



Evaluation of thermal and radiation stability of EPDM in the presence of some algal powders

Traian Zaharescu¹ · Carmen Mateescu¹ · Andreea Dima¹ · Gustavo H. C. Varca²

Received: 30 January 2020 / Accepted: 28 September 2020 / Published online: 27 October 2020
© Akadémiai Kiadó, Budapest, Hungary 2020

Abstract

In this paper, ecological-friendly materials based on ethylene–propylene–diene terpolymer (EPDM) with improved thermal and radiation stabilities by *Chlorella vulgaris* (CV) and *Spirulina platensis* (SP) powders were investigated by complementary procedures: FTIR spectroscopy and isothermal and nonisothermal chemiluminescence (CL). The stabilization potential of microalgae was evaluated at several degrees of γ -radiolysis by 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging assay, while the polymer resistances were studied on a large range of algal concentrations (1, 3, 5 and 10 mass%). The carbonyl and hydroxyl indices of all degraded EPDM formulations were found to be two times smaller in the presence of algal powders, if compared to the pristine material. Some dissimilarities between the oxidation development in pristine and modified EPDM appeared, especially in unirradiated samples. The activation energies required for the oxidation of EPDM and the lifetime of these samples at various temperatures between room temperature and 100 °C were calculated. The antioxidant compounds existing in the studied microalgae proved a significant influence on the stability of EPDM, mainly in the presence of SP, which was confirmed by the activation energies calculated from our CL results. The investigation of cycling thermal degradation revealed the obvious contribution of additives towards delaying EPDM ageing.

Keywords *Chlorella vulgaris* · *Spirulina platensis* · Antioxidants · EPDM · Thermal and radiation stabilization

Introduction

The quality of packaging materials is mainly determined by their oxidation resistance, which hinders material degradation and the contamination of foodstuff. The growth of the microbial population and the generation of predominant hazardous oxidation products such as alcohols and ketones from polymeric material packaging are some of the main concerns related to the material degradation that often require the addition of protectors to their compositions. Additionally, the handling of perishable food requires suitable packaging

materials, which are properly stabilized themselves. Concerning the improvement of thermal stability, various alternatives for the protection of polymers have been proposed: synthesis antioxidants [1–3], plant extracts [4–7] or inorganic additives [8, 9]. Despite the high antioxidant content of algal additives with the efficient ability for the extension of material shelf life and durability, the attempts on their implementation are still scarcely reported [10], and regardless of their abundance, marine algae [11] have not been largely qualified as the protectors against degradation in packaging materials. However, the friendly antioxidants added in their composition can provide important benefits in the food packaging industry and commodities.

The oxidation of polymers is one of the most important processes responsible for the ageing of materials. The degradation mechanism of polyolefins, the predominant products through the large spectrum of packaging materials, is presented elsewhere [12]. The relation between the performance of the materials and the lifetime prediction is essential, when specific applications are envisaged [13]. Accordingly, the conditions under which the oxidative degradation occurs must be well defined for avoiding the accelerated process

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s10973-020-10319-4>) contains supplementary material, which is available to authorized users.

✉ Carmen Mateescu
carmen.mateescu@icpe-ca.ro

¹ National Institute for Electrical Engineering, INC DIE ICPE CA, 313 Splaiul Unirii, P. O. Box 149, Bucharest, Romania

² IPEN-CNEN/SP, Cidade Universitaria, Avenida Lineu Prestes, São Paulo 5508-000, Brazil

including overexposure during operation. The understanding and explanation of material resistance make possible the prediction of a lifetime by controlling the environmental agents (heat, UV exposure) acting during the product lifetime. This basic approach explains the meaning of the protective action of stabilizers.

The oxidation inhibitors are purposely added to the polymer compositions towards changing the course of ageing. The addition of microalgae powders as degradation delayers in the formulations of polymers has been not extensively studied, although the above-mentioned effect has attracted a noticeable interest concerning biological purposes [14–16]. The presence of polyphenols (catechin, gallate, flavonoids), polysaccharides, vitamins, carotenes and many other active components (nutrients) is a reliable argument for the inhibition of polymer degradation. Their proportion is specifically determined by the growing conditions [17]. Several microalgae are industrialized in the production of biofuel [18]. Despite extensive interest in the conversion of algal mass into energy, their useful potential in the warranty extension of organic substrates including polymer materials must not be discarded.

The distinct question related to the oxidative protection of polymers refers to evaluating the contribution of various components, such as *CV* and *SP*, over the inhibition degree. The previous comparative investigation on the antioxidant properties of *Chlorella vulgaris* and *Spirulina platensis* was reported in relation to the improvement effects in rainbow trout [19]. Moreover, polysaccharides (arabinose, glucosamine, galactose, mannose, xylose, glucose) from *CV* were studied for the in vitro and in vivo protection of the oxidation stress involved in the development of degenerative diseases [20]. The improvement effects of lipids, proteins and nucleic acids in the treatment of Alzheimer's disease [21] suggested the friendly peculiarity of microalgae as major with peculiar antioxidant capacities. Similarly, the seaweeds from the Danish coast act efficiently as screening factor for oxidation due to the presence of phenolic compounds and tocopherols [22].

It is well known that the protective activity of the main antioxidant components in algal biomass depends strongly on the type of algae and the place where they were grown and harvested. Some examples of extracts containing *Chlorella vulgaris* or *Spirulina platensis* with high antioxidant capacities or stabilizing potential used for medical purposes have been previously reported: polyphenol and carotenoid contents [23, 24], carbohydrates and sulphated polysaccharides [25], plant protein, carbohydrates, fat as essential oils, vitamins, volatile components [26], flavonoids, β -carotene, vitamin A, α -tocopherol, fatty acids, namely palmitic and linoleic acids [27], proteins, vitamins, γ -linoleic acid, essential fatty acid precursors for prostaglandin, phycocyanin, β -carotene, γ -tocopherol and phenolic compounds [28].

The present study describes the benefits of adding microalgae powders as ecological stabilizers for increasing the stability of polymeric materials. Accordingly, the investigation was focused on the effects of *CV* or *SP* biomass, which were added as nanofillers into the ethylene–propylene terpolymer. It was chosen as an illustrative example of polyolefin-based products. The advantages of this study involve an eco-friendly alternative for material modification and safe handling of polymeric products ameliorated by natural antioxidants.

Experimental

Ethylene–propylene–diene monomer (EPDM) was provided by DSM Elastomers (The Netherland) as KELTAN 8340/A, whose formulation contains 5mass% 5-ethylidene 2-norbornene as third diene component. The initial ethylene/propylene ratio was 3:1. *CV* and *SP* were donated by the R & D National Institute of Chemistry and Petrochemistry (Bucharest, Romania). For the preparation of stock polymer solution, raw EPDM was first solubilized in pure CHCl_3 . A proper amount of mother solution was then subjected to the separation of the insoluble polymer by pouring drop by drop a small amount of water. After drying in an oven at 105 °C for 1 h, the new CHCl_3 mother solution free of manufacturing antioxidants can be prepared in the same manner. This purification is required for avoiding the formation of synergistic antioxidant couples with algal stabilizers. The daughter samples were prepared by transferring aliquots of 25 mL stock polymer solution into glass bottles followed by the addition of corresponding amounts of *CV* or *SP* powders to obtain final loadings (1, 3, 5 and 10 phr) of each algal additive. These separate bottles were the wet sources for dry films. The proper volumes of daughter solutions were poured in large stainless steel trays for the preparation of films for infrared spectroscopic measurements and in small round aluminium pans for the accomplishment of chemiluminescence determinations. The drying of samples was carried out by evaporation at room temperature. γ -Irradiation was performed inside an irradiator Ob Servo Sanguis (Hungary) equipped with a ^{60}Co source. The exposures were accomplished in the air at room temperature. The permanent rotation of irradiation assured uniform processing for all samples. The available dose rate was 0.5 kGy h^{-1} . The applied heating cycling treatment was accomplished in an electrical oven by isothermal processing at 180 °C. One thermal cycle consisted of 3 h of heating followed by the 6 h of storage on the laboratory table at room temperature.

The antioxidant activity was assessed by UV-Vis spectroscopy with a JASCO A-4200 (Japan) instrument after 50 scans. The thermal stability of each sample was determined by

isothermal chemiluminescence (proper temperatures between 130 °C and 180 °C) and nonisothermal chemiluminescence (3.7, 5.0, 10.0 and 15.0 °C min⁻¹) using CL spectrometer LUMIPOL 3 (Slovak Academy, Bratislava). The errors for temperature measurements were placed within ± 0.5 °C. All heating rates were carefully selected based on the diffusion contribution on the oxidation of EPDM. A special mention must be done for the rate of 3.7 °C min⁻¹, a low value, which is convenient for the slow oxygen diffusion, which requires a slight corresponding increase in the temperature. From the CL isothermal spectra recorded on all compounded EPDM samples at 160, 170 and 180 °C, the activation energies were calculated according to Arrhenius equation (Eq. (1)):

$$t_x = t_0 e^{-\frac{E_a}{RT_x}} \quad (1)$$

where t_x and t_0 are the values of oxidation induction times (the moments when the degradation starts effectively with significant measurable CL emission) for working temperature, T_x , and initial temperature, T_0 , respectively. E_a is the activation energy (kJ mol⁻¹) involved in the studied process, and R is the universal constant of gases (8.314 kJ K⁻¹ mol⁻¹).

For the lifetime calculation of EPDM samples, a rearranged relationship of the Arrhenius equation was applied (Eq. (2)):

$$t_x = t_{\text{ref}} \exp \left[-\frac{E_a}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T_x} \right) \right] \quad (2)$$

here T_{ref} is the temperature considered as the reference value. In our calculation, T_{ref} was chosen as 433 K (160 °C). The activation energies required for the oxidative degradation of irradiated EPDM based on onset oxidation temperatures, OOT (the temperatures when the degradation starts effectively), are calculated with Eq. (3), the Kissinger relationship:

$$\frac{d(\ln(\beta/T_p^2))}{d(1/T_p)} = -\frac{E_a}{R} \quad (3)$$

where β is the heating rate (K min⁻¹) and T_p is the OOT value corresponding to each heating rate. E_a and R have the same meanings as above.

Results and discussion

The DPPH assay measurements confirm the presence of compounds with antioxidant activity in microalgae, showing a linear increase in the inhibition action of DPPH on free radicals with the increase in the irradiation dose. The proportionality between the radical scavenging activity and irradiation dose (Fig. 1) can be explained by the conversion

of some initial phenolic structures into other related configurations which also exhibit the stabilization activity. This assumption is based on the analogous behaviour of rosemary [29] and carnosic acid [30]. The beneficial contribution of γ -exposure of *Spirulina platensis* was proved for the doses less 1 kGy [31] by its stimulated growth. It was previously demonstrated [32] that the former descendant structures of natural antioxidants are themselves oxidation protectors. Therefore, the similarity in the slopes of inhibition degree vs dose for both algal powders suggests the conversion of active molecules either into the same number of molecules with higher stabilization efficiency or into a higher amount of smaller molecular mass antioxidants, but with overall higher radical scavenging activity.

The antioxidant availability of biological components in ripe avocados attracted attention due to their protective capacity [33]. The extension of this type of investigation onto algae powders is a new step on the manufacture way of ecological polymer products. The prediction of longer shelf life is disentangled by the characterization of the positive contribution of natural extracts [34], in our case—the algal powders. It was previously demonstrated that various thermal analysis methods can depict functional features involved in the improvement of material stability [35].

FTIR spectroscopy

The modifications induced by exposure of polymer composites during the action of incidental γ -radiation are the consequences of the accelerated degradation in the polymer substrate. The formation of free radicals during irradiation follows a classical mechanism even the material is a pristine form or it contains fillers or stabilizers [36, 37]. The higher values of transmission for the hydroxyl band define the

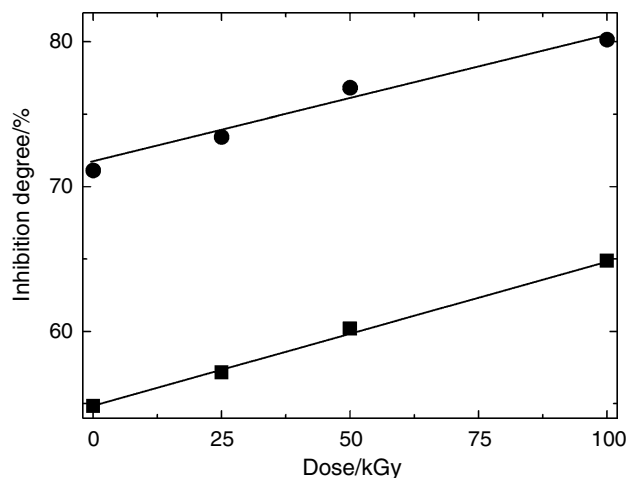


Fig. 1 Modification in antioxidant activities by of algal powders γ -irradiation. (1) *Spirulina platensis*; (2) *Chlorella vulgaris*

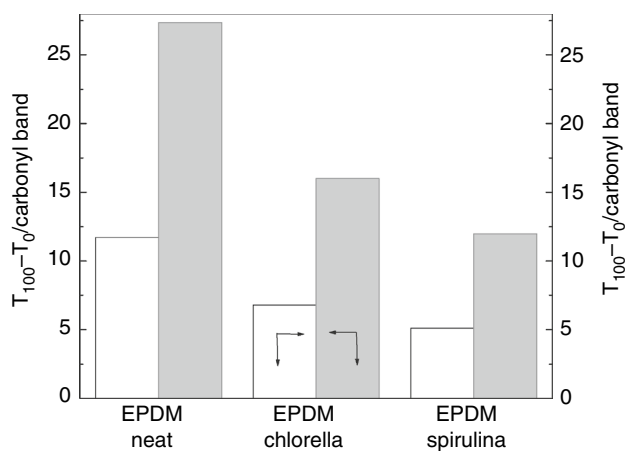


Fig. 2 Transmission differences for pristine and aged EPDM/algae mass

presence of phenolic compounds in the initial formulation, while the carbonyl band is a large one with several peaks illustrating the polymer degradation during storage and handling (Fig. 1 S). There is not any difference between the shapes and peak structures of the carbonyl band for the three unirradiated EPDM samples. The accumulation of main

oxidation products, the alcohol and ketone configurations, is comparatively presented in Fig. 2. The sustained increase in the transmission values of carbonyl units indicates the formation of degradation products directly by the reaction between free radicals and diffused molecular oxygen.

However, the evolution of the hydroxyl band is the result of the simultaneous generation of degradation compounds and the decay of phenolic structures initially contained in the algal mass. The overall behaviour of EPDM/algae powder samples indicates turning onto an ageing process, when the former structures are partially consumed. Even on the advanced stage of degradation, the performed complementary thermal or radiochemical investigations reveal the presence of stabilizing components. The resistance of algal mass against degradation is also proved by the values of activation energies involved in oxidative degradation.

Thermal degradation

It is generally agreed that the permanently exposed polymer materials are affected by chaining environmental factors. For example, the temperature modification by the alternation of day and night, mostly in wintertime, requires the investigation of cyclic heating that would demonstrate the material

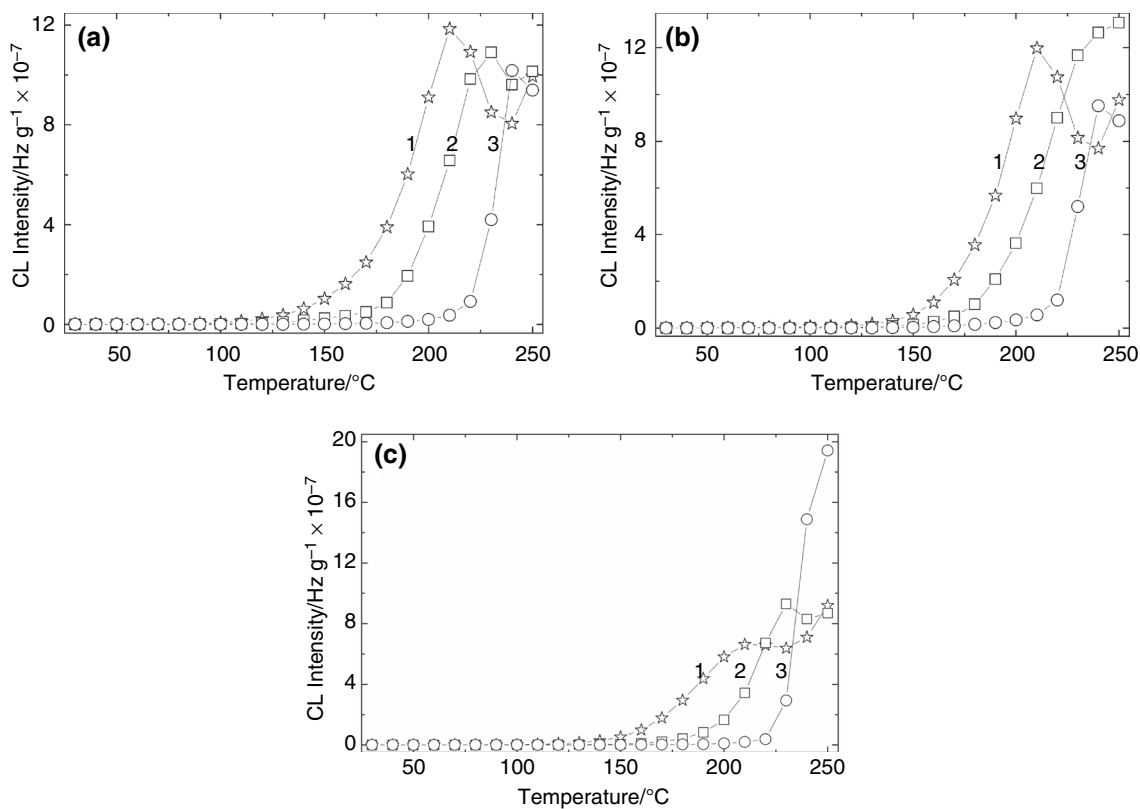


Fig. 3 Nonisothermal CL spectra recorded on thermally aged EPDM samples. Powder concentration: 5 phr; heating rate: 10 °C min⁻¹; environment: air. (1) pristine EPDM; (2) EPDM *Chlorella vulgaris*;

(3) EPDM/*Spirulina platensis*. **a** after one cycle; **b** after three cycles; **c** after six cycles

behaviour subjected to the sharp modification of operation conditions. The alternation of heating and cooling applied on the EPDM/algae specimens reveals the aiding effect of natural phenols existing in *Chlorella vulgaris* and *Spirulina platensis*. In Fig. 2 S, the higher stabilization efficiency of *SP* concerning the contribution of *CV* at low concentration (1 phr) is noticeable, when the protective action of added algal powders enables a slight cross-linking. The increase in the algae loading up to 5 phr causes visible differences in the thermal resistance of EPDM samples (Fig. 3). After several heating cycles the onset oxidation temperatures of neat polymer decreased from 160 to 150 °C, when these samples were measured after one and six cycles, respectively. After the same heating treatment, the increases in OOT values from 165 to 200 °C for EPDM/*CV* and from 220 to 230 °C for EPDM/*SP* were noticed (Fig. 3).

The isothermal chemiluminescence spectra recorded on unirradiated samples (Fig. 4) pointed out a great difference that appears between the neat samples and the polymer in the presence of *CV* or *SP* particles. The most obvious contrast between the oxidation progresses is illustrated by the comparison between the isothermal spectra recorded at

160 °C. While the oxidation evidently started after 120 min in pristine EPDM, the same process becomes effective after around 210 min in EPDM modified with *Chlorella vulgaris* powder. The presence of *Spirulina platensis* starts the inhibition of degradation later on (after 250 min). The good protection efficiency of algal powders can be remarked at 180 °C. The most efficient contribution of *Spirulina platensis* can be highlighted at 170 °C, when a small increase in the photoemission may be noticed at the oxidation peak after 190 min.

The best improvement in polymer strength against oxidation was achieved by the addition of *SP*. According to the spectroscopic assay, when the higher content of phenolic compounds is revealed, the nonisothermal CL curves for EPDM/*SP* are places on the right side indicating the highest contribution to the material protection. The obvious consequence of the interaction between host polymer and algal microparticles is depicted by the extension of product durability and shelf life as well as in the longer period of constancy in the physical characteristics.

The option of natural antioxidants for the manufacture of food package attracts more and more interest [10, 38,

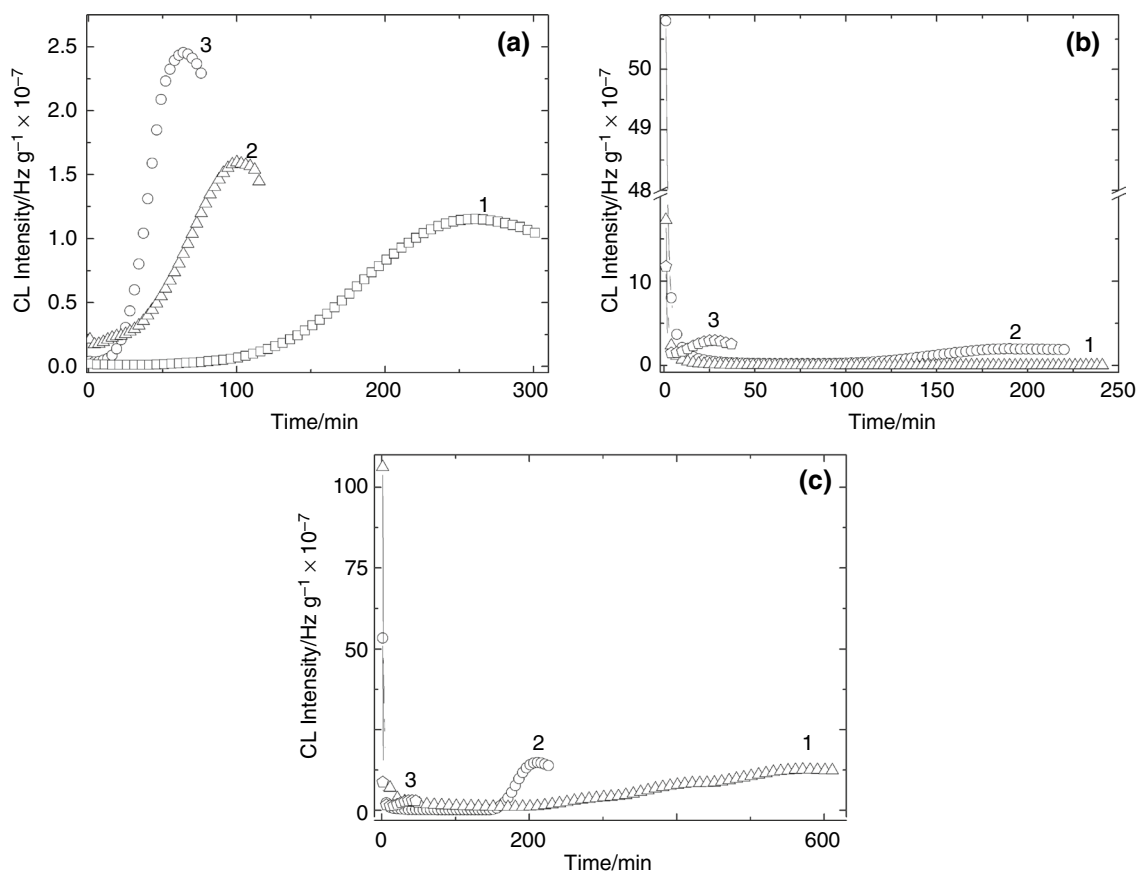


Fig. 4 Isothermal chemiluminescence spectra recorded for various states of modified EPDM samples. Filler concentration: **a** neat EPDM; **b** EPDM with *Spirulina platensis*; **c** EPDM with *Chlorella vulgaris* (1) 160 °C, (2) 170 °C, (c) 180 °C

Table 1 The oxidation induction times (OIT) and corresponding activation energies for thermal degradation of nonirradiated EPDM from isothermal CL measurements

Sample	OIT/min			Linear regression	Correlation factor	Activation energy/kJ mol ⁻¹
	160/°C	170/°C	180/°C			
Neat EPDM	150	55	10	$y = -3.08 + 3.95x$	0.99033	32.84
EPDM + CV	220	100	15	$y = -6.39 + 5.44x$	0.99995	45.23
EPDM + SP	320	180	10	$y = -9.91 + 7.07x$	0.98742	58.78

39]. Despite large applications of microalgae extracts for medical purposes, their extended usage as polymer protectors is currently little addressed, even though the oxidation prevention is closely associated with the ecological features of green products.

The oxidation induction time of evaluated for oxidative degradation as the main kinetic parameter depicting the thermal stability can be satisfactorily used in the calculation of activation energies. In Table 1, these values show a noticeable contribution of algal powders towards stability improvement. If the activation energy value obtained for the EPDM matrix stabilized with CV increases by 50%, the protection activity of PS causes growth in its activation energy by 85%. These results allow us to consider algal extracts as very efficient antioxidants. The evaluation of the lifetime of EPDM samples under different stabilization states (Table 2) reveals once again the appropriate activities of algae (CV and SP) as a minimizing factor in the thermal degradation of polymers.

Radiation degradation

The large variety of algal components having antioxidant properties provides a consistent argument for their implementation in polymer protection. The oxidation reactions occurring in the degradation mechanisms can be hindered by the inhibiting step involving the hydroperoxide output. The autocatalytic chain followed in the oxidation of polymers can be broken, when the additive scavenges intermediates (R· and RO₂·) [40]. The efficiency of stabilization is mainly proved by the evaluation of kinetic process parameters describing the progress of alteration.

Table 2 Life time of modified EPDM at various temperatures

Regular temperature/°C	Durability/day		
	Neat EPDM	EPDM + CV	EPDM + SP
20	7.76	61.83	543.30
40	3.31	18.88	116.26
60	1.56	6.64	29.94
80	0.80	2.63	8.99
100	0.44	1.15	3.07

The accelerated oxidative degradation accomplished by γ -irradiation reveals the contribution of algal components on the delay of oxidative ageing. The isothermal CL spectra recorded on irradiated samples (25 kGy–Fig. 3 S; 100 kGy–Fig. 5) demonstrate the real stimulation of protection by the addition of algal fraction in the formulations of EPDM. As it was noticed in all stability investigations on EPDM substrate, SP presents the best activity in the hindering of oxidation. The efficiency of oxidation delay was assessed by the calculation of activation energies required by the degradation process (Table 3). The significant increase of this picture proves the relevant effect of added algal powders to the relevant dropping down of energetic restrictions. These values are in a good agreement with other reported figures [41].

As it was previously proved with various plants, the studied seaweeds have a noteworthy effect on the slowing down oxidation process [42]. In the microalgae-stabilized EPDM, the increase in the oxidation temperature causes an early peak at 140 °C (Fig. 6). This peak is not present in the pristine EPDM. It may be ascribed to the easily oxidized components of SP or CV powders, but not to phenolic compounds and flavonoids, which are more resistant. After γ -irradiation this peak disappears and the chemiluminescence curves are shifted towards lower temperatures because of the accelerated degradation of the matrix. The irradiation effect is more accentuate because the stabilizing compounds are absent. The two powders act similarly in the irradiated material on the higher-temperature range. However, the diminution of oxidation peak at 140 °C takes place slower in the presence of SP proving that its active antioxidant content of nutrients is greater than in CV. If the nonisothermal chemiluminescence curves recorded for the same dose of the different compositions, it is easy to note that in the stabilized polymer starts later than in unmodified EPDM. The direct consequence of partial oxidation restraining is the extension of operation temperature with a minimum 20 °C, which can be reliably interpreted by an enlarged temperature limits for the regular and light fatigable environment.

As it was reported with several modified polymers, the structural effects brought about by the contribution of protection additive were noticed for a HDPE-based nanohybrid, where the POSS filler content FTIR differentiates on the

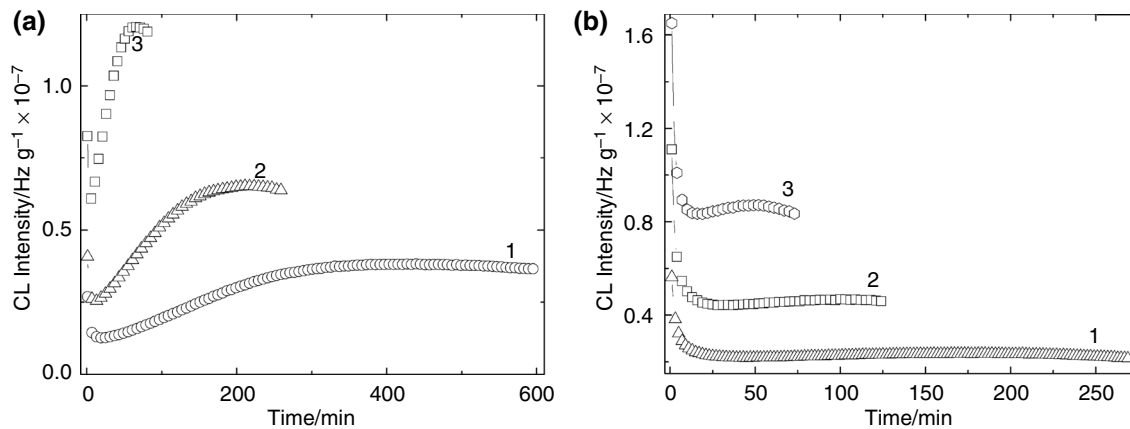


Fig. 5 Isothermal CL spectra recorded on EPDM samples irradiated at 100 kGy. Filler concentration: 3 phr; environment: air **a** neat EPDM, **b** EPDM/*Spirulina platensis*, **c** EPDM/*Chlorella vulgaris* (1) 140 °C, (2) 150 °C, (3) 160 °C

Table 3 The onset oxidation temperatures (OOT) and activation energies required for radiochemical oxidation of EPDM/algae microparticle compounds from nonisothermal CL measurements

Sample	Dose/kGy	OOT/°C				Correlation coefficient	Activation energy/kJ mol ⁻¹
		3.7/°C min ⁻¹	5.0/°C min ⁻¹	10.0/°C min ⁻¹	15.0/°C min ⁻¹		
Control EPDM	0	209	215	225	230	0.99549	96.22
	25	193	194	206	215	0.98673	118.14
	50	180	183	190	198	0.98737	123.55
	100	170	175	186	190	0.99464	108.66
EPDM/SP	0	206	217	220	233	0.95362	156.14
	25	205	208	215	222	0.99242	155.30
	50	181	187	191	198	0.97125	147.24
	100	176	181	188	192	0.99357	146.76
EPDM/CV	0	201	208	218	225	0.99548	143.49
	25	195	200	204	212	0.99242	148.90
	50	181	186	193	198	0.99554	142.58
	100	174	179	185	190	0.99258	148.82

1400–900 cm⁻¹ spectral region of various blending compositions [37], for reclaiming PP wastes, whose thermal behaviour is strongly influenced by the mixing ratio [43] or for improvement of wearing resistance of EPDM [44].

The concentration of stabilizer is a main factor in modifying the kinetic parameters of oxidation resistance. In the cases of *Chlorella vulgaris* and *Spirulina platensis*, the assessment of optimal loadings up to 10 phr confirms the stabilization potential of algal mass over a large concentration scale (Fig. 7). The protection efficiency of microalgae lutein was already reported [45], but only for the range of food. There is limited information on the trigger of oxidation effectively done by active components of microalgae. Now, this hole is filled by the evaluation of contribution brought about algae additives (*Chlorella vulgaris* and *Spirulina platensis*) embedded in EPDM (Fig. 7). The lowest concentration (1 phr) may be a proper option for

Chlorella vulgaris microparticles over the operating temperatures less 175 °C, while the similar content of *Spirulina platensis* has proved its inability to show satisfactory protection effects. The higher loadings present increasing antioxidant activities as their concentrations are greater. Nevertheless, on the temperature exceeding 200 °C, there is dissimilarity in the effectiveness of oxidation slowing down. While SP maintains oxidation state at lower levels, CV does not attain a similar performance. This behaviour would be ascribed to the differences in their compositions that exist being proved by FTIR assay (see Sect. 3.2). In regular situations, the degradation of polymer packaging materials supposes the temperature of less than 100 °C, when the material resists with or without a protector. But over a long-term degradation or after the processing of several repeated thermal cycles, the material ageing leads to a significant accumulation of oxidation products [46],

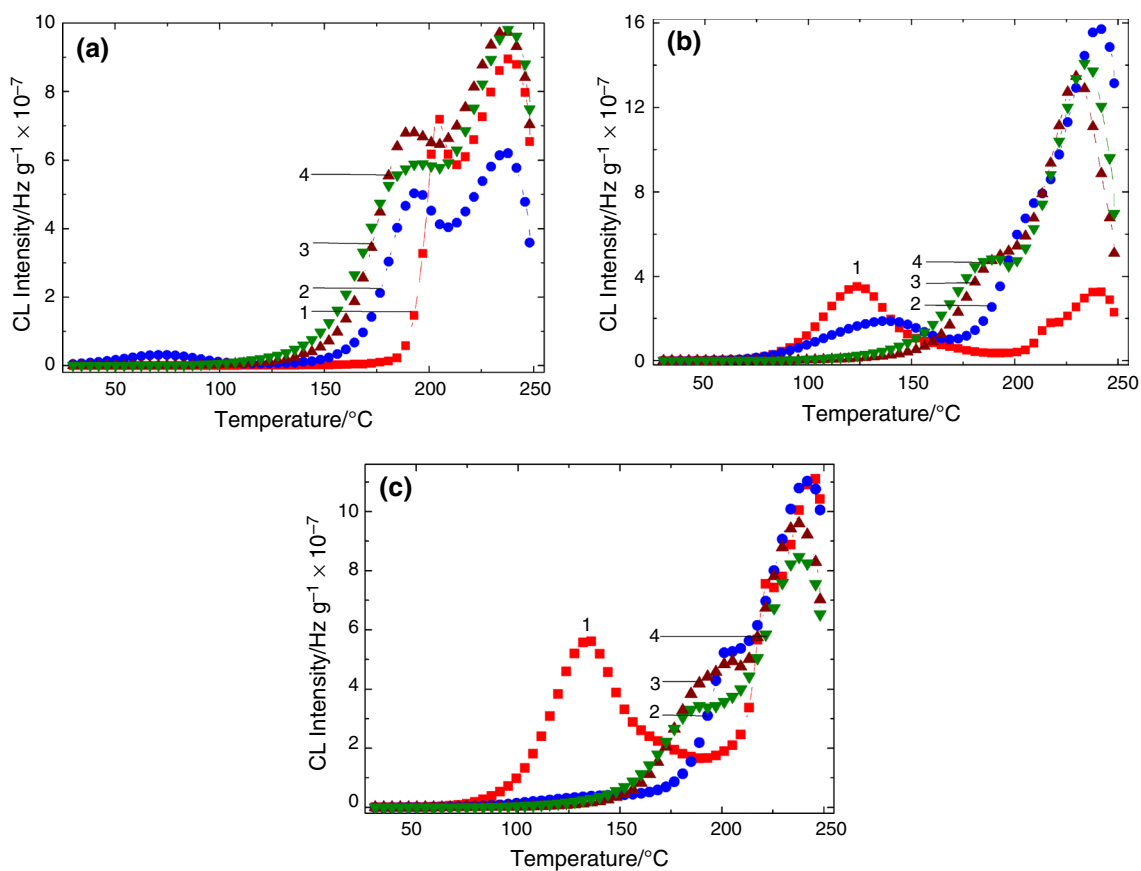


Fig. 6 Nonisothermal CL spectra recorded on EPDM/algae mass samples. Powder concentration: 1 phr, heating rate: $10\text{ }^{\circ}\text{C min}^{-1}$, environment: air. (1) 0 kGy; (2) 25 kGy; (3) 50 kGy; (4) 100 kGy

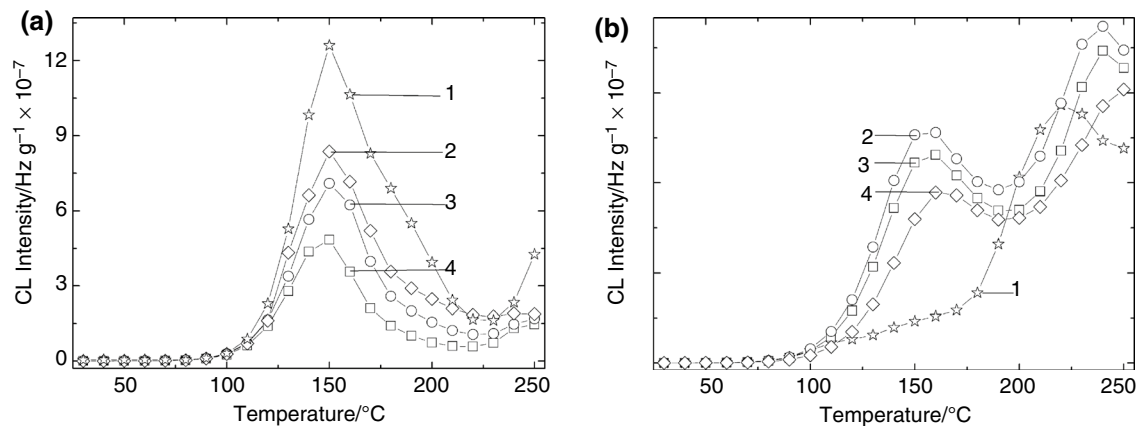


Fig. 7 Nonisothermal CL spectra recorded on unirradiated EPDM/algae mass samples Heating rate: $10\text{ }^{\circ}\text{C min}^{-1}$, environment: air. (1) 1 phr, (2) 3 phr, (3) 5 phr, (4) 10 phr

whose effect is similar to the consequence at higher temperatures. The addition of ageing inhibitors like *SP* or *CV* extracts, friendly products, is compulsory for avoiding the structural deterioration of packaging sheets normally accompanied by their migration into sealed food. Though

a comparative analysis of the efficiency of natural antioxidants in polypropylene was published [41], the scavenging effects of seaweeds extracts were never reported.

The sterilization dose (25 kGy), an efficient treatment usually applied for destroying micro-organisms and

their pathogenic products, modifies only the activity of CV (Fig. 4 S). If the nonisothermal chemiluminescence spectrum of EPDM with a low concentration (1 phr) of SP reveals the strongest protection contribution, the samples containing CV present similar concern, mostly at the temperature less 200 °C. In these cases, the formation of oxygen-containing products depends not only on the filler amount, but also on the interaction efficiency of the active component of added algal powders. It may assume that the difference in the antioxidant activities of *Spirulina platensis* and *Chlorella vulgaris* [19] is extended under γ -irradiation.

Conclusions

This paper analyses the protection effects of *Spirulina platensis* and *Chlorella vulgaris* on the improving EPDM thermal stability as an example of polyolefin class of plastics. These natural antioxidants show their efficiency either in thermal degradation or in hazardous circumstances where ionizing radiation causes profound damages in polymers. In the case of polymer sheets destined to the manufacture of food packaging, where environmental stressors act permanently on the damaging polymer sheets, the stabilization version with these microalgae would be preferred over a large scale of concentration. The increase in the activation energies of oxidation and the enhanced durability in the presence of algae extracts attained at high temperatures (up to 100 °C) are the significant advantages for the selection of *Spirulina platensis* and *Chlorella vulgaris* as the protector additive in several polymer formulations. The ageing that degrades polymers is efficiently delayed by SP and CV due to their polyphenolic contents. The presented results of this kinetic study recommend these algae as proper oxidation protectors providing longer shelf life and handling durability. These features are confirmed by the increase in the activation energy values concerning neat EPDM. The CL assay is a proper way by which the protection activity against oxidative degradation can be relevantly demonstrated.

Acknowledgements The authors thank the Education and Research Ministry for funding this study in the frame of project PN-III-P1-1.2-PCCDI-2017-0541, “The energetic efficiency growth of biogas equipments by the design of biogas-microalgae-biofuels based on the refinery concept”.

References

- Jeon DH, Park GY, Kwak IS, Lee KH, Park HJ. Antioxidants and their migration into food simulants on irradiated LLDPE film. *LWT-Food Sci Technol*, 2007; 40: 151–56.
- Brodowska M, Guzek D, Jóźwik A, Głowska D, Godziszewska J, Wojtasik-Kalinowska I, Zarodkiewicz M, Ganter M, Wierzbička A. The effect of high-CO₂ atmosphere in packaging of pork from pigs supplemented with rapeseed oil and antioxidants on oxidation processes. *LWT-Food Sci Technol*, 2019; 99: 576–82.
- Wang K, Zheng ZJ, Liu CH, Wang Y, Li JW, Li IF. Identification and qualification of synergistic antioxidants and their application in sunflower oil. *LWT-Food Sci Technol*. 2020;118: 108726.
- Zaharescu T, Pleșa I, Jipa S. Improvement in the degradation resistance of LDPE for radiochemical processing. *Radiat Phys Chem*. 2014;94:151–5.
- Kirschweg B, Tátraaljai D, Földes E, Pukánszky B. Natural antioxidants as stabilizers for polymers. *Polym Degrad Stab*. 2017;14:525.
- Masek A, Latos M. The potential of quercetin as an effective natural antioxidant and indicator for packaging materials. *Food Packag Shelf life*. 2018;16:51–8.
- Pelter M, Wagner JR, Jiménez A. Thermal characterization of UHMWPE stabilized with natural antioxidants. *J Therm Anal Calorim*. 2007;87:493–7.
- Zaharescu T, Iliș D-L, Roșu T. Thermal and spectroscopic analysis of stabilization effect of copper complexes in EPDM. *J Therm Anal Calorim*. 2016;123:231–6.
- Zaharescu T, Dumitru A, Marinescu V, Velciu G, Panaitescu D, Sbarcea G. Radiochemical stability and lifetime of HDPE-based flexible composite filled with Ce-doped PbZrTiO₃. *J Therm Anal Calorim*. 2019;138:2419–28.
- Bajić M, Ročnik T, Oberlintner A, Scognamiglio F, Novak U, Likazar B. Natural plant extract as active components in chitosan-based film. A comparative study. *Food Packag Shelf Life* 2019; 21: 100365.
- Chu WL. Potential applications of antioxidant compounds derived from algae. *Curr Top Nutraceut Res*. 2011;9:83–988.
- Bernstein R, Thornberg SM, Assink RA, Mowery DM, Alam MK, Irwin AN, Hochrein JM, Derzon DK, Klamo SB, Clough RL. Insights into oxidation mechanisms in gamma-irradiated polypropylene, utilizing selective isotopic labeling with analysis by GC/MS, NMR and FTIR. *Nucl Instrum Meth Phys Res B*. 2007;265:8–17.
- Celina MC. Review of polymer oxidation and its relationship with materials performance and lifetime prediction. *Polym Degrad Stab*. 2013;98:2419–29.
- Li X, Wang L, Fan Y, Feng Q, Cui FZ, Watari F. Nanostructures scaffolds for bone tissue engineering. *J Biomed Mater Res Part A*. 2013;101:2424–35.
- de Moraes MG, da Silva Vaz B, de Moraes EG, Costa JAV. Biological effects of *spirulina (arthrospira)* biopolymers and biomass in the development of nanostructured scaffolds. *BioMed Res Int*. 2014; 762705. <https://doi.org/10.1155/2014/762705>.
- Casadey R, Challier C, Senz A, Criado S. Antioxidant ability of tyrosol and derivative-compounds in the presence of O₂(¹Δ_g)-specie. Studies of synergistic effect with commercial antioxidants. *Food Chem*. 2019; 285: 275–81.
- Ángeles R, Rodero R, Carvajal A, Muñoz R, Lebrero, R. Potential of microalgae for wastewater treatment and its valorization into added value products. In: Gupta KS, Box F, eds. Application of microalgae in the wastewater treatment. Vol. 2: Biorefinery approaches of wastewater treatment. Cham: Springer, 2019, pp 281–315.
- Mateescu C, Zaharescu T. Comprehensive overview of biomethane production potential of algal biomass cultivated in wastewater. In: Gupta KS, Box F, editors. Application of microalgae in the wastewater treatment. Vol. 2: Biorefinery approaches of wastewater treatment. Cham: Springer, 2019, pp 427–444.
- Taghavi Takyar, MB, Khajavi ShH, Safari R. Evaluation of antioxidant properties of *Chlorella vulgaris* and *Spirina platensis* and

- their application in order to extend the self life of rainbow trout (*Oncorhynchus mykiss*) fillets during refrigerated storage. *LWT-Food Sci Technol.* 2019;100:244–9.
20. Yu MG, Chen MJ, Gui JG, Huang SD, Liu YM, Shentu HF, He J, Fang ZY. Preparation of *Chlorella vulgaris* polysaccharides and their antioxidant activity in vitro and in vivo. *Int J Biol Macromol.* 2019;137:139–50.
 21. Olasehinde TA, Olaniran AO, Okah AI. Therapeutic potentials of microalgae in the treatment of Alzheimer's disease. *Molecules.* 2017;22:480.
 22. Sabeena Sarvin KH, Jacobsen Ch. Phenolic compounds and antioxidant activities of selected species of seaweeds from Danish coast. *Food Chem.* 2013;138:1670–81.
 23. Li HB, Cheng KW, Wong CC, Fan KW, Chen F, Jiang Y. Evaluation of antioxidant capacity and total phenolic content of different fractions of selected microalgae. *Food Chem.* 2007;102:771–6.
 24. Gioris K, Muylaert K, Fraeye I, Foubert I, de Brabanter J, de Cooman L. Antioxidant potential of microalgae in relation to their phenolic and carotenoid content. *J Appl Phycol.* 2012;24:1477–86.
 25. Rajasekar P, Palanisamy S, Anjali R, Vinosha M, Elakkiya M, Marudhupandi T, Tabarsa M, You SG, Prabhu NM. Insulation and structural characterization of sulfated polysaccharide from *Spirulina platensis* and its bioactive potential: In vitro antioxidant, antibacterial and Zebrafish growth and reproductive performance. *Int J Biol Macromol.* 2019;141:809–21.
 26. Soni RA, Sudhakar K, Rana RS. *Spirulina*—from growth to nutritional product: a review. *Trends Food Sci Technol.* 2017;69:157–71.
 27. Wang L, Pan B, Sheng JC, Xu J, Hu QH. Antioxidant activity of *Spirulina platensis* extracts by supercritical carbon dioxide extraction. *Food Chem.* 2007;105:36–41.
 28. de Marco ER, Steffolani ME, Martínez CS, León AE Effects of spirulina biomass on the technological and nutritional quality of bread wheat pasta. *LWT-Food Sci Technol.* 2014; 58: 102–8.
 29. Petiwala S, Johnson JJ. Diterpenes from rosemary (*Rosmarinus Officinalis*): defining their potential for anti-cancer activity. *Cancer Lett.* 2015;367:93–102.
 30. Jipa S, Zaharescu T, Gorghiu LM, Dumitrescu C, Setnescu R, Esteves MA, Gigante B. Kinetic characterisation of radiation resistance of stabilised LDPE. *J Appl Polym Sci.* 2005;95:1571–7.
 31. Hu TC, Yang SJ, Mao YL. The effect of γ -irradiation on spirulina. *Acta Agric Nucl Sinica.* 1990;4:120–4.
 32. Jipa S, Zaharescu T, Kappel W, Dumitrescu C, Mariş M, Mantsch A, Lungulescu M. Scavenger capacity of natural phenols in some selected labiateae herbs. *Optoelectron Adv Mater Rapid Commun.* 2008;2:669–73.
 33. Forero-Doria O, Flores Garcia M, Vergara CE, Guzman L. Thermal Analysis and antioxidant activity of oil extracted from pulp of ripe avocados. *J Therm Anal Calorim.* 2017;130:959–66.
 34. Souza VC, Santos EBC, Mendonça AV, Silva LB. Thermal behavior and decomposition kinetic studies of biomedical UHMWPE/vitamin C compounds. *J Therm Anal Calorim.* 2018;134:2097–105.
 35. Schirald A, Fessas D. Calorimetry and thermal analysis in food science. *J Therm Anal Calorim.* 2019;138:2721–32.
 36. Zaharescu T, Giurginca M, Jipa S. Radiochemical oxidation of ethylene-propylene elastomers in the presence of some phenolic antioxidants. *Polym Degrad Stab.* 1999;63:245–51.
 37. Baatti A, Erchiqui F, Godard F, Bussiéres D, Bèbin P. DMA analysis, thermal study and morphology of polymethylsilsesquioxane nanoparticles reinforced HDPE nanocomposites. *J Therm Anal Calorim.* 2020;139:789–97.
 38. Behera B, Balasubramanian P. Natural plant extract as an ecological and friendly alternative for harvesting microalgae. *Bioresource Technol.* 2019;283:45–52.
 39. Mira-Sánchez MD, Castillo-Sánchez J, Morillas-Ruiz J.M. Comparative study of rosemary extract and several synthetic and natural food antioxidants. Relevance of carnosic acid/carnosol ratio. *Food Chem.* 2019; 309: 125688.
 40. Rychlý J, Rychlá L, Novák I, Vanko V, Prešo J, Janigová I, Chodák I. Thermooxidative stability of hot melt adhesive based on metalocene polyolefin grafted with polar acrylic acid moieties. *Polym Test.* 2020;85:106422.
 41. Cerruti P, Malinconico M, Rychlý J, Matisová-Rychlá L, Carfagna C. Effect of natural antioxidants on the stability of polypropylene films. *Polym Degrad Stab.* 2009;94:2095–100.
 42. Teixeira TS, Vale RC, Almeida RR, Ferreira TPS, Guimaraes LGL. Antioxidant potential and its correlation with the contents of phenolic compounds and flavonoids of methanolic extracts from different medicinal plants. *Rev Virtual Quim.* 2017;9:1546–59.
 43. Stoian SA, Gabor AR, Albu A-M, Nicolae CA, Raditoiu V, Panaitescu DM. Recycled polypropylene with improved thermal stability and melt processability. *J Therm Anal Calorim.* 2019;138:2469–80.
 44. Sowińska A, Maciejewska M. Thermal analysis applied to study the influence of ionic liquids on the vulcanization, thermal stability and damping properties of ethylene-propylene-diene rubber. *J Therm Anal Calorim.* 2019;138:2669–811.
 45. Low KL, Idris A, Mohd YN. Novel protocol optimized for microalgae lutein as food additives. *Food Chem.* 2020;307:125631.
 46. Philippart JL, Sinturel C, Armand R, Gardette JL. Influence of the exposure parameters on the mechanism of photooxidation of polypropylene. *Polym Degrad Stab.* 1999;64:213–25.

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.