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RESEARCH ARTICLE

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Evaluation of the activity of natural phenolic antioxidants, extracted from industrial coffee residues, on the stability of poly(1,4-butylene succinate) formulations

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Abstract

In this work, the evaluation of the antioxidant activity of natural phenolic compounds is performed and compared to that of a conventional antioxidative agent. Phenolic molecules, extracted from industrial processing coffee residues, are added to a matrix of poly(1,4-butylene succinate) (PBS). The apparent activation energy (E_a) of the thermo-oxidative degradation is calculated by employing different methods like Kissinger-Akahira-Sunose, Flynn-Wall-Ozawa and Friedman. The results are compared with the antioxidant activity evaluation obtained through the ABTS radical scavenging assay. From the average activation energies, it is observed that the addition of the natural antioxidants led to an increase in the activation energy of the degradation process as a function of the phenolic compound content. This trend is confirmed by the results of the ABTS assay. Hence, this study proves that the active molecules extracted from agri-food waste could be employed to improve the antioxidant capacity of the biopolymer, even if the composition of the extract must be evaluated in order to mitigate the effects of other components.

KEYWORDS

ABTS assay, biodegradable polymer, kinetic methods, natural antioxidant, thermal oxidization

1 | INTRODUCTION

Nowadays the management of plastics is a global hot topic. In particular, the end-of-life of plastic materials is an increasingly pressing issue due to the environmental impact of the plastic rubbish.

Various ways of plastic recycling are being explored, but, unfortunately, the intrinsic properties of polymers and the large array of polymeric materials with different physical and chemical characteristics complicate the process and only a limited portion of plastic waste is recycled.[1,2] According to the EPA report, in 2018, 36 million tons of plastic waste were generated and only 3 million tons are actually recycled.[1] This certainly leads to an increased interest in biodegradable polymers that, for this property, can be a valid alternative to

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replace conventional and non-biodegradable materials in different applications, for example in the packaging field.

In this context, a specific attention must be spent on the additives used in polymer formulation: they have to be non-toxic and biodegradable too. Therefore, it could be a good strategy to test natural molecules as eco-friendly additives for biopolymers.

In particular, in polymer formulation, the presence of antioxidants is essential to retard the oxidation process and to allow the material to better preserve for longer times. In the green chemistry perspective, antioxidants from renewable sources and, better, from agro-industrial residues are increasingly studied.[3–5]

The exploitation of phenolic compounds, that are known to have antioxidant characteristics,[6–10] extracted from industrial processing coffee residues, is exactly one of the purposes of the H2020 PROLIFIC project which funded the research described in this paper.

PBS is a polymer both bio-derived and biodegradable, therefore owning all the sustainability characteristics; in addition, it exhibits high flexibility and impact strength. A further benefit of PBS matrix consists in its relatively low melting temperature that can prevent the degradation of polyphenols during the melting processing. Moreover, PBS has good chemical resistance and controllable rate of biodegradation. For these reasons, PBS is considered an interesting high-performance environment-friendly biodegradable plastic.[11] According to literature, oxidative degradation of PBS proceeds through the radical-radical coupling of an oxygen molecule on a carbon atom centered free radical, leading the formation of peroxyl radicals. Primary radicals, that are initiators of the degradative mechanism, can be produced on the polymer backbone in presence of oxygen.[12,13] Free-Radical Scavengers (like sterically hindered phenols) can react with the chain-propagating radicals interrupting this degradation process. Phenolic compounds are able to scavenge reactive oxygen species.[5,12,14–16] Thus, phenolic molecules extracted from coffee beans may provide an antioxidant activity toward the PBS matrix.

The aim of this work is to evaluate the effective antioxidant activity of the natural phenolic compounds, extracted from coffee residues and dispersed in a PBS matrix in different small amounts by melt mixing. A kinetic approach has been used, by calculating the apparent activation energy (E_a) of the thermo-oxidative degradation. The results were compared with those obtained through the ABTS radical scavenging assay. In addition, a comparison with the activity of a conventional antioxidative agent was carried out.

2 | EXPERIMENTAL

2.1 | Materials

Poly(1,4-butylene succinate) (PBS) material was the BioPBS FZ91PM provided by PTTMCC Biochem (Thailand), produced from polymerization of bio-based succinic acid and 1,4-butanediol and characterized by M_w of 170 kDa and melt flow index (190°C, 2.16 kg) of 22 g 10 min^{-1}.

A sample extracted from milled coffee green beans (CGB) by a subcritical water extraction (SWE), carried out by following a procedure reported in literature,[17] was used as additive (labeled exCGB). The chemical composition, determined by HPLC-DAD as previously described and expressed as mg g^{-1},[18] was: 40.0 mg of chlorogenic acid, 58.7 mg of neochlorogenic acid, 57.1 mg of cryptochlorogenic acid and 27.2 mg of caffeine. The corresponding total amount of phenolic compounds in the exCGB extracted was 16 wt%. The antioxidant activity of the extract, measured by the ABTS method (see section 2.3.5), is 75 ± 7 μgAA mg^{-1} of the sample.

Irganox 1010, 2,2-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) (≥ 98% HPLC grade), chloroform (HPLC grade) and water (HPLC grade) have been purchased by Merck.

2.2 | Sample preparation

Composites containing PBS and exCGB or Irganox 1010 were prepared using a Haake Minilab II micro-compounder (Thermo-Scientific Haake GmbH). The micro twin-screw extruder was used to mechanically mix the materials at 140°C for 1 min to favor a good dispersion of additives within the matrix. PBS and exCGB were dried overnight at 60 and 80°C, respectively, before processing.

The melted materials were transferred from the mini extruder with a preheated cylinder into a MegaTech Tecnica DueBi injection molding machine. Tensile specimens Haake type 3 dog-bone bar were prepared. The size of dog bond specimens was: width 10 mm, width in the narrow section 4.8 mm, thickness 1.35 mm, length 90 mm.

Increasing amount of exCGB powder was introduced reaching a maximum of 5%. The PBS sample containing Irganox 1010 was prepared with 1% of additive. In addition, a control sample (pure PBS) without the addition of any amount of antioxidant was also prepared. The composition and the name of the prepared samples are reported in Table 1.

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TABLE 1 Composition of the poly(1,4-butylene succinate)-based samples

Name	Additive	Additive amount [wt%]	Phenolic antioxidants [wt%]
PBS	-	-	-
PBS-exCGB1	Extracted CGB	1	0.2
PBS-exCGB3	Extracted CGB	3	0.5
PBS-exCGB5	Extracted CGB	5	0.8
PBS-Irg1	Irganox 1010	1	-

2.3 | Characterization

2.3.1 | Gel permeation chromatography

Gel permeation chromatography (GPC) measurements were performed at 30°C on a GPC Hewlett Packard Series 1100 using a PL gel 5 μm Minimixed-C column with chloroform ($CHCl_3$) as eluent with a 0.3 mL min^{-1} flow; the Refractive Index detector was used and a calibration plot was constructed with monodisperse polystyrene standards. The samples were dissolved in $CHCl_3$ and filtered on Teflon syringe filter with a pore size of 0.45 μm to eliminate the insoluble residue. The UV detector at 254 nm was used to measure the amount of Irganox 1010.

2.3.2 | Determination of the composition of the PBS-based samples

The quantity of exCGB present in the composites was verified by exploiting the different solubility of exCGB and PBS in chloroform. 1 g of PBS-exCGB sample was dissolved in 100 mL of chloroform at room temperature for 3 h under magnetic stirring. The murky suspension, due to the presence of insoluble exCGB, was filtered under vacuum. The insoluble fraction was recovered and weighed.

In the case of the PBS-Irg1 sample, Irganox 1010 was quantified by GPC analysis in chloroform, using the peak recorded by UV detector at 254 nm and a calibration curve. A similar method has been reported in the literature.[12]

2.3.3 | Differential scanning calorimetry

Calorimetric analysis was carried out by means of a Perkin Elmer DSC6 calorimeter, calibrated with high-purity standards. The measurements were performed under nitrogen. Melting temperature (T_m) and enthalpy (ΔH_m) were collected during the first scan from 25 to 150°C at 20°C min^{-1}.

2.3.4 | Thermogravimetric analysis

The thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA4000 apparatus in nitrogen (gas flow: 40 mL min^{-1}) or in air (gas flow: 50 mL min^{-1}) at 10°C min^{-1} heating rate, from 30 to 600°C. The degradation temperature (T_D) was calculated as the temperature of the maximum degradation rate, whereas the onset degradation temperature (T_{onset}) was defined as the initial temperature of degradation, corresponding to the intercept of the tangent drawn at the inflection point of the decomposition step with the horizontal zero-line of the thermal gravimetric curve. In addition, $T_{5\%}$ has been determined as the temperature at which 5% weight loss was reached.

For kinetic studies, samples of 5.0 ± 0.5 mg were heated from ambient temperature to 600°C under air atmosphere (50 mL min^{-1}). Heating rates of 2, 5, 7 and 10°C min^{-1} were used and continuous records of the sample weight as a function of the temperature and the first derivative were taken.

2.3.5 | ABTS radical scavenging assay

Antioxidant activity of exCGB extract was measured using the ABTS method by incubating an aliquot of exCGB suspension with 1 mL of ABTS solution for 30 min at 30°C.[19] Dog-bone bar were cut in 200 $\pm$ 35 mm^2 parts for antioxidant property assessment. Each piece was incubated in 1 mL of ABTS solution (2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) at 30°C in a shaking thermostatic bath. The absorbance was measured at 734 nm and the results were expressed as micrograms of ascorbic acid (AA) equivalents per surface unit (μg AA eq cm^{-2}) by means of a dose–response calibration curve (between 0 and 2 μg of AA).[19,20]

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2.4 | Kinetic analytical methods

Activation energy (E_a) was evaluated with different iso-conversional (model-free) methods. In particular, Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO) and Friedman's method were used, as reported in several papers.[21–25] The mathematical treatment of each iso-conversional methods will not be discussed in depth since it is not the focus of this article and has been extensively covered in the scientific literature.[21,22]

The KAS method is a non-isothermal iso-conversional technique which is widely used and based on the following equation[26]:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT} \quad (1)$$

where β is the heating rate, T is the kelvin temperature, A is the preexponential factor, R is the universal gas constant and $g(\alpha)$ is the integral form of the conversion function. At least three heating rates are needed to apply this equation and the respective conversion curves must be evaluated from the measured TG curves. The apparent E_a can be obtained by plotting $\ln\left(\frac{\beta}{T^2}\right)$ versus $1/T$ which delivers a straight line for a constant value of degree of conversion. The slope of the line is equal to $(-E_a/R)$ for a given value of conversion thus the activation energy is obtained as a function of conversion.

The iso-conversional FWO method was also employed.[27,28] It is a "model free" method because assumes that for all values of conversion (α), the conversion function $f(\alpha)$ does not change with the variation of the heating rate. In this method the temperatures corresponding to fixed values of α from TG scans are measured at different heating rates. The plots of $\ln(\beta)$ versus $1/T$ at a constant conversion value in the form of:

$$\ln(\beta) = \ln\left(\frac{AE_a}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E_a}{RT} \quad (2)$$

give straight lines with slope equal to $1.052\ E_a/R$.[21] Therefore, for a constant degree of conversion, a plot of $\ln(\beta)$ versus $1/T$ obtained from thermal curves recorded at several heating rates should be a straight line whose slope can be used to evaluate the activation energy.

The third iso-conversional method used was the Friedman's method that is one of the most common differential iso-conversional method.[29] This method applies the logarithm of conversion rate as a function of the reciprocal T at different degrees of conversion. Friedman's equation can be described as

$$\ln\frac{d(\alpha)}{dt} = \ln[Af(\alpha)] - \frac{E_a}{RT} \quad (3)$$

By plotting the left side of the equation against $1/T$ at different heating rates, the value of the $(-E_a/R)$ for a given value of α can be directly obtained.

The main parameters of the methods used are summarized in Table 2.

3 | RESULTS AND DISCUSSION

3.1 | Description of the samples

Four samples of PBS with increasing content of antioxidants extracted from coffee green beans were prepared by melt mixing at 140°C and analyzed: pure PBS, PBS + 1 wt%, PBS + 3 wt% and PBS + 5 wt% of phenolic compounds, as summarized in Table 1 and described in the scheme reported in Figure 1. As reported in the Experimental part (section 2.1), the total amount of antioxidant components presents in the exCGB sample is 160 mg per gram, corresponding to the 16 wt%, while the remaining fraction is mainly composed of proteins, peptides and sugars. This means that the effective amounts of antioxidants in the composites are equal to 0.2, 0.5 and 0.8 wt%, respectively, as reported in Table 1.

During the extrusion, the melt is homogeneous and uniformly colored with a yellow-brown tone (due to the brown color of the extract) whose intensity increases with increasing the amount of exCGB. In the final specimens, the exCGB appears well dispersed within the polymeric matrix (as confirmed by SEM analysis not reported in this work) and, then, the interaction of exCGB with the PBS matrix seems good. From the tests performed to verify the composition after extrusion process, the inclusion of exCGB in the PBS matrix results almost quantitative (>90 wt% for all compositions).

To compare the stabilizing activity of exCGB with the one of a conventional antioxidative agent, a sample containing 1 wt% of Irganox 1010 was formulated. In this case the melt is white and homogeneous and the inclusion of Irganox 1010 in the PBS matrix is quantitative.

The molecular weight (M_w) of the PBS-based samples was determined by GPC analysis after a filtration procedure to remove the insoluble residue. In general, the PBS-exCGB samples and the PBS-Irg specimen maintain high-molecular weight values, close to the one of pristine PBS.

The results obtained by differential scanning calorimetry (DSC) analysis, reported in Table 3, show similar behavior both for PBS and PBS-based samples, indicating that the presence of additives does not influence the

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TABLE 2 Summary of the approaches used for the determination of the apparent activation energy of the thermo-oxidation degradation[26,27,29]

Methods	Equation	Plot
Kissinger-Akahira-Sunose (KAS)	$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT}$	$\ln\left(\frac{\beta}{T^2}\right) = f\left(\frac{1}{T}\right)$
Flynn-Wall-Ozawa (FWO)	$\ln(\beta) = \ln\left(\frac{AE_a}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E_a}{RT}$	$\ln(\beta) = f\left(\frac{1}{T}\right)$
Friedman	$\ln\frac{d(\alpha)}{dt} = \ln[Af(\alpha)] - \frac{E_a}{RT}$	$\ln\left(\frac{d\alpha}{dt}\right) = f\left(\frac{1}{T}\right)$

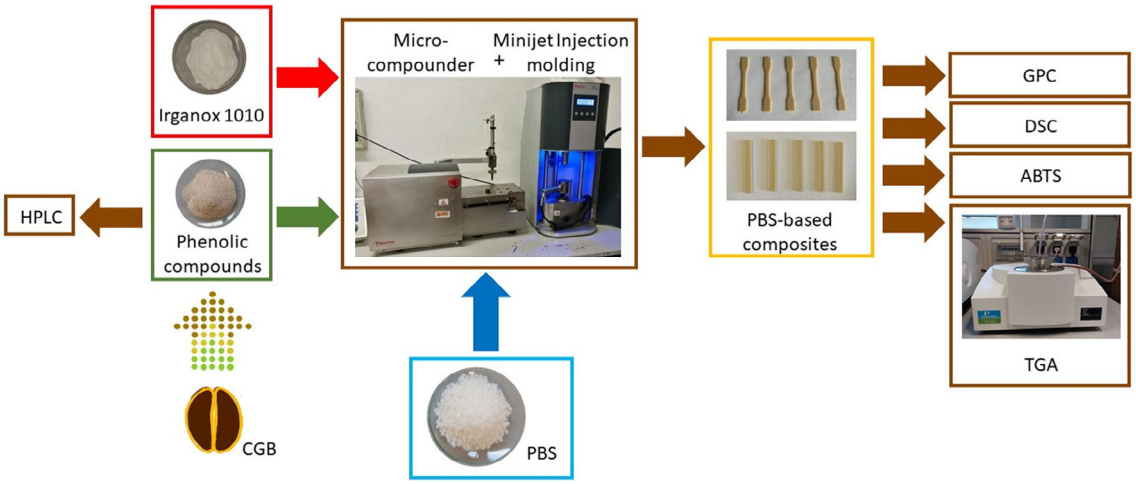

FIGURE 1 Scheme of the work [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 Thermal characterization of the PBS-based samples

	TGA in nitrogen			TGA in air			DSC (first scan)	
	$T_{5\%}$ [°C]	T_{onset} [°C]	T_D [°C]	$T_{5\%}$ [°C]	T_{onset} [°C]	T_D [°C]	T_m [°C]	ΔH_m [J g^{-1}]
PBS	360	376	403	336	360	393	118	68
PBS-exCGB1	353	375	401	340	367	398	116	68
PBS-exCGB3	336	369	396	334	362	391	116	69
PBS-exCGB5	330	362	394	324	358	388	117	74
PBS-Irg1	359	378	407	344	370	399	115	68

Abbreviations: DSC, differential scanning calorimetry; PBS, poly(1,4-butylene succinate); TGA, thermogravimetric analysis.

crystallization and the melting processes of the matrix. Indeed, the crystallization degree is similar for all the samples and, then, does not affect the thermo-oxidation analyses.

A preliminary thermogravimetric analysis is carried out in nitrogen and in air atmosphere at 10°C min^{-1}. The results extrapolated from TG e dTG curves are reported in Table 3. Figure 2 shows the TG curves recorded for PBS-exCGB samples and for exCGB under nitrogen (a) and air (b) (dTG curves in air can be viewed in Figure S1). From the TG curve of exCGB, it is evident that the additive starts to lose weight at low temperatures (about 120°C) and that the first remarkable decomposition process takes place at around 260°C. Considering that the effective amount of antioxidant molecules present in the exCGB additive is about 16 wt% and that these active molecules degrade at temperatures above 300°C,[30] this significant weight loss at about 260°C should be mainly due to the degradation of other components present in the exCGB extract, such as proteins and sugars.

Concerning the behavior of PBS-exCGB samples in nitrogen (Table 3), it is possible to notice a continuous decrease in the $T_{5\%}$, T_{onset} and T_D values with the increment of the additive content. As reported in literature, PBS degradation under inert atmosphere proceeds mainly

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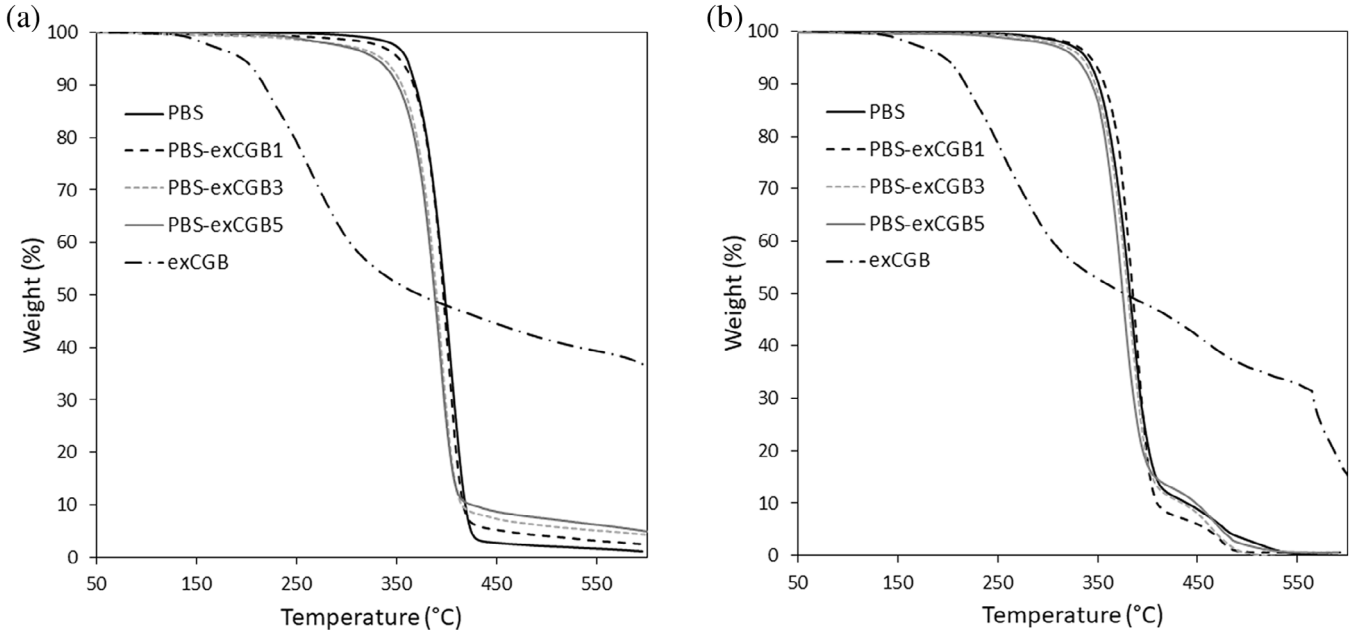

FIGURE 2 Thermogravimetric curves recorded at 10°C min^{-1} for the PBS-exCGB samples and exCGB under (a) nitrogen and (b) air

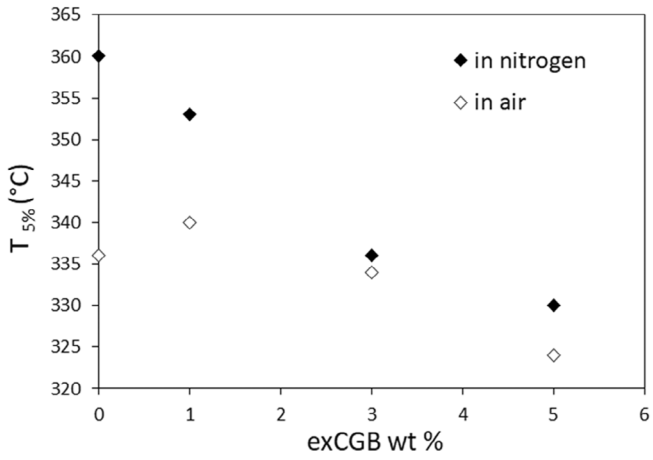

FIGURE 3 $T_{5\%}$ data of PBS-exCGB samples extrapolated from thermogravimetric curves in nitrogen and in air

by β-hydrogen-transfer bond scission, which is not affected by the presence of antioxidants.[5,12,13,24] Therefore, the decrease of the thermal stability of the samples in nitrogen atmosphere could be attributed to the low stability of some components of the exCGB extract itself. On the other hand, the thermal stability in nitrogen of the PBS-Irg1 sample is similar to the one of the PBS, in agreement with the literature.[5,12]

Regarding the analyses performed under air flow, $T_{5\%}$, T_{onset} and T_D for the PBS-exCGB1 sample are higher than those of the PBS reference. Moreover, these data are very similar to those obtained with the addition of Irganox 1010. Comparing these results with those reported in the literature,[5] it can be asserted that the phenolic compounds used in this work have a stabilizing effect over the oxidative degradation. In addition, the values tend to return near the PBS ones increasing the amount of exCGB up to 3 wt% while they decrease with concentration of 5 wt%.

The different behavior of the samples observed in nitrogen and air atmospheres is highlighted by the graph shown in Figure 3, reporting the $T_{5\%}$ data.

The gap of 25°C, between the $T_{5\%}$ values of the PBS matrix recorded in nitrogen and in air, is not maintained in the samples containing exCGB. The reduction of this gap should indicate the stabilizing effect of phenolic compounds. Indeed, two contrasting effects have to be considered to explain the composites behavior due to the addition of exCGB: the effect of the phenolic molecules, which stabilize the material over the thermo-oxidative process, and the effect of the fraction of exCGB, which degrades at low temperature and whose degradation mechanism is not affected by the presence of the phenolic compounds. Therefore, to study more in depth the antioxidant effect of the quantities of phenolic compounds on the PBS matrix overcoming the not converged action, kinetic studies were performed and discussed in the following section.

3.2 | Kinetic analysis

In order to study the influence of the characteristics and amounts of the antioxidant on the thermo-

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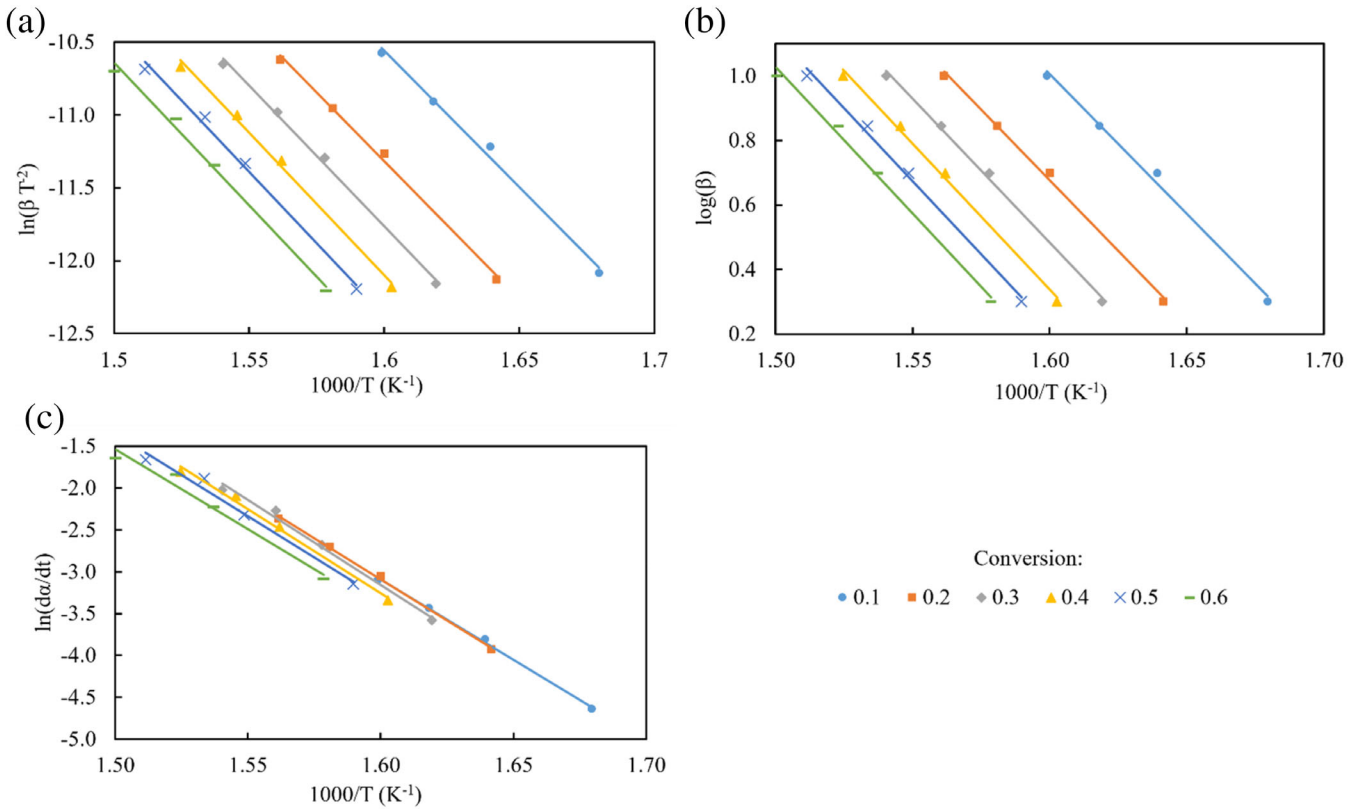

FIGURE 4 Iso-conversional plots for the PBS-exCGBB3 sample obtained for each mathematical model: (a) Kissinger-Akahira-Sunose (b) Flynn-Wall-Ozawa (c) Friedman [Color figure can be viewed at wileyonlinelibrary.com]

oxidative degradation reaction of the material, thermogravimetry and derivative thermogravimetry (TG/dTG) analysis under non-isothermal conditions at four heating rates (2, 5, 7 and 10°C min^{-1}) were used (the corresponding TG curves and the extrapolated data are reported in Figure S2 and Table S1). For all the samples and at all the heating rates, the mass loss vs. temperature occurs in two steps as already observed in Figure 2b, obtained in non-isothermal conditions. The main weight loss process takes place at about 400°C whereas the second phenomenon is less important and occurs at around 480°C. The effect of the presence of the antioxidant molecules can be observed in the first degradation step: for this reason, the analysis has been carried out in this initial phase up to a weight loss of 60%. Moreover, to avoid degradation processes which are due to the different components, the conversion starting from 0.1 has been considered. Magnifications of the dTG profiles showing the exclusion of this effect are reported in Figure S3.

The KAS, FWO and Friedman's model-free methods have been employed to obtain the activation energy (E_a) of the thermo-oxidation degradation reaction. A conversion ranges from 0.1 to 0.6 was considered for the iso-conversional plots in order to calculate E_a.

As an example, the iso-conversional plots for the sample with 3 wt% of exCGB extract for the kinetic models employed in this work are shown in Figure 4.

The E_a and the coefficient of determination (R^2) obtained from the KAS, FWO and Friedman iso-conversional plots at different conversion values are shown in Tables 4, 5 and 6, respectively. It is worth mentioning that the correlation coefficient (R^2) for all the samples and for each method were found to be greater than 0.97. These results demonstrate that the KAS, FWO and Friedman's methods could be highly reliable for calculating E_a for PBS samples.

In agreement with the scientific literature, comparing the E_a values obtained through KAS and FWO methods, it can be observed that the FWO values are slightly higher and an excellent agreement between the E_a for both methods is notable, in agreement with publications on kinetic methods.[31]

The data reported in Tables 4, 5 and 6 can be discussed, firstly, by considering the comparison of the behavior of different samples at the same degree of the conversion.

A significant increment in E_a for each conversion values can be observed as the exCGB content increases. High E_a values can be observed also for the PBS sample

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TABLE 4 Activation energy (E_a) and coefficient of determination (R^2) calculated through Kissinger-Akahira-Sunose method

Conversion	PBS		PBS-exCGB1		PBS-exCGB3		PBS-exCGB5		PBS-Irg1	
	E_a [J Kmol^{-1}]	R^2	E_a [J Kmol^{-1}]	R^2	E_a [J Kmol^{-1}]	R^2	E_a [J Kmol^{-1}]	R^2	E_a [J Kmol^{-1}]	R^2
0.1	133	0.9778	141	0.9910	156	0.9932	172	0.9899	129	0.9942
0.2	140	0.9900	153	0.9882	157	0.9964	164	0.9948	142	0.9946
0.3	147	0.9910	160	0.9970	161	0.9966	164	0.9947	156	0.9966
0.4	152	0.9881	161	0.9985	163	0.9954	165	0.9947	163	0.9983
0.5	152	0.9876	161	0.9998	163	0.9941	167	0.9951	170	0.9973
0.6	153	0.9884	162	0.9994	163	0.9931	172	0.9933	176	0.9960

containing Irganox, mainly at high conversions. This behavior suggests that the thermo-oxidation process of the polymeric matrix in oxygen is contrasted by the presence of exCGB additive, also in a small amount.

To compare the data of E_a as a function of the exCGB amount, the average values were calculated in 0.1–0.6 range of conversion and reported in Table 7. The values of kinetic parameters evaluated by the three methods are almost the same and in good agreement among them. All methods show that the virgin PBS sample presents the lowest E_a and a noticeable increase in E_a can be observed for all the samples.

It is interesting to observe that the same E_a value has been calculated for both PBS-exCGB1 and PBS-Irg1 samples, using KAS and FWO methods. This means that the antioxidant activity of the additive investigated in this work is comparable to that observed with 1 wt% of Irganox 1010, a conventional antioxidant product. By considering that the real amount of phenolic compounds contained in this sample is about 0.1 wt%, this result indicates a very high antioxidant activity of the natural extracted molecules. This result is in agreement with the literature in which the protective effect of 0.1% caffeic and 0.1% chlorogenic acids is reported.[10]

By comparing the results obtained for the PBS-exCGB samples, it is possible to notice that the E_a data increase with the exCGB content up to the composition containing 5% of additive.

To explain this behavior, it is possible to consider that the phenolic compounds act as radical scavengers by the hydrogen atom donation from the phenolic hydroxyl group. Therefore, in the presence of phenolic molecules the thermal oxidative PBS degradation is inhibited and a different mechanism, probably similar to that occurring in inert atmosphere, characterized by a higher E_a, takes place.[24] Accordingly, by observing the data reported in Table 7, it is possible to observe that the averaged E_a value is about 150 J Kmol^{-1} for PBS whereas it is about 170 J Kmol^{-1} for PBS-exCGB5. If the amount of radical scavengers is not enough high, the two mechanisms can occur simultaneously and the E_a data have intermediate values, as it occurs for PBS-exCGB1 and PBS-exCGB3 samples.

Similar results are reported in literature for agro-wastes rich in natural antioxidants.[7] In particular it is also reported that the antioxidant activity reaches a maximum with increasing the antioxidant concentration. Iyer et al. found the best value between 4 and 12 wt% of natural compounds, depending on the agro-waste used. In our case, composites with higher concentrations of exCGB additive could be prepared to reach this maximum value but the presence of the less stable fraction in the exCGB extract must also be taken into account. Finally, it is noteworthy to underline that E_a data indicate also that the natural phenolic antioxidants investigated in this work remain active after the mixing with the polymeric matrix at 140°C: therefore, thanks to the relatively low processing temperature of PBS, the exploitation of exCGB in PBS formulation does not require specific strategies of natural additive protection, for example by encapsulation in inorganic lamellar structures.[32]

3.3 | Antioxidant properties by ABTS radical scavenging assay

The 2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) assay is one of the most widely used methods of antioxidant capacity measurement. The ABTS-based assay is experimentally and instrumentally easy to apply, give fast and reproducible data and is rather cheap.[33]

The approach of the ABTS assay is based on an electron transfer and involves reduction of a colored oxidant. In specification, the ABTS assay is based on the generation of a blue/green $ABTS^{\bullet+}$ that can be reduced by antioxidants present in the reaction mixture. The amount of decolorization is related to the concentration of the added antioxidant.[34] The basic chemistry of

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TABLE 5 Activation energy (E_a) and coefficient of determination (R^2) calculated through Flynn-Wall-Ozawa method

Conversion	PBS		PBS-exCGB1		PBS-exCGB3		PBS-exCGB5		PBS-Irg1	
	E_a [J Kmol^{-1}]	R^2	E_a [J Kmol^{-1}]	R^2	E_a [J Kmol^{-1}]	R^2	E_a [J Kmol^{-1}]	R^2	E_a [J Kmol^{-1}]	R^2
0.1	136	0.9806	144	0.9898	158	0.9939	173	0.9910	133	0.9949
0.2	143	0.9913	156	0.9973	159	0.9941	165	0.9955	145	0.9953
0.3	150	0.9921	162	0.9986	163	0.9924	166	0.9954	159	0.9970
0.4	154	0.9895	163	0.9998	165	0.9939	167	0.9954	166	0.9985
0.5	155	0.9891	164	0.9998	165	0.9987	169	0.9957	172	0.9976
0.6	156	0.9898	167	0.9995	165	0.9979	172	0.9941	177	0.9964

TABLE 6 Activation energy (E_a) and coefficient of determination (R^2) calculated through Friedman's method

Conversion	PBS		PBS-exCGB1		PBS-exCGB3		PBS-exCGB5		PBS-Irg1	
	E_a [J Kmol^{-1}]	R^2	E_a [J Kmol^{-1}]	R^2	E_a [J Kmol^{-1}]	R^2	E_a [J Kmol^{-1}]	R^2	E_a [J Kmol^{-1}]	R^2
0.1	141	0.9869	152	0.9802	160	0.9981	165	0.9928	147	0.9897
0.2	154	0.9918	156	0.9997	163	0.9975	164	0.9984	175	0.9956
0.3	168	0.9813	162	0.9981	169	0.9898	176	0.9930	186	0.9970
0.4	159	0.9821	166	0.9977	167	0.9920	170	0.9923	188	0.9940
0.5	153	0.9882	167	0.9969	164	0.9816	178	0.9867	190	0.9917
0.6	158	0.9918	168	0.9934	164	0.9741	187	0.9739	194	0.9911

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TABLE 7 Average activation energy (E_a) as exCGB content increases, calculated by KAS, FWO and Friedman's method

Methods	Average E_a PBS [J Kmol^{-1}]	Average E_a PBS-exCGB1 [J Kmol^{-1}]	Average E_a PBS-exCGB3 [J Kmol^{-1}]	Average E_a PBS-exCGB5 [J Kmol^{-1}]	Average E_a PBS-Irg1 [J Kmol^{-1}]
Kissinger-Akahira-Sunose (KAS)	146	156	160	167	156
Flynn-Wall-Ozawa (FWO)	149	159	162	169	159
Friedman	155	162	164	173	180

the ABTS-based assay is the interaction between an antioxidant and the pre-generated $ABTS^{\bullet+}$ radical cation. $ABTS^{\bullet+}$ scavenging can be easily quantitatively detected due to the bleaching of absorption spectrum characteristic maxima at 414, 417, 645, 734, and 815 nm.[33] According to the literature the higher wavelength range is recommended to avoid possible interference.[35] Some reviews have pointed out the issues related to the ABTS-based assay, nevertheless the ABTS assay proves to be very useful for tracking changes within the same antioxidant system and for composition effect evaluation.[33] These factors together with the simplicity, rapidity, low cost and good reproducibility, have led to the widespread use of this approach for the evaluation of antioxidant activity.[36,37]

In order to verify the results obtained with TG analysis, antioxidant properties were evaluated by the widely used ABTS radical scavenging assay.[36,37] The analyses have been carried out on the extract, the virgin PBS and the PBS samples mixed with 1%, 3% and 5% of exCGB. It is interesting to notice that the extract is very active (75 ± 7 μgAA mg^{-1} of the sample).

Figure 5 shows the obtained results in the first round of assay. The addition of additives increases the basal PBS antioxidant activity of 2.3, 4.9 and 5.3-times for 1%, 3% and 5% respectively. Pure PBS had an almost constant radical scavenging activity (on average 0.22 μgAA cm^{-2}), which was reached by all composite formulation in the second (0.20–0.42 μgAA cm^{-2}) and third (0.18–0.25 μgAA cm^{-2}) rounds of analyses. It seems to suggest that all the antioxidant molecules exposed on the specimen surface react the first time as they are put in contact with the radical reagent.

For the PBS-exCGB5, the error is high probably due to the presence of a large amount of not phenolic molecules that could contrast the efficiency of the antioxidant molecules.

Therefore, the ABTS assay confirms the results obtained through kinetic analysis up to 3 wt% in CGB extract.

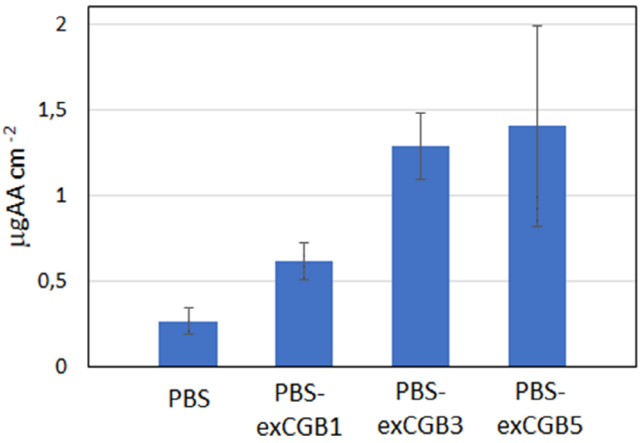

FIGURE 5 Results obtained via ABTS assay; data are the average ± SD of five determinations for poly(1,4-butylene succinate) (PBS) and of three determinations (three pieces each different specimen) for PBS + extracts: average of 1%, 3% or 5% exCGB [Color figure can be viewed at wileyonlinelibrary.com]

4 | CONCLUSIONS

In this study the antioxidant activity of natural phenolic compounds, extracted from coffee bean by-products, against the thermo-oxidative degradation of the PBS matrix was evaluated by TG analysis, employing model free iso-conversional mathematical methods. The results were compared with the antioxidant activity evaluation done by ABTS assay. Moreover, a comparison with the activity of a traditional antioxidant (Irganox) has been also carried out.

The thermogravimetric evaluation of the behavior of the PBS matrix by kinetic analyses shows that the activation energy of the degradation process increases with the increment of the amount of the phenolic molecules, indicating an antioxidant activity of the natural extract. This result is confirmed by the ABTS method. Moreover, the natural phenolic molecules appear to be very active, with an efficiency similar to the one of Irganox compound.

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This result is significant because it highlights that the low PBS processing temperature (140°C) maintains the properties of the phenolic compounds avoiding degradation phenomena. Similar investigations are necessary for formulations based on polymeric matrixes with higher melting temperature.

As a conclusion, the present study demonstrates that natural molecules extracted from agri-food waste can be valorized as antioxidants for biopolymers, thus facilitating their application in the packaging field. However, it is noteworthy to underline that the extract contains only a percentage of phenolic molecules: it is characterized also by the presence of other compounds, such as peptides, proteins and sugars, that tend to degrade at low temperatures. Therefore, the use of natural extracts must be always carefully evaluated in order to mitigate this negative effect.

AUTHOR CONTRIBUTIONS

Paola Marchese: Conceptualization (equal); data curation (equal); supervision (equal); validation (equal); writing – original draft (equal); writing – review and editing (equal). **Stefano Bianchi:** Data curation (equal); formal analysis (lead); investigation (equal); writing – original draft (equal); writing – review and editing (equal). **Micaela Vannini:** Supervision (equal); writing – review and editing (equal). **Laura Sisti:** Supervision (equal); writing – review and editing (equal). **Annalisa Tassoni:** Data curation (supporting); formal analysis (supporting); writing – original draft (supporting). **Maura Ferri:** Data curation (supporting); formal analysis (supporting); writing – original draft (supporting); writing – review and editing (supporting). **Norma Mallegni:** Formal analysis (supporting). **Patrizia Cinelli:** Formal analysis (supporting). **Annamaria Celli:** Conceptualization (lead); data curation (equal); funding acquisition (lead); supervision (equal); writing – review and editing (equal).

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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