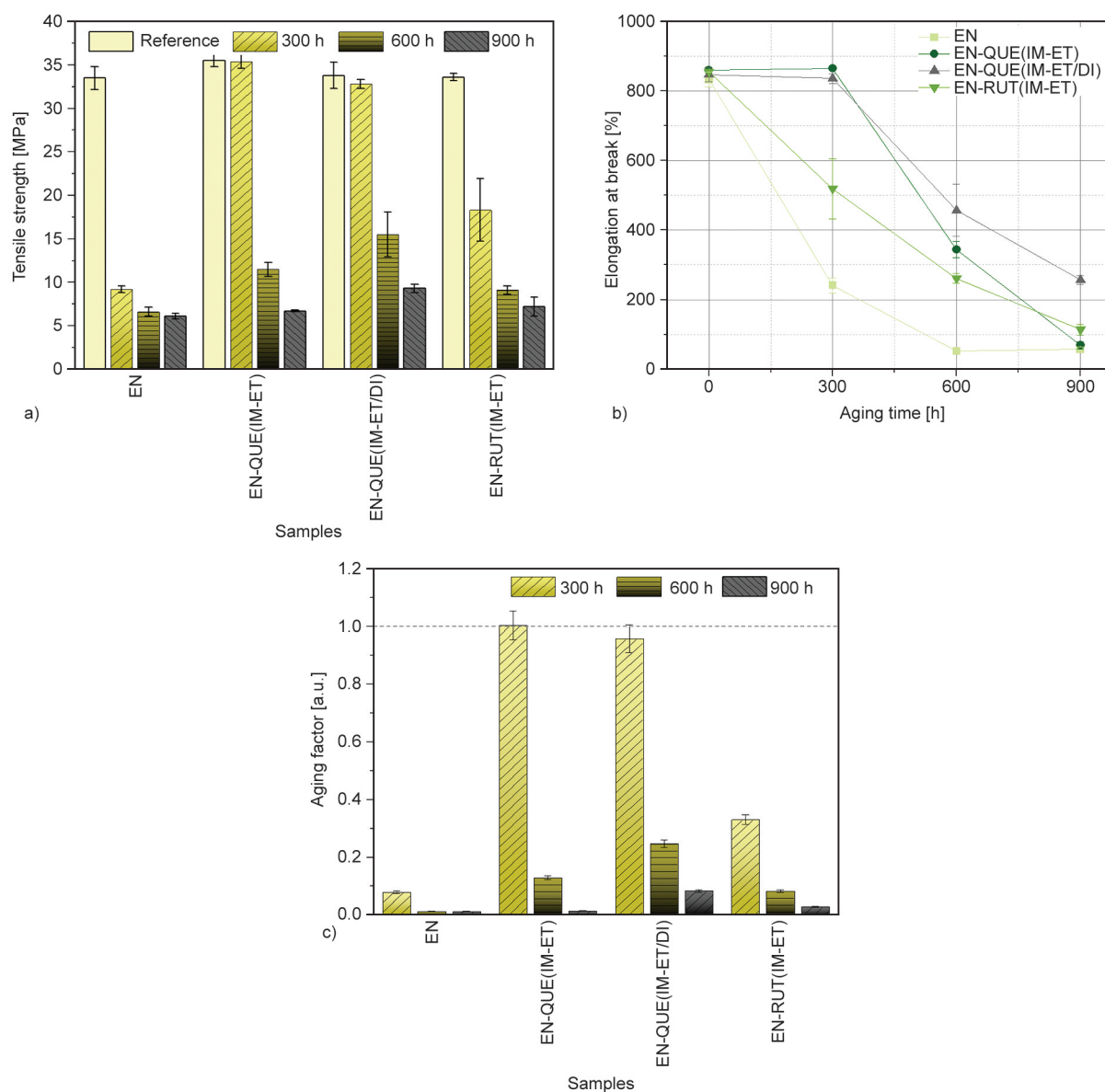


Figure 10. Static mechanical properties of the EN-based samples: tensile strength (a), elongation at break (b), and aging factor values (c).

less pronounced. Only after 600 h of photoaging, these differences were more apparent.

Furthermore, in order to more accurately demonstrate the influence of specific aging conditions on the functional characteristics of EN-based samples, aging factors (A_f) were calculated, which provide insight into the degradation progress (Figure 10c). If the value of A_f approaches 1, it indicates that the tested sample exhibits high resistance to aging. In the case of the reference EN, an almost complete loss of mechanical properties was observed after the first aging stage (A_f below 0.1). In contrast, for samples containing quercetin, the A_f value after 300 h of photoaging was approximately 1, indicating their exceptional resistance to UV light. In comparison, for EN-RUT(IM-ET), the A_f value was equal to 0.3. As previously indicated, this may be attributed to the different chemical structures of these flavonoids, particularly the additional OH group present in the C ring of quercetin, which may underpin its enhanced antioxidant efficacy. The replacement of the hydrogen atom in the OH group with a sugar group at the C3 position in the C ring may result in a reduction in the antioxidant effect of rutin. This substitution may result in a slight increase in bond dissociation enthalpies for all OH groups, which subsequently led to a reduction in the activity of this compound. Moreover, it is noteworthy that quercetin, introduced into EN in the form of impregnated granules using a mixture of solvents (ethanol and dioxane), demonstrated the highest stabilizing activity throughout the entire aging period. This finding is in accordance with the results of the FTIR analysis. It can be assumed that the greater susceptibility to swelling of

the EN in a mixture of two solvents may affect the further aging behavior of the final polymer product.

3.5. Antioxidant effect of quercetin and rutin

Quercetin and rutin are hydroxylated phenolic compounds whose activity depends on their chemical constitution. They can facilitate the retardation of the degradation of polymers by virtue of their capacity to scavenge reactive oxygen species (ROS), chelate metal ions and impede the catalytic activity of enzymes involved in the formation of ROS. Hence, when a free radical is produced as a consequence of the photooxidation process, the flavonoids move towards this labile point in the polymer to intercept further degradation and thus provide a stabilizing effect. The most important structural characteristics of flavonoids are the presence of a catechol moiety in the B ring (marked in blue in Figure 11), the existence of OH groups that are capable of binding transition metal ions (marked in purple), and the presence of a C2-C3 double bond (marked in yellow) in conjunction with the 4-oxo function (marked in green) in the C ring [51]. Nevertheless, it should be noted that not all OH groups present in these substances are equally effective in their capacity as free radical scavengers. As depicted in Figure 11, the initial step involves the oxidation of the OH group at the C3' position in the B ring, which is followed by the oxidation of the OH group at the C4' position in the B ring. Subsequently, in the case of quercetin, the hydroxyl group at the C3 position in the C ring is oxidized, and the OH groups located in the A ring at C5 and C7 positions contribute only minimally to the antioxidant activity. This is because the A ring is

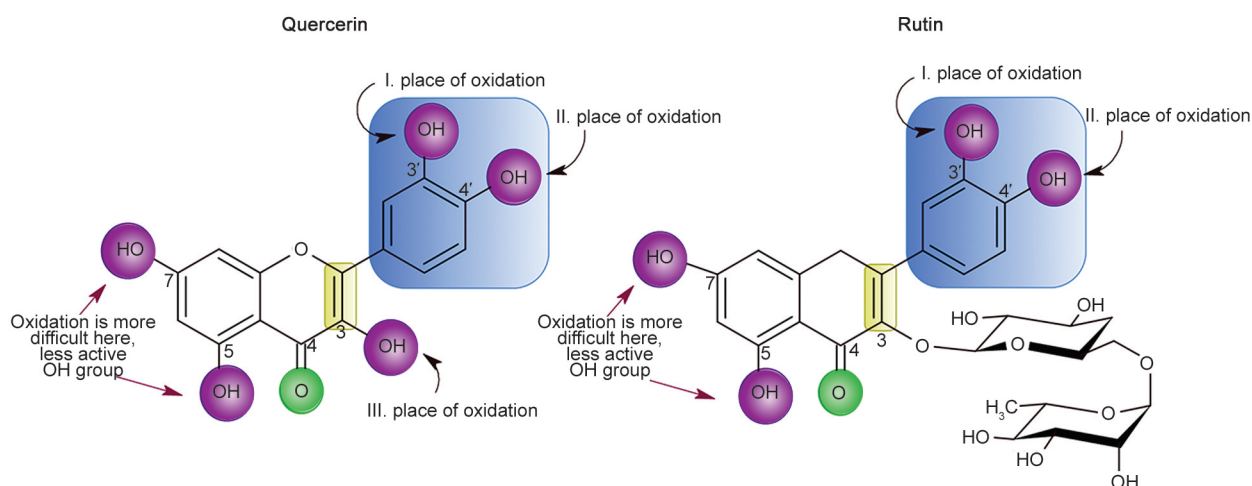


Figure 11. Demonstration of chemical structures of quercetin and rutin and their places responsible for the antioxidant effect.

not a good electron donor, and oxidation is more difficult here [52]. Therefore, the higher stabilizing effect provided by quercetin in this work may be related to the presence of hydroxyl group at the C3 position in the C ring, which could increase the reactivity of the catechol structure of the B ring.

4. Conclusions

The novel approach of incorporating natural flavonoids into polymers through a pre-impregnation process prior to processing was found to be effective. TGA measurements showed that the EN polymer, when filled with the proposed compounds, exhibits enhanced thermal stability (with a 5–27 °C increase in $T_{5\%}$), with the most noteworthy resistance to elevated temperatures observed in materials comprising impregnated pellets. This trend was also confirmed by the determined OIT values. Furthermore, the results from the microbial colonization assessment indicated that the number of dead cells of *E. coli* bacteria increased from 8 to 59% following the introduction of quercetin-impregnated pellets into the EN polymer. Another advantage of the produced materials was their good photostability, which was definitely higher compared to the reference EN and filled with the stabilizing compound in a traditional powder form. This may be a direct result of the enhanced dispersion degree of samples containing impregnated pellets and their more gradual, controlled release from the EN during operation. It can be posited that the flavonoids incorporated into the EN through the pre-impregnation process demonstrated superior anti-migration performance, as evidenced by the findings of the migration test. If we compare the stabilizing effect of both polyphenols, quercetin was more efficient, which may be attributed to the presence of hydroxyl group at the C3 position in the C ring, which could increase the reactivity of the catechol structure of the B ring. In addition, the introduction of quercetin in the form of impregnated pellets using a mixture of solvents resulted in the highest stabilizing activity. In summary, the proposed approach effectively solves the issues that arise during the commonly used processing techniques and may facilitate the broader utilization of natural stabilizers in the polymer industry.

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