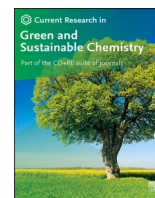




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Potential of caffeic acid as an effective natural antioxidant for polypropylene-polyethylene copolymers: A DFT and experimental study

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ABSTRACT

Caffeic acid (CAF) is a polyphenolic compound commonly found in plants, valued for its ability to act as an antioxidant. This study focused on investigating the impact of a natural antioxidant, specifically caffeic acid (CAF), compared to two synthetic antioxidants, butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), on the thermal stability of propylene/ethylene copolymer (C-PP/PE), aiming to establish a theoretical framework for the advancement of novel polymeric antioxidant compounds. Theoretical calculations were conducted to determine each compound's thermodynamic properties and antioxidant activity. The phenolic hydroxyl bond dissociation enthalpy (BDE) values revealed that BHA had the lowest value (325.6 kJ mol⁻¹), trailed by CAF (328.2 kJ mol⁻¹) and BHT (341.3 kJ mol⁻¹), indicating a higher electron-donating capacity of BHA. Transition energy (TS) calculations indicated that BHA had the lowest TS energy (49.29 kJ mol⁻¹), succeeded by CAF (57.61 kJ mol⁻¹) and then BHT (75.57 kJ mol⁻¹), suggesting greater efficiency in radical scavenging. Additionally, the obtained rate constants showed that CAF had the highest hydrogen abstraction rate ($k = 1.05 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), followed by BHA ($k = 1.17 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$), and then BHT ($k = 4.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$). These results support the effectiveness of CAF as a potentially more active antioxidant. In the experimental part of this study, it was observed that C-PP/PE with BHA showed a lower melt flow index (MFI) (8.51), indicating more excellent thermal stability. On the other hand, samples containing natural caffeic acid extracts exhibited a gradual decrease in MFI with increasing CAF concentration (MFI of 9.4, 8.82, 7.59, 6.44, and 5.98 for concentrations of 0.025, 0.05, 0.075, 0.1, and 0.125 ppm, respectively), suggesting a progressive improvement in the thermal stability of C-PP/PE with increasing natural antioxidant. In TGA analyses, decomposition was observed around 340 °C in samples without additives and those containing 0.1 ppm of BHA. In contrast, samples with different concentrations of CAF showed delayed degradation, observed in the temperature range of 380–400 °C. This delay in degradation indicates that CAF imparts more excellent thermal stability to C-PP/PE copolymer, as it reaches temperatures above 400 °C before starting its decomposition. These findings support the feasibility of using natural antioxidants such as CAF to improve the thermal properties of copolymers.

1. Introduction

While there is increasing attention towards biodegradable polymers, particularly in certain applications, polyolefins continue to dominate the industrial field [1]. Within these, polypropylene and polyethylene compounds (C-PP/PE) stand out as the leading thermoplastics in the

packaging industry thanks to their outstanding mechanical properties and impact resistance, which have led to a significant increase in demand for these materials in recent years. European plastic converters requested around 20 million tons of C-PP/PE in the past year alone. This demand arises mainly from the need for various industrial products, such as confectionery and wrappers, microwave containers, and

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automotive parts. It is important to note that C-PP/PE is widely used in manufacturing products that contribute rapidly to the significant accumulation of plastic waste. However, over 70 % of these wastes are effectively recovered through industrial recycling processes (covering 31 % of plastic waste) and energy recovery (accounting for 42 % of plastic waste), which aligns with the principles of a circular economy [2, 3]. Over 8.7 million tons of plastics are recycled yearly [2]. Nevertheless, polyolefins are prone to degradation throughout the recycling process and traditional industrial methods, including injection molding, extrusion, and film creation. Thermooxidative degradation forms unwanted brittle material [4,5], leading to prolonged reprocessing time and an increase in the molecular weight and melt viscosity of C-PP/PE. As a result, this causes a decrease in the mechanical efficiency of the polymer [6].

The degradation of C-PP/PE is an irreversible process, often characterized by oxidation as the primary mechanism, along with other possible additional processes [7]. Oxidative stress entails the assault by free radicals, which are highly reactive and unstable entities characterized by possessing an unpaired electron in their outermost shell [8]. Antioxidants play a crucial role in counteracting this process by donating an electron to the free radicals and neutralizing and deactivating them [9]. However, antioxidants frequently used in industrial settings are primarily derived from petroleum and unsuitable for specific purposes, such as those found in toy, childcare, medical, or food packaging industries. Common synthetic antioxidants, such as *butylated hydroxytoluene* (BHT) and *butylated hydroxyanisole* (BHA), have raised growing concerns due to their potential carcinogenicity and toxicity [10]. This apprehension has prompted the introduction of the most recent REACH environmental safeguard certification by the EU, aimed at ensuring human safety. Consequently, certain aforementioned synthetic antioxidants have faced regulatory restrictions in the US and Japan [11]. These traditional synthetic antioxidants have been employed as efficient supplements in moderate quantities (i.e., ranging from 0.1 to 0.5 % by weight) to safeguard the polymer framework during processing [12,13]. Consequently, there is a global inclination to replace artificial antioxidants with harmless alternatives derived from renewable sources. This alteration arises from migration, whereby some of the supplementary substances transfer to the product it encounters, potentially eliciting toxicity concerns [14,15].

To mitigate this issue, natural antioxidants (NAs) are being utilized as a preventive strategy [7,14–16]. Therefore, integrating NAs as additives into polymers has arisen as a promising approach to shield the polymer matrix from thermal oxidative degradation and UV radiation throughout its usage (See Fig. 1). Additionally, the simultaneous use of these additives lessens the footprint of the final product due to their regenerative properties [8,17]. Flavonoids are the primary contributors to synthesizing most natural antioxidants and polyphenolic compounds. These compounds are receiving increasing attention in plastic

processing as substitutes for antioxidants regularly used to promote environmentally responsible practices [8,9,16,18]. Samper et al. found that flavonoids, such as *silibinin* and *quercetin*, had a more significant stabilizing effect on the PP matrix than flavanone glucosides, such as *hesperidin* and *naringin*. The stabilizing effect of these flavonoids is equivalent to that of petroleum-derived antioxidants, such as ethane 330 and Irganox 1010, which are frequently used in industrial settings [16].

With growing concerns over environmental issues, the substitution of synthetic additives with eco-friendly alternatives becomes imperative. Natural antioxidants, present in a diverse array of natural sources including fruits, petals, flowers, and even animal products like cow's milk and honey [12], represent a sustainable and increasingly attractive option across various industries. *3,4-dihydroxycinnamic acid* (*caffeic acid*, CAF) is a compound widely occurring in nature. It is found in various plant products, including fruits, vegetables, wine, olive oil, and coffee beans [19]. This acid has been the subject of study by various research groups, highlighting its efficacy as a therapeutic agent due to its antioxidant properties [20] and its ability to chelate metal ions [21].

Furthermore, recent research has revealed a broad spectrum of pharmacological effects associated with CAF. Its ability to inhibit enzymatic activity, as well as its anti-inflammatory and antitumor effects, has been demonstrated [22]. Studies also suggest its potential antimetastatic effects [23] and its ability to inhibit HIV replication [24]. Caffeic acid has shown remarkable efficacy in neutralizing free radicals present in edible oils and fats [25,26], surpassing the potency of BHT and BHA [27]. Because of its widespread presence in different origins and its varied biological functions, CAF has risen as a key and extensively utilized compound in the enhancement of biomass molecules' functionality. Peng Fei and collaborators boosted the antimicrobial and antioxidant features of chitosan by integrating CAF onto it through a non-radical method of synthesis [28].

Theoretical studies on antioxidants have been conducted using Density Functional Theory (DFT), which is related to the structural properties influencing antioxidant activity [29,30]. This methodology has demonstrated cost and time reductions compared to traditional experimental methods. Additionally, molecular simulations offer the advantage of conducting virtual experiments straightforwardly, allowing for capturing aspects that may elude conventional experimental techniques at the microscopic level. In antioxidant studies, bond dissociation energy (BDE) has been used as an indicator to predict the antioxidant activity of phenols through the hydrogen atom transfer mechanism (HAT) [31–35]. Generally, this antioxidant activity is associated with a lower BDE value for the phenolic hydroxyl group.

Furthermore, a second hydrogen atom positioned orthogonally may impact the BDE and improve the efficacy of transferring hydrogen atoms to the peroxy radical [36]. Despite the extensive studies on caffeic acid, there still exists a significant gap in the field of polyolefins, such as polypropylene, and even more so in copolymers. To our knowledge, no

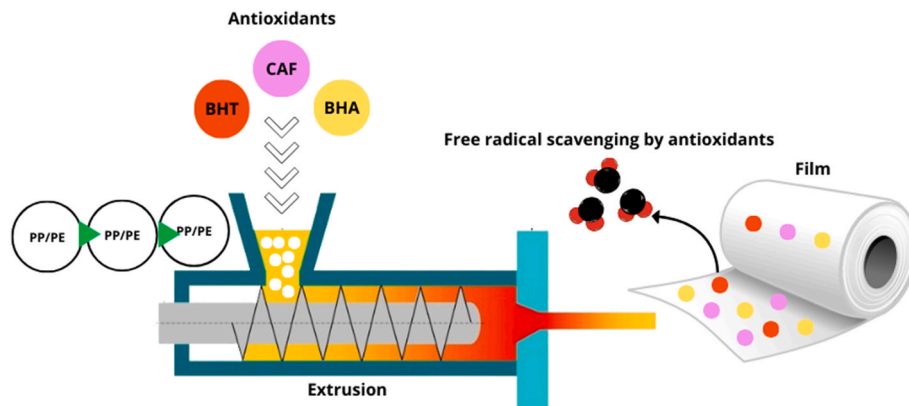


Fig. 1. The degradation process of C-PP/PE.

theoretical-experimental investigations have addressed caffeic acid as an antioxidant in polypropylene and polyethylene copolymers. This gap represents the central innovation of our work.

To replace synthetic antioxidants with high-potency natural versions, it is imperative to compare these species to identify the most effective alternatives. Likewise, detailing the antioxidant potential of these species is crucial. Consequently, we will compare two synthetic antioxidant additives (BHT and BHA) with a natural one (*caffeic acid*) using computational tools. Additionally, it is essential to consider that free radicals are primarily responsible for copolymer degradation. Computational research aims to elucidate the mechanisms underlying caffeic acid's ability to eliminate these free radicals. Among these mechanisms are Hydrogen Atom Transfer (HAT), Sequential Proton Loss Electron Transfer (SPLET), and Sequential Electron Transfer - Proton Transfer (SET-PT). To carry out this task, Density Functional Theory (DFT) calculations were employed to determine the enthalpies associated with each of these steps. Based on theoretical results suggesting that caffeic acid may outperform BHA as an antioxidant, we aim to confirm this hypothesis through practical experiments. To this end, we designed a study using small amounts of natural *caffeic acid* extracts as additives to improve the stability of polypropylene and polyethylene copolymers (C-PP/PE). Therefore, mixtures containing C-PP/PE and caffeic acid extracts in varying amounts (0.025, 0.05wt percent, 0.075 percent, 0.1, and 0.125 percent) were created. Subsequently, these combinations were subjected to a hot extrusion technique to replicate the conditions seen in industrial processing. The thermo-oxidative behavior of these mixtures was evaluated using the hot melt flow index, thermogravimetric analysis, and kinetic analysis, which is advantageous for examining the rate at which polymers undergo thermal degradation. The apparent activation energy (E_a) was determined through the Horowitz-Metzer and Coats-Redfern method [37,38]. Furthermore, pure polypropylene (PP) fortified with commercial BHA, a synthetic antioxidant widely used in various industrial sectors, was compared to gather data on the feasibility of replacing frequently used traditional antioxidants in the industrial sector with the natural antioxidants proposed in this study.

2. Materials and methods

2.1. Computational methodology

The structures of all compounds were sourced from the National Institutes of Health (NIH) PubChem database, forming the research dataset. Conformational analysis and geometry optimizations were conducted using Gaussian 16. Two DFT methods were applied: the B3LYP hybrid [39] in combination with the 6-311+G(d,p) basis set and the *meta*-GGA hybrid M06-2X [40] in combination with the 6-311++G(d,p), 6-311+G(d,p), and 6-311+G(d,p) basis sets. The values of $H(H^+)$, $H(H\bullet)$, and $H(e^-)$ in the gas phase were calculated with the M06-2X/6-311++G(d,p) level of theory, yielding 0.4963 au, -0.4979 au, and -0.4981 au, respectively.

After generating the initial configurations of CAF, BHA, and BHT, the geometric structures of the three polyphenols, along with their radicals, anions, and dehydrogenation cations, were optimized. The energy was calculated using B3LYP/6-311++G(d,p) and M06-2X with different bases (6-31G+(d,p), 6-311++G(d,p), and 6-311+G(d,p)). The most stable conformations were identified. We selected these methods to assess the antioxidant potential of the species under study due to their previously demonstrated effectiveness in comparable systems [41–44]. Frequency analysis indicated the presence of no imaginary frequencies, suggesting a stable position on the potential energy surface. Detailed discussions on the antioxidant properties of the polyphenols were conducted, taking into account factors such as molecular geometry, bond dissociation energy (BDE), ionization potential (IP), proton dissociation energy (PDE), proton affinity (PA), and electron transfer enthalpy (ETE) of each phenolic hydroxyl group in the gas phase, as well as frontier

molecular orbitals. Furthermore, optimization of transition state structures of phenolic hydroxyl groups at different positions in the presence of $\cdot OOH$ was carried out.

2.1.1. Exploration of antioxidant mechanisms

In the literature, three relevant mechanisms are found to describe the process of radical scavenging in molecules with antioxidant properties: HAT, SET-PT, and SPLET. The fundamental principle of the HAT mechanism involves “breaking the O–H bond homolytically”, where the hydrogen is directly “donated by the antioxidant” “to neutralize the free radical” ($R\bullet$) (1). The antioxidant capacity of a compound can be determined by the “BDE associated with the O–H bond”. A lower BDE value indicates that the strength of the O–H bond is weaker, suggesting a higher antioxidant capacity of the compound.

The alternative mechanism is the SET-PT process, delineated in two steps: the electronic dissociation of the antioxidant (OH) and the proton transfer from the radical cation ($A_{Ox}OH^{+\bullet}$) (2). The significance of IP and PDE values cannot be overstated in determining scavenging efficacy. Compounds exhibiting low IP and PDE values demonstrate heightened effectiveness in radical scavenging.

SPLET represents the third mechanism, which can be broken down into three stages: the creation of the antioxidant anion and the generation of the radical. These processes are influenced by the values of PA and ETE [45–47].



Various parameters, including molecular descriptors, are employed in evaluating the antioxidant characteristics of a compound. These include softness (S), electronegativity (χ), hardness (η), electron affinity (A) and electrophilicity index (ω). These factors play a critical role in elucidating the antioxidant potential of compounds. η and χ values are determined by Parr and Pearson. Additionally, Koopman's theory is applied in this investigation to compute the ionization potential (I) and electron affinity values [45].

$$\eta = \frac{I - A}{2} \quad (4)$$

$$\chi = \frac{I + A}{2} \quad (5)$$

Calculations of ω and S are obtained through the following formulas:

$$\omega = \frac{\mu^2}{2\eta} \quad (6)$$

$$S = \frac{1}{\eta} \quad (7)$$

I used the M06-2X functional, which is fully parametrized and incorporates an empirical exchange correlation, along with the 6-311++G(d,p) basis set. This method was chosen for its recognized accuracy in calculating rate constants for radical reactions in solution, as indicated by previous research [48–50]. For the kinetic analysis, the quantum mechanics-based Quantum Mechanics for Global Free Radical Scavenging Activity (QM-ORSA) test was employed, validated experimentally [51–53]. The rate constants (k) were calculated at 298.15 K using the conventional transition state theory (TST) [54–58].

$$k = \alpha_k \frac{K_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (8)$$

Where: α reaction symmetry numbers; k tunneling corrections; K_B Boltzmann constant; h Planck constant.

2.2. Materials

The polypropylene and polyethylene compounds (C-PP/PE) utilized in this study were sourced from Propilco (Colombia) as additive-free granules. Caffeic acid compounds were extracted from coffee processing byproducts obtained from facilities in Colombia using supercritical fluid extraction. Ciba (Colombia) provided the synthetic antioxidant BHA, with a purity of 98 %.

2.2.1. Supercritical fluid extraction: equipment and procedure description

The laboratory-scale equipment previously described by Tello et al. [59] was used to perform the supercritical fluid extraction. This apparatus consisted of a CO₂ supply line, a 50 mL 316 stainless steel extractor, a pressure regulation device, and a sample collection mechanism, as shown in Fig. 2.

Liquid phase CO₂ was introduced from the pressurized container and brought to a temperature of 258 K in a temperature-regulated bath via a diaphragm pump with a cooled head. Before entering the container, the pressurized CO₂ was heated in a coil within a thermal jacket. The container was also maintained at the appropriate temperature with another thermal jacket. Both devices had a temperature control accuracy of ± 1 K and were monitored with a type K thermocouple in direct contact with the fluid and the solid inside the reactor. A manometer with an accuracy of ± 6 bar was used to measure the pressure. For pressure and flow control, a heated micro-dosing valve was used in conjunction with a pump. A pressure release device set to 370 bar was installed to prevent the pressure from exceeding the established limits. The CO₂ flow, determined by the mass flow meter, was controlled at the end of the line with an accuracy of ± 0.7 g/min.

The coffee husks, after being weighed and properly prepared, were placed in the extractor to form a stationary bed. A total of 9.0 ± 0.3 g of whole husks and 15.0 ± 2 g of ground husks were loaded into the extractor, respectively. Distribution devices made from stainless steel mesh, equivalent in size to the cross-section of the extractor, were placed approximately every 2 cm during tests with ground material. The extractor was then sealed and preheated. After preheating, CO₂ was introduced by pumping, and once the target pressure was reached, the back pressure regulator (BPR) was activated, allowing a constant flow through the bed. After the valve, the CO₂ pressure was released, decreasing the solvent capacity of the supercritical fluid and precipitating the extract into a pre-weighed glass flask. After the designated treatment time, the device was depressurized, the extract was quantified, and the coffee husks were removed. The total amount of CO₂

circulated was recorded using the mass flow meter.

2.2.2. Preparation of polypropylene/polyethylene compound mixtures with varying concentrations of caffeic acid extracts

Blends comprising caffeic acid extracts and polypropylene/polyethylene compounds were prepared by mixing ground polypropylene/polyethylene compounds with different concentrations of caffeic acid extracts (0.025, 0.05 wt percent, 0.075 percent, 0.1, and 0.125 percent) in a standard mixer set to 25 °C for 8.5 min. Subsequently, each sample underwent processing using an extruder equipped with five temperature zones: 189 °C, 196 °C, 200 °C, 210 °C, and 220 °C. Films measuring 315 mm in diameter and 1.2 mm in thickness were then manufactured by compressing the composite materials. An unmodified PP film was also produced using identical processing conditions for comparative analysis.

2.3. Characterization techniques

2.3.1. Water contact angle

The contact angles of the polypropylene/polyethylene compounds-caffeic acid extract films with water were carried out with an Easydrop model FM140 equipment (Krüss GmbH). To carry out the test, the sample was placed on the surface, and a camera was placed on its opposite side to capture an image of the drop applied to each sample illuminated from one side. The Easydrop team worked with DSA1 software that helped determine the contact angle for each polymeric composite of interest.

2.3.2. Analysis of melt flow index (MFI)

The MFI was measured following the specifications of ISO 1133 [60]. The plastometer cylinder was kept at a temperature of 230 °C, and a consistent load of 2.2 kg was applied. Measurements were performed on a Tinius Olsen MP1200 plastometer equipped with a nozzle of 3 mm diameter and 9 mm length.

2.3.3. Thermal analysis characterization

Thermal gravimetric analysis (TGA) were conducted to assess the impact of CAF on the thermal resistance of the copolymers. The Perkin Elmer TGA 7 instrument was utilized for the evaluation. with samples weighing between 17 and 21 mg. The analysis involved subjecting the samples to a dynamic heating cycle from 28 to 650 °C at a steady rate of 15 °C/min under a nitrogen atmosphere, with a flow rate of 50 mL/min. The starting point of thermal decomposition (T5%) was identified when

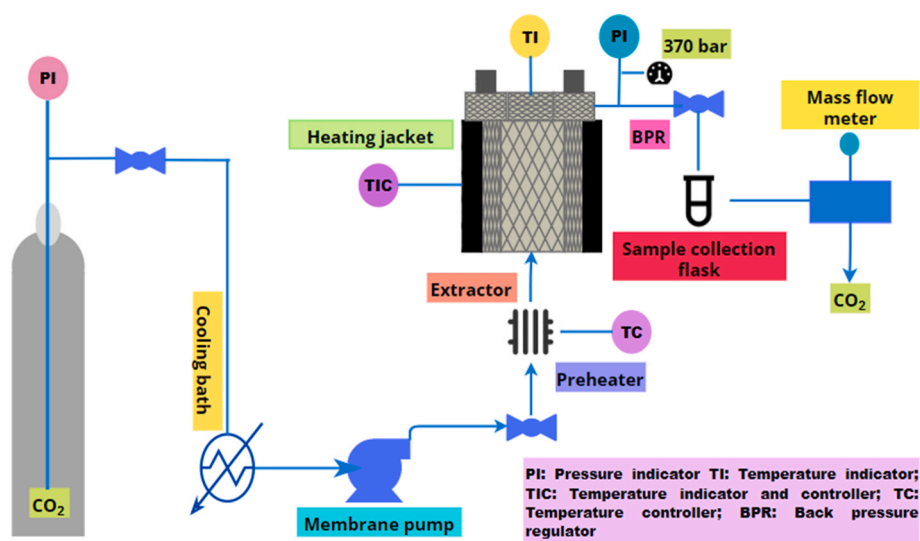


Fig. 2. Extraction of CAF using supercritical fluid.

a 5 % mass loss occurred, while the temperatures of peak degradation rate (Tmax) were determined from the corresponding peak in the first derivative of the TGA curves (DTG). To comprehend the scientific study, Horowitz-Metzer, and Coats-Redfern methods were employed to determine the kinetic parameters that will aid in estimating valuable lifespan and the degree of degradation of the produced thermoplastics [16,17, 61]. Equation (9) presents the Horowitz-Metzer model:

$$\ln \left[\ln \left(\frac{1}{1-\alpha} \right) \right] = \frac{E_a \theta}{RT_s^2} \quad (9)$$

The equation illustrates the relationship between several variables. θ signifies the temperature difference, T_s signifies the actual temperature, E_a signifies the apparent activation energy (kJ mol^{-1}), R signifies the gas constant ($\text{J K}^{-1} \text{mol}^{-1}$), and α signifies the reaction fraction. This method involves integrating the acquired thermogravimetric curve and utilizing the general reaction kinetics equation.

$$\ln \left[\frac{\alpha}{T^2} \right] = \ln \left[\frac{AR}{\beta E_a} \right] \left[1 - \left(\frac{2RT}{E_a} \right) \right] - \left(\frac{E_a}{RT} \right) \quad (10)$$

In this context, T represents temperature, A is the pre-exponential factor, β is the heating rate, and α is determined by the equation $\alpha = (W_0 - W_t)/(W_0 - W_f)$. Here, W_0 is the initial weight of the sample, W_t is the remaining weight of the sample at the observed temperature, and W_f represents the final weight of the sample.

2.3.3.1. Differential Scanning Calorimetry (DSC). A Perkin Elmer DSC 4000 Differential Scanning Calorimeter (DSC) was used to determine the oxidation induction time (OIT) following a previously described method [62]. Samples weighing between 5 and 10 mg were analyzed under controlled conditions. Initially, the DSC was set in isothermal mode at 60°C for 5 min. Subsequently, it was heated from 60 to 200°C at a rate of 20°C per minute in a nitrogen atmosphere with a flow rate of 50 mL per minute, followed by a stabilization at 200°C for 15 min. Finally, the

internal gas conditions were changed to oxidation with a flow rate of 50 mL per minute, maintaining the temperature at 200°C for 30 min.

3. Results

3.1. Structural optimization

We employed the M06-2X/6-311++G(d,p) method to optimize the CAF, BHA, and BHT molecules. Fig. 3 visualizes the optimized structural formula, while Table 1 details the main structural parameters.

CAF exhibits a higher number of hydroxyl groups than BHT and BHA, initially suggesting that its antioxidant activity may be more potent than that of synthetic antioxidants.

According to the theory of molecular valence bonds, the strength of a molecule's bonds correlates strongly with its length. Longer bonds tend to be easier to break, suggesting higher reactivity. Upon analyzing the structural characteristics of the molecules in Tables 1 and it is observed that the lengths of the phenolic hydroxyl group bonds in CAF are significantly greater compared to those of BHT and BHA. Based on this, it is presumed that the three polyphenols' antioxidant activity follows the order: CAF > BHA > BHT.

Table 1
Binding length of CAF, BHT, and BHA.

CAF		BHT		BHA	
RO(1)-H	0.96427	RO(1)-H	0.95704	RO(1)-H	0.96052
RO(2)-H	0.96058				
RO(3)-H	0.96621				

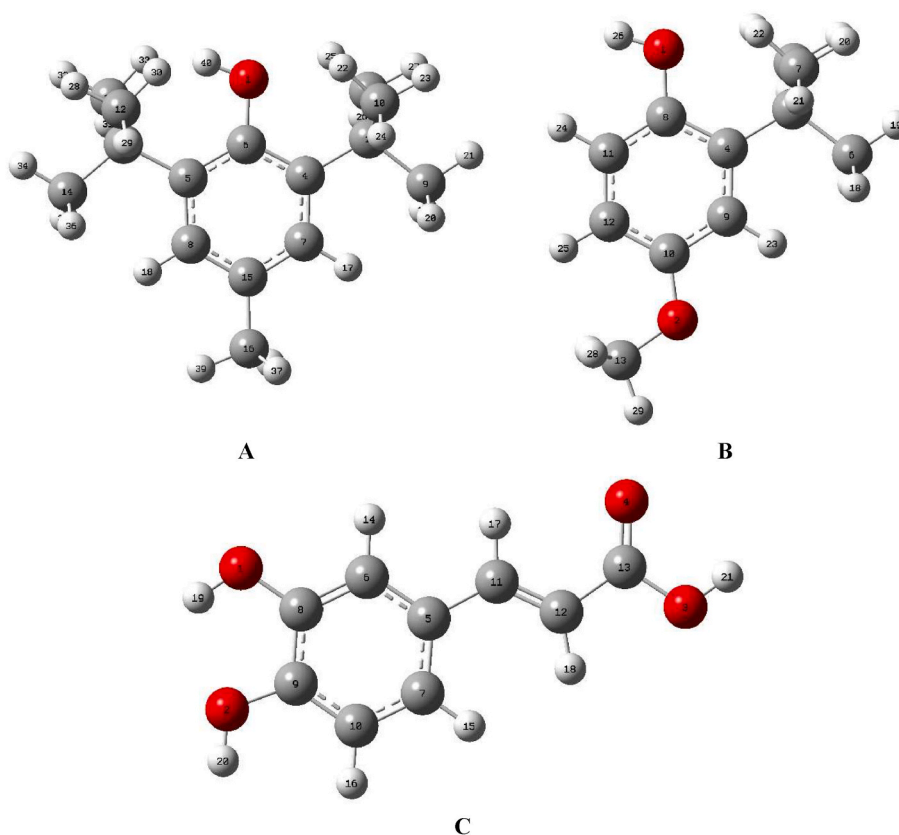


Fig. 3. Optimized geometry: A: BHT, B: BHA, C: CAF.

3.2. Hydrogen extraction reaction mechanism

3.2.1. Binding dissociation energy calculation

The evaluation of BDE reflects the ability of O–H to donate hydrogen during the removal of free radicals by phenolic compounds. A lower BDE in the O–H bond indicates greater ease of breaking this bond, leading to a more efficient reaction in hydrogen extraction and a more potent antioxidant activity. According to the information presented in Table 2, it is observed that the BDE of the hydroxyl group in CAF (RO(1)-H) is lower than that of BHA and BHT, suggesting that CAF is more prone “to dissociation” and possesses higher antioxidative potential. The free radical neutralization capacity for polyphenols largely relies on the BDE of the phenolic hydroxyl group with the lowest value. Based on the order of the lowest BDEs (CAF < BHT < BHA), it is concluded “that the antioxidative potential” of the polyphenols follows the pattern: CAF > BHT > BHA.

3.2.1.1. Selection and validation of an accurate approach. Research was undertaken employing four different theoretical approaches to validate methodologies for evaluating the antioxidant capacity of compounds including BHA, BHT, and caffeic acid (CAF). Experimental enthalpy values of O–H bond dissociation for BHA, BHT, and CAF were utilized as benchmarks to validate the computations and identify the most suitable combination of method and basis set for subsequent analyses. In each instance, comparisons were made between the data obtained in the gas phase, revealing close alignment between the calculated values and the experimental outcomes (refer to Table 3).

It was identified that the least suitable combination was the B3LYP method along with the 6-311+G(d) basis set, as the calculated values showed a difference exceeding 19 kJ/mol for CAF, 22 kJ/mol for BHA, and 22.2 kJ/mol for BHT compared to the experimental values. However, employing the theoretical level M06-2X/6-311++G(d,p) and M06-2X/6-311+G(d,p) seemed to provide a better approximation for BHA and BHT, with differences of less than 2.1 kJ/mol. In the end, it was concluded that the M06-2X/6-311++G(d,p) approach proved to be the most precise, showing negligible disparity between the calculated and experimentally obtained values, with just a 2.1 kJ/mol variance for the O–H bond in BHT and BHA, and 0.9 kJ/mol for CAF.

3.2.2. Proton and electron transfer mechanism in stages

IP and PDE signify the capacity of base molecules to contribute electrons when antioxidants neutralize free radicals. The lower these values, the greater the antioxidant efficacy. Examination of Table 4 reveals that BHA exhibits the lowest IP but the highest PDE. According to IP, the sequence of antioxidant effectiveness is CAF > BHT > BHA. Conversely, the sequence of PDE magnitude is BHA > BHT > CAF, it contrasts with the IP assessment result. Nevertheless, given the importance of the initial step in the transfer reaction mediated by electron transfer, it is presumed that the sequence of antioxidant activity is CAF > BHT > BHA. Additionally, the smallest PDE of the phenolic hydroxyl moiety at position C8 in CAF suggests that this moiety exhibits the

Table 2

Bond Dissociation Energy (BDE) and Proton Dissociation Energy (PDE) values (in kJ mol⁻¹) for the molecules under investigation were determined using B3LYP/6-311+G (d,p), M06-2X/6-31+G*, M06-2X/6-311+G(d,p), and M06-2X/6-311++G(d,p) methods in the gas phase.

Molecule	Bond	BDE				PDE			
		B3LYP/6-311+G (d,p)	M06-2X/6-31+G*	M06-2X/6-311++G (d,p)	M06-2X/6-311+G (d,p)	B3LYP/6-311+G (d,p)	M06-2X/6-31+G*	M06-2X/6-311++G (d,p)	M06-2X/6-311+G (d,p)
Caffeic Acid	RO(1)-H	308.2	321.4	328.2	325.6	1620.9	1634.1	1636.7	1634.1
	RO(2)-H	355.5	368.6	372.8	370.2	1668.2	1681.4	1681.4	1678.7
BHA	RO(1)-H	321.4	321.4	341.3	341.3	1634.1	1634.1	1644.6	1644.6
BHT	RO(1)-H	310.8	310.8	328.2	328.2	1623.6	1623.6	1636.7	1639.3

Table 3

Comparison of BDE Values for BHT, BHA, and CAF using Different Levels of Computational Theory.

Compound	BDE (-OH) kJ.mol ⁻¹				Experimental
	B3LYP/6-311+G (d,p)	M06-2X/6-31+G*	M06-2X/6-311++G (d,p)	M06-2X/6-311+G (d,p)	
Caffeic Acid	308.2	321.4	328.2	325.6	327.3
BHA	321.4	321.4	341.3	341.3	343.4
BHT	310.8	310.8	328.2	328.2	333.0

Table 4

Ionization Potential (IP) Values (in kJ mol⁻¹) of the Examined Molecules using B3LYP/6-311+G(d,p), M06-2X/6-31+G*, M06-2X/6-311+G(d,p), and M06-2X/6-311++G(d,p) methods in the Gas Phase.

Method	Caffeic Acid	BHA	BHT
B3LYP/6-311+G (d,p)	758.8	708.9	711.5
M06-2X/6-31+G*	803.4	743.0	740.4
M06-2X/6-311++G (d,p)	785.0	727.3	732.5
M06-2X/6-311+G (d,p)	782.4	729.9	732.5

highest activity.

3.2.3. Mechanism of electron transfer with selective proton release

PA symbolizes the thermal energy liberated by the antioxidant when it binds to an isolated proton (H⁺), whereas ETE signifies the energy fluctuation during electron transfer within an antioxidant reaction. Reduced PA and ETE values signify heightened antioxidant efficacy of the compound. As observed in Table 5, BHA and BHT, having only one phenolic hydroxyl group, generate fewer anions compared to CAF, which possesses two phenolic hydroxyl groups, thereby exhibiting weaker antioxidant activities. The order of PA magnitude is BHA > BHT > CAF, whereas the order of ETE magnitude is the reverse. However, since the entire reaction relies on electron transfer as the primary step, the order of antioxidant activity is inferred to be CAF > BHT > BHA based on ETE magnitude.

3.3. Global descriptors and molecular orbitals

A lower E_{HOMO} indicates a diminished capacity for proton donation, while a higher E_{HOMO} suggests an increased ability for electron donation. Additionally, we have observed a correlation between antioxidant activity and the distributions of frontier orbitals. The frontier energy values obtained, along with their distributions for the examined molecules, are provided in Table 6 and illustrated in Fig. 4. As demonstrated in Fig. 4A, the electron clouds in the phenolic hydroxyl moiety at position C13 of CAF are fewer, whereas the LUMO and HOMO display a broader distribution in the phenolic hydroxyl moiety at positions C8 and C9. The reactive center of the molecule is anticipated to be the atom

Table 5
ETE and PA of CAF, BHA, and BHT (unit: kJ·mol⁻¹).

Molecule	Bond	PA			ETE		
		B3LYP/6-311+G (d, p)	M06-2X/6-311++G (d, p)	M06-2X/6-311+G (d, p)	B3LYP/6-311+G (d, p)	M06-2X/6-311++G (d, p)	M06-2X/6-311+G (d, p)
Caffeic Acid	RO(1)-H	1337.4	1347.9	1355.8	288.8	294.0	283.5
	RO(2)-H	1421.4	1431.9	1429.3	252.0	254.6	254.7
BHA	RO(1)-H	1447.7	1447.7	1447.7	191.6	202.2	202.2
BHT	RO(1)-H	1416.2	1418.8	1416.2	212.7	223.2	225.8

Table 6
Global descriptors of the studied compounds.

Molecule	Method	E _{HOMO}	E _{LUMO}	ΔE _{HOMO-LUMO}	χ	η	S	ω	μ
Caffeic Acid	B3LYP/6-311+G (d,p)	-0.2310	-0.0784	-0.1526	0.1546	-0.0763	-13.1001	-0.15674	-0.1546
	M06-2X/6-31+G*	-0.2812	-0.0487	-0.2324	0.1649	-0.1162	-8.6036	-0.11706	-0.1649
	M06-2X/6-311++G (d,p)	-0.2766	-0.0414	-0.2352	0.1589	-0.1176	-8.5012	-0.10743	-0.15898
BHA	M06-2X/6-311+G (d,p)	-0.2767	-0.0413	-0.2353	0.159	-0.1176	-8.4990	-0.10743	-0.159
	B3LYP/6-311+G (d,p)	-0.2087	-0.0158	-0.1929	0.1122	-0.0964	-10.3680	-0.06532	-0.11225
	M06-2X/6-31+G*	-0.2088	-0.0089	-0.1999	0.1088	-0.0999	-10.0030	-0.05927	-0.1088
BHT	M06-2X/6-311++G (d,p)	-0.2578	-0.0074	-0.2504	0.1326	-0.1252	-7.9872	-0.07022	-0.1326
	M06-2X/6-311+G (d,p)	-0.2578	-0.0055	-0.2633	0.1261	-0.1316	-7.5944	-0.06044	-0.1261
	B3LYP/6-311+G (d,p)	-0.2144	-0.0085	-0.2058	0.1114	-0.1029	-9.7139	-0.06035	-0.1114
	M06-2X/6-31+G*	-0.2646	-0.0108	-0.2537	0.1377	-0.1268	-7.8827	-0.07476	-0.1377
	M06-2X/6-311++G (d,p)	-0.2625	-0.0067	-0.2557	0.1345	-0.1278	-7.8207	-0.07082	-0.1345
	M06-2X/6-311+G (d,p)	-0.2625	-0.0083	-0.2707	0.1271	-0.1353	-7.3874	-0.05968	-0.1271

significantly contributing to both the LUMO and HOMO. Consequently, it is inferred that the phenolic hydroxyl moiety at position C9 is the most pivotal reactive site of CAF, while the phenolic hydroxyl moiety at position C13 exhibits diminished activity. Likewise, the electron cloud distribution in the phenolic hydroxyl moiety at position C1 of BHA and BHT is lower compared to that of CAF.

Significant differences are observed in several key parameters when comparing the electronic properties of the antioxidants BHA, BHT, and caffeic acid (CAF). Regarding orbital energies, BHA exhibits the lowest E_{HOMO} (-0.2578 eV) among the three antioxidants, while caffeic acid shows the highest E_{LUMO} (-0.0414 eV). However, BHA has the slightest difference between E_{HOMO} and E_{LUMO} (ΔE_{HOMO-LUMO}) at approximately -0.2504 eV, suggesting more excellent stability. Regarding electronegativity (χ) and hardness (η), BHT has the highest value of χ (0.1345) and the lowest of η (-0.1278), indicating a more remarkable ability to attract electrons but less resistance to changes in electron density. Regarding globality (S) and charge transfer capability (ω), caffeic acid shows the most negative values at approximately -8.5012 hartrees and -0.10743 hartrees, respectively, suggesting more excellent softness and charge transfer capability. Finally, regarding molecular polarity (μ), BHT exhibits the lowest value (-0.1345), indicating a more asymmetric charge distribution.

The electronic properties of antioxidants, such as E_{HOMO}, E_{LUMO}, hardness, electronegativity, and molecular polarity, can significantly influence their reactivity and antioxidant activity. A lower E_{HOMO} suggests a more remarkable ability to donate electrons and act as a reducing agent, which could enhance its ability to neutralize reactive oxygen species (ROS) and protect against oxidative stress. Similarly, a lower difference between E_{HOMO} and E_{LUMO} (ΔE_{HOMO-LUMO}) indicates more excellent antioxidant stability and, therefore, a more remarkable ability to stabilize free radicals. Additionally, higher electronegativity can enhance an antioxidant's ability to attract electrons and thus react with oxidizing species.

3.4. Analysis of dynamic simulation for ·OOH neutralization

Given the high reactivity of ·OOH radical, along with the localization of the unpaired electron on the oxygen atom at the terminal site, it is deduced that these three polyphenols can effectively neutralize the ·OOH radical (See Fig. 5).

IRC calculations were executed for every transition state using the M06-2X/6-311++G(d,p) method to validate the authenticity of the actual structure at the transition state. Upon inspection, it was observed that the molecular arrangements depicted on both ends of the IRC calculation curve represented the respective reactive (Reac.) and product (Prod.) states, thereby confirming the accuracy of the obtained TS configuration. Fig. 4 illustrates the IRC curves of TS for the ·OOH elimination reaction of CAF, BHA, and BHT.

Examining Fig. 6A and Table 7, it is notable that when ·OOH interacts with the phenolic hydroxyl moiety at the O1 site of CAF, the distance separating O in the ·OOH interaction complex from H in the phenolic hydroxyl moiety of CAF initially measures 1.553 nm, gradually decreasing to 1.199 nm. Simultaneously, the distance between the O of the phenolic hydroxyl moiety and the H gradually increases to 1.161 nm, resulting in the formation of a transition state (TS). Eventually, a quinone structure and H₂O₂ are produced through the product complex. A similar mechanism is observed in the hydrogen abstraction process in the phenolic hydroxyl moiety at the O2 position of CAF. The energy difference (E_a[‡]) between the TS and the reactive state (Reac.) is 56.03 kJ mol⁻¹, while the energy difference (ΔE_a) between the product (Prod.) and the reactive state (Reac.) is -147.7 kJ mol⁻¹, suggesting an exothermic reaction, promoting the efficient progression of the CAF elimination process.

3.5. Potential energy surfaces

Based on the data provided in Tables 1 and it is observed that the primary mechanism for radical elimination in the gas phase is hydrogen atom transfer (HAT). Therefore, we have focused our analysis on the potential energy surface associated with this mechanism, as shown in

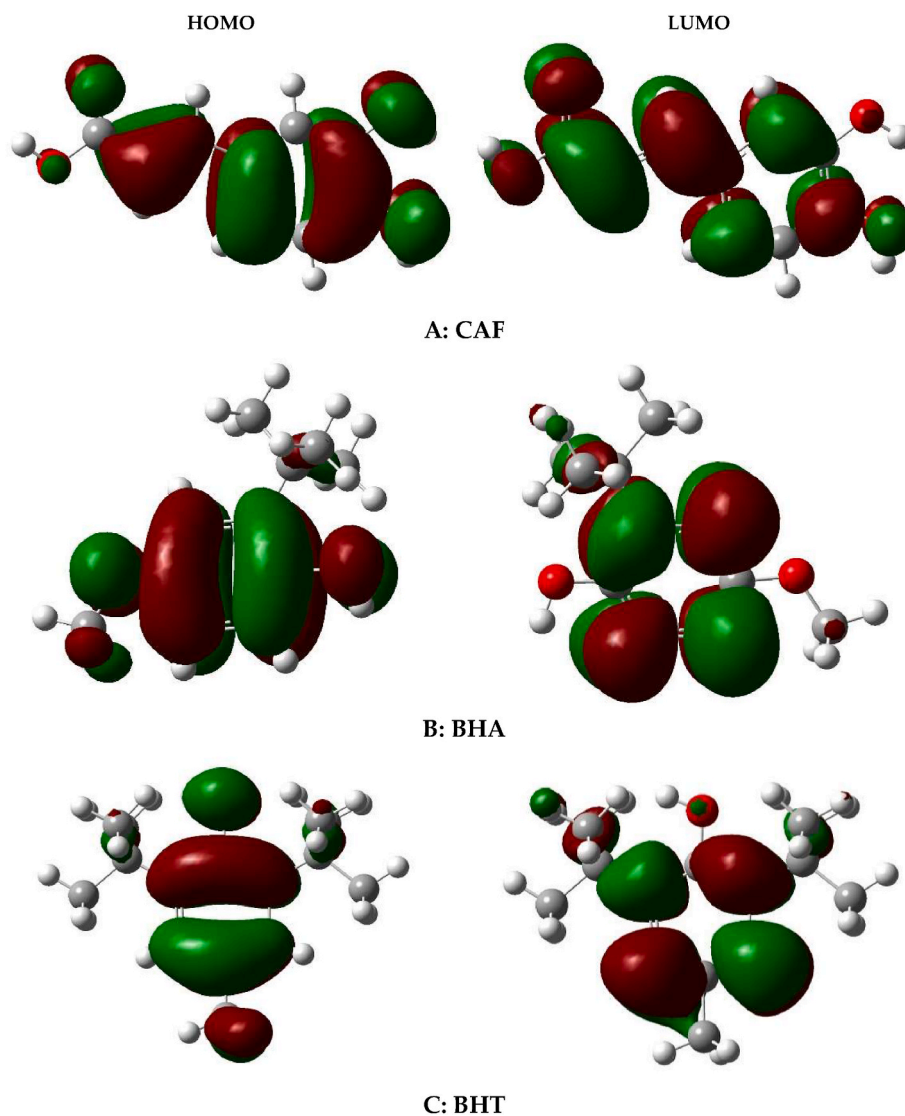


Fig. 4. Molecular frontier orbitals of A: CAF, B: BHA, and C: BHT.

Fig. 6, where the corresponding transition states (TS) have been depicted. The results obtained reveal that the energies of the transition states (TS) lie in a range of 49.29–76.39 kJ mol⁻¹ (Fig. 7), with BHA presenting the lowest TS energy, at 49.29 kJ mol⁻¹, followed by CAF-O2 with 57.61 kJ mol⁻¹, which is lower than BHT with 75.57 kJ mol⁻¹. This observation suggests that BHA could have higher efficacy as an antioxidant than BHT and CAF-O2 due to its lower TS energy, indicating greater ease for the radical elimination process.

3.6. Kinetic study

To corroborate the preceding findings, kinetic calculations were conducted to investigate the interactions between the phenolic antioxidants and the HOO• radical. The results are detailed in Table 7. The rate constants for all reactions range between 1.02×10^{-1} and 1.05×10^5 M⁻¹ s⁻¹. It is noteworthy that the H atom abstraction rate by HAT of CAF is the highest, with $k = 1.05 \times 10^5$ M⁻¹ s⁻¹, followed by compound BHA with 1.17×10^4 M⁻¹ s⁻¹, while the lowest rate constant corresponds to BHT, with $k = 4.2 \times 10^3$ M⁻¹ s⁻¹. These results indicate a clear hierarchy in antioxidant efficacy, suggesting that CAF is the most effective in protection against oxidation, followed by BHA, and finally BHT. This can guide the selection of antioxidants for industrial applications where protection against oxidation is crucial. This result is consistent with the

findings of the thermodynamic study.

3.7. Experimental section

3.7.1. Analysis of wetting behavior

A detailed analysis of the surface aging properties of the samples was carried out, focusing on variations in their wetting behavior. Before the aging process, differences in wettability were observed in the copolymer due to the different substances present. The PE, PP, and C-PP/PE demonstrated hydrophobic characteristics. During the aging process, an increase in hydrophilicity was observed in the C-PP/PE with the addition of different concentrations of caffeic acid extracts.

Caffeic acid is a natural phenolic compound that contains two hydroxyl groups (-OH) in its structure (Fig. 8B), which gives it some polarity and capacity to interact with water. Therefore, compared to synthetic antioxidants BHA, BHT, and TBHQ, which are generally more hydrophobic, caffeic acid tends to be less hydrophobic and more hydrophilic due to the presence of these hydroxyl groups. The octanol-water partition coefficient (LogP) is a measure of a molecule's hydrophobicity or lipophilicity, and it is calculated as the logarithm of the ratio of a molecule's concentration in octanol to water. The higher the LogP value, the greater the tendency of the molecule to dissolve in octanol (an organic solvent) rather than water (an aqueous solvent),

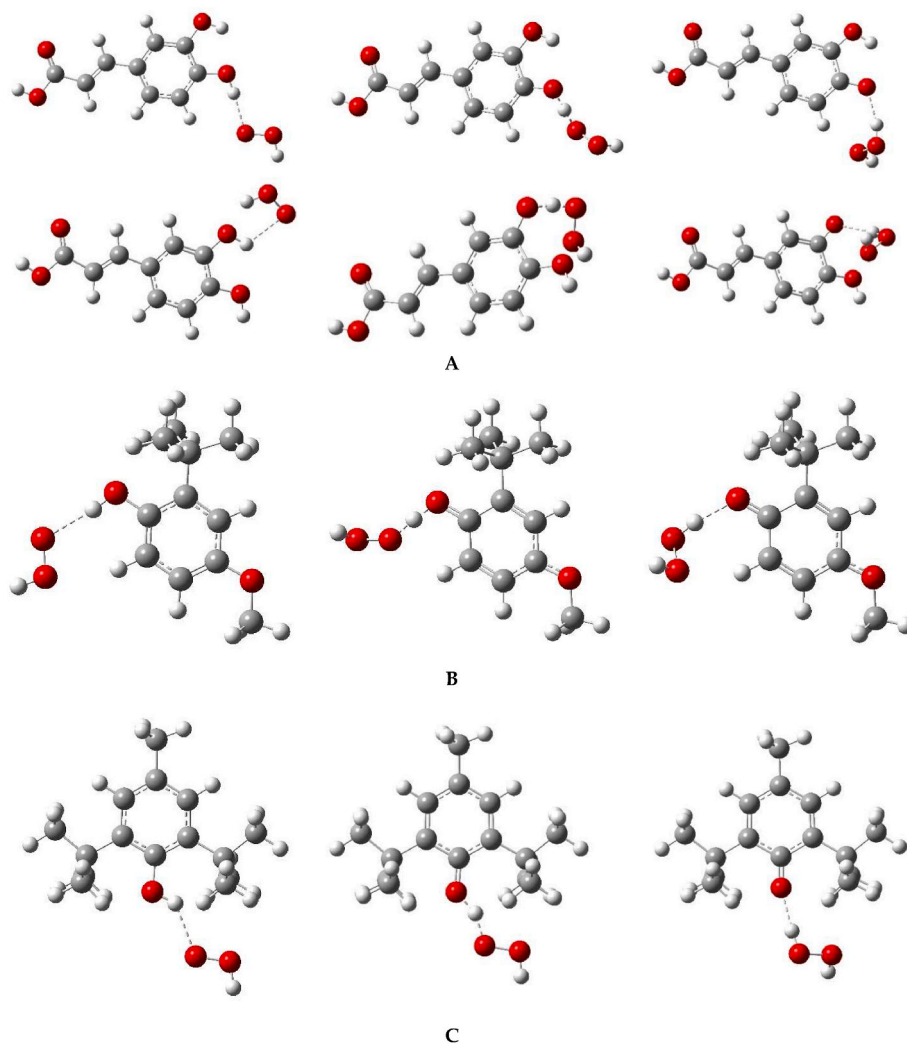


Fig. 5. Optimized structures of reactants (react.), transition state (TS), and products (prod.) for A: CAF, B: BHA, C: Bht.

indicating greater hydrophobicity. In the case of caffeic acid (CAF), its LogP value is 1.584, suggesting moderate hydrophobicity. On the other hand, BHA has a LogP value of 3.137, indicating higher hydrophobicity compared to caffeic acid (Fig. 8B). Therefore, caffeic acid is considered a hydrophilic antioxidant.

The production of more hydrophobic films is related to the ability of the materials used to repel water or resist the penetration of water vapor through their surface. In the context of the mentioned antioxidants (BHA and CAF), their ability to influence the hydrophobicity of the films is related to their own hydrophobicity or hydrophilicity. When more hydrophobic antioxidants, such as BHA, are incorporated into the film matrix, these compounds tend to preferentially distribute on the film surface, forming a barrier that hinders the entry of water or water vapor. This results in the production of films with improved hydrophobic properties. On the other hand, more hydrophilic antioxidants, such as caffeic acid, can interact more easily with water, which can affect the hydrophobicity of the film differently. The $-OH$ groups in caffeic acid have a natural affinity for water and can form hydrogen bonds with water molecules. When caffeic acid is added to the polymeric material, these hydroxyl groups can interact with water molecules on the material surface, forming a layer that can help repel additional water and improve the hydrophobic stability of the surface.

We can say that both caffeic acid and BHA can contribute to improving the hydrophobic stability of the polymeric material by interacting with water in different ways. Caffeic acid does so through its

hydrophilic properties that form a protective layer, while BHA does so by forming a hydrophobic barrier on the material surface.

3.7.2. Thermal properties

Evaluation of thermal characteristics is crucial as it impacts both polymer production and their recyclability after they have served their purpose [1,63]. A necessary consequence is the potential modification of the melt flow index (MFI) of polymer formulations, as this feature is crucial for material melting [1]. The MFI data are shown in Fig. 9, and it is evident that, overall, the MFI decreases when antioxidants are added. Unstabilized C-PP/PE had a melt flow index of 10.5. The mixture of C-PP/PE, when combined with 0.1 % of the industrial synthetic antioxidant BHA, showed a melt flow index (MFI) value of 8.51. Combinations of C-PP/PE containing 0.025, 0.05, 0.075, 0.1, and 0.125 % of natural caffeic acid extracts exhibited MFI values of 9.4, 8.82, 7.59, 6.44, and 5.98, respectively. The findings indicate that natural caffeic acid extracts can effectively rival a commonly used synthetic antioxidant in the petrochemical industry.

It has been observed that the decomposition temperature at 99 % is significantly higher for pure PP compared to PE. This disparity in decomposition temperatures indicates that PP has relatively superior thermal stability compared to PE [64]. The thermal degradation of polyethylene typically begins with the scission of C–C bonds at the allylic position to a double bond. This process involves the cleavage of a carbon atom adjacent to a vinyl group, leading to the formation of an

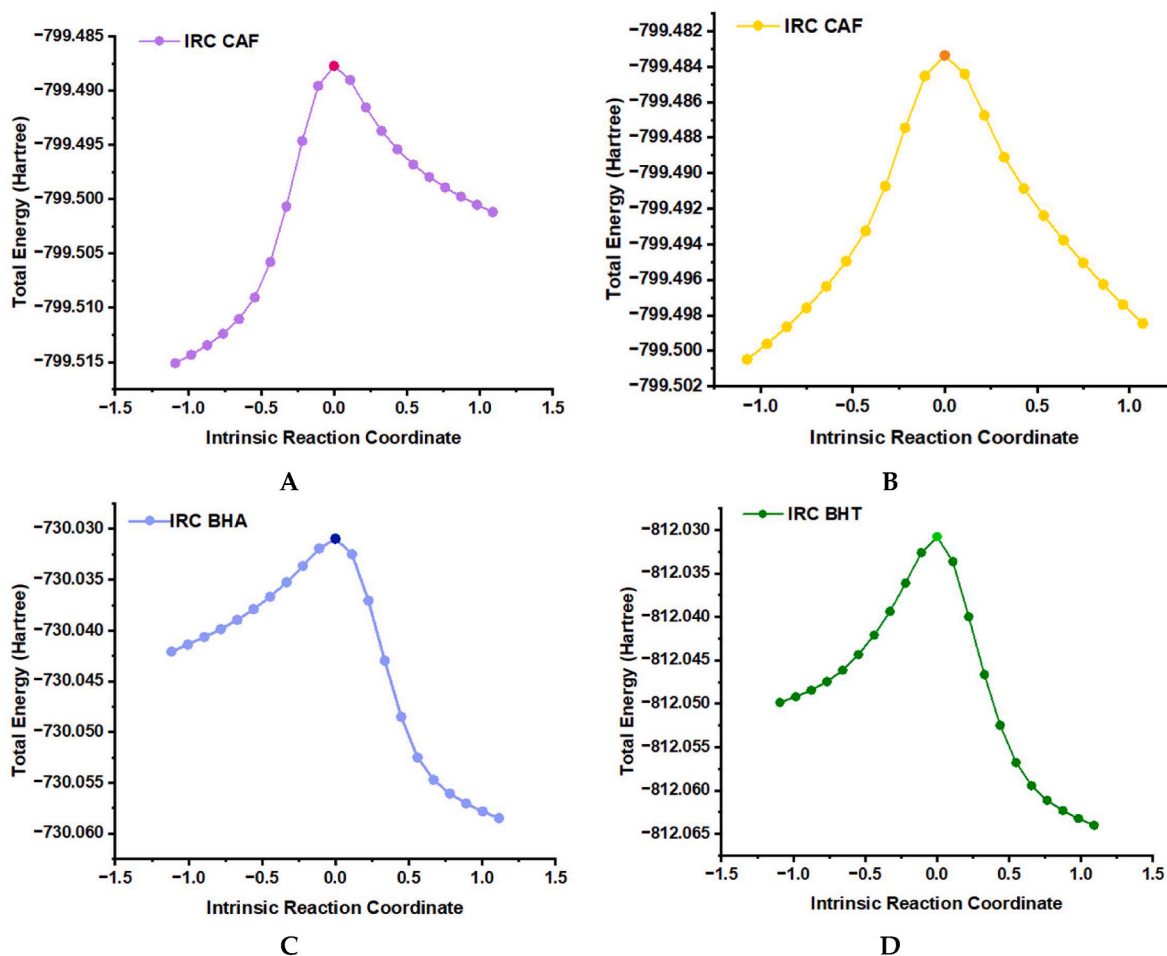


Fig. 6. IRC of A: CAF-O1, B: CAF-O2. C: BHA, D: BHT at the established M06-2X/6-311++G(d,p) level base.

Table 7

ΔG^\ddagger (kJ/mol) and k ($M^{-1} s^{-1}$) were calculated for the reaction between phenolic antioxidants and $HOO\bullet$.

	R	TS	P	E_a^+	E_a^-	ΔE_a	k
CAF (O2)	-2098784.49	-2098728.46	-2098820.13	56.03	-91.67	-147.7	1.05×10^5
CAF (O1)	-2098789.52	-2098713.13	-2098777.28	76.39	-64.15	-140.54	1.02×10^{-1}
BHA	-1916173.88	-1916124.58	-1916213.48	49.3	-88.9	-138.2	1.17×10^4
BHT	-2131215.45	-2131139.88	-2131254.23	75.57	-114.35	-38.78	4.2×10^3

allyl radical and an alkyl radical, without a significant change in the molecular weight of the polymer. The allyl radical can further react or volatilize at high temperatures during PE processing, resulting in a reduction in the quantity of vinyl groups without significantly altering the MFI. The addition of an alkyl radical to the vinyl group leads to the formation of a secondary radical [65,66], which can interact with another alkyl radical, thereby promoting chain branching and increasing the material's viscosity [67].

Alkyl radicals generated in the first step of degradation react with the minimal amounts of oxygen present during operation. In addition to oxygen, our atmosphere contains other more reactive species such as O_3 , $HOO\cdot$, $OH\cdot$, and $NO\cdot$, although in low but relevant concentrations. All these species are capable of reacting with polyolefins, and many can promote degradation through different mechanisms. Similar to ozone, hydroperoxyl radicals are also found in small amounts in the troposphere, along with hydroxyl radicals. These radicals form when O_3 interacts with polymers (Fig. 10A). In 2016, Chen and colleagues suggested that the formation of peroxy groups during the thermo-oxidation of poly(ethylene oxide) could be explained by hydrogen

transfer between $ROO\cdot$ and $HOO\cdot$.

The peroxy radicals are eliminated by the hydrogen atoms donated by the OH groups of caffeic acid. The resulting hydroperoxide groups are decomposed by the secondary antioxidant into stable products. After the oxidation of all the secondary antioxidant molecules, the addition reaction (2) becomes predominant, resulting in the formation of long-chain branches accompanied by a decrease in MFI (Fig. 10B). The beneficial effect of CAF on the melt stability of the copolymer is twofold. The reaction of CAF with alkyl radicals prevents the oxidation of the copolymer and the formation of long-chain branches.

3.7.3. Thermal stability

A comprehensive thermogravimetric analysis was conducted to investigate the impact of antioxidants (CAF and BHA) on the thermal stability of the C-PP/PE copolymer. Figs. 11A and 10B present the weight loss curves and their derivatives (DTG), respectively, for the C-PP/PE copolymer with different concentrations of CAF. A notable aspect is that all TG curves exhibit a single stage of mass decrease, indicating an unfaceted decomposition process.

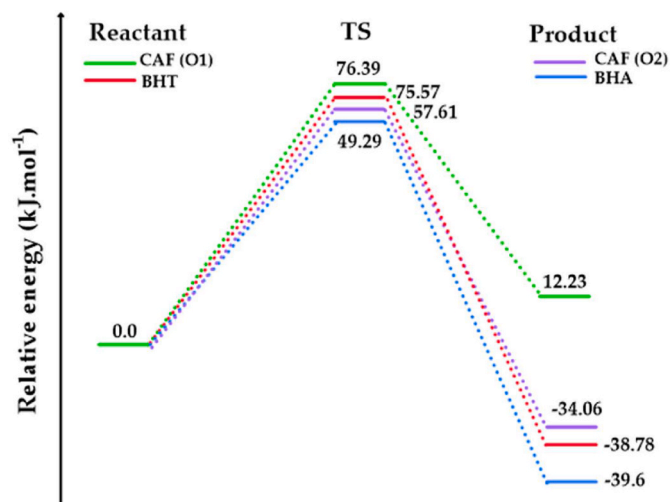


Fig. 7. Potential energy surface (PES) of the reaction between the selected compounds and the HOO• radical.

It is important to note that within the temperature range of 100 °C–350 °C, no significant mass loss is observed in any of the samples, suggesting relative stability of the polymer within this interval. However, around 340 °C, decomposition initiates in the samples without additives and those containing 0.1 ppm of BHA. In contrast, samples with different concentrations of CAF show delayed degradation, observed in the temperature range of 380–400 °C. This delay in degradation indicates that CAF confers more excellent thermal stability to the C-PP/PE copolymer, as it reaches temperatures above 400 °C before starting its decomposition (Table S1).

3.7.3.1. DSC analysis. To evaluate the ability of caffeic acid to protect PP from the thermo-oxidative process, isothermal DSC tests were conducted at a processing temperature of 200 °C (Fig. 12). The isothermal DSC curves indicate that both the commercial additive and the natural antioxidant delay degradation. In fact, the longer the oxidation induction time (OIT), the more stable the PP/PE-based blend. Additionally, significant differences were observed in the induced oxidation times for each composition. The results highlight that the OIT value for pure PP was 0.5 min.

A notable difference was observed when comparing the effect of BHA and CAF. CAF exhibited a higher oxidation induction time (OIT) value, reaching 8 min, compared to BHA's 5 min. This superiority of CAF is attributed to its molecular structure, which is very similar to that of *p*-

coumaric acid, but with an additional hydroxyl group. This extra functional group grants CAF a more robust antioxidant capacity during thermal processing. Polyphenols, such as CAF, can act as radical scavengers for PP, reacting with alkyl (R•), alkoxy (RO•), or peroxy (ROO•) radicals through hydrogen donation and resonance stabilization. This results in the formation of products such as hydroperoxides (ROOH), alcohols (ROH), and stabilized polymer radicals (RH), which interrupt the degradation chain and preserve the integrity of the copolymer during thermal processing [68].

The process by which PP/PE is protected against thermo-oxidative degradation by antioxidant agents depends on the arrangement and total number of hydroxyl groups present. As previously discussed, the structure of CAF exhibits a greater number of active OH groups on the phenolic rings compared to BHA. Additionally, the conjugation of C=C double bonds and the presence of carboxyl groups play a crucial role in the substituent groups. The ability to scavenge free radicals is primarily attributed to the high reactivity of the hydroxyl substituents, which actively participate in these reactions.

3.7.4. Coats-Redfern and Horowitz-metzger method

The kinetic parameters calculated using the Coats-Redfern and Horowitz-Metzger methods are shown in Table 8. It was found that the

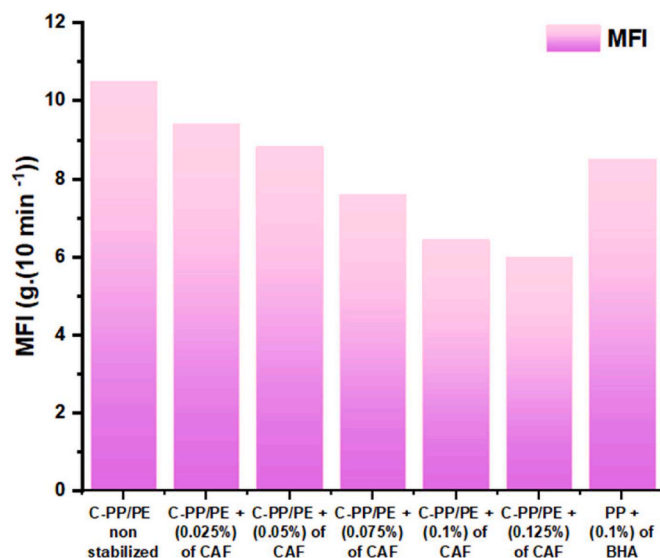


Fig. 9. Comparative MFI trends of C-PP/PE and its blends with CAF and BHA.

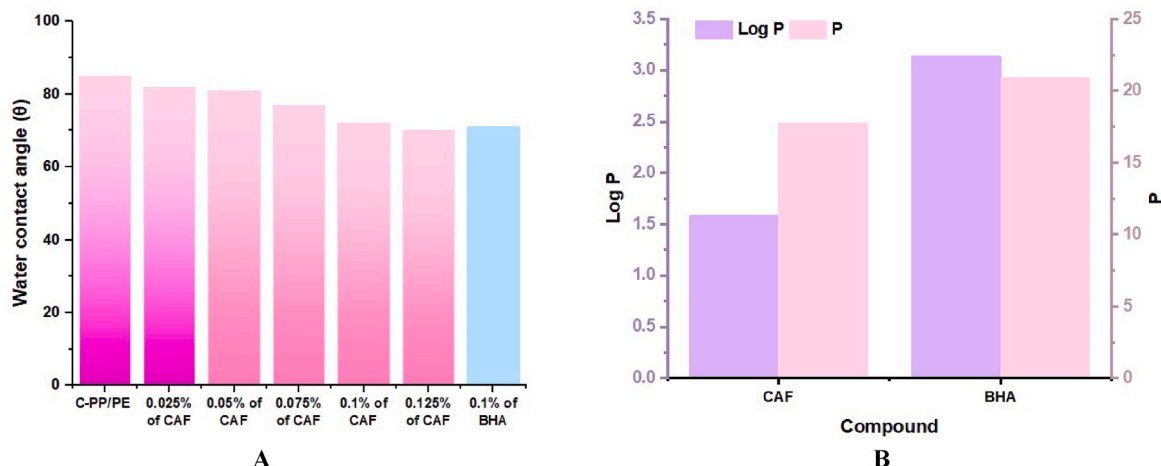


Fig. 8. A: The water contact angle of C-PP/PE - caffeic acid extracts based films; B: Log P and polarizability (μ) of CAF and BHA.

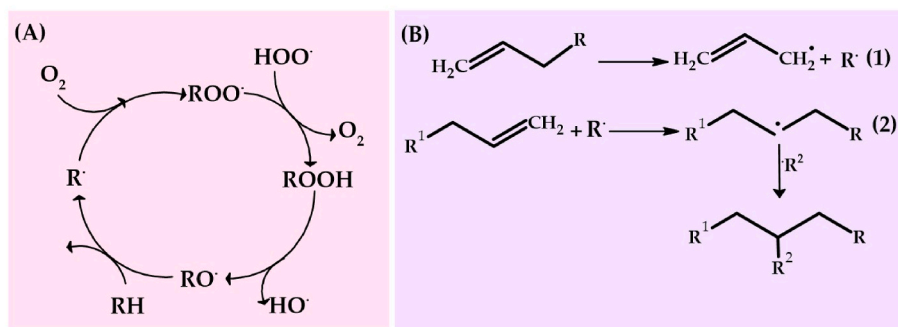


Fig. 10. Secondary Propagation Step Mediated by $\text{HOO}\cdot$ (A); generation of alkyl radicals during the manufacturing of polyolefins (B).

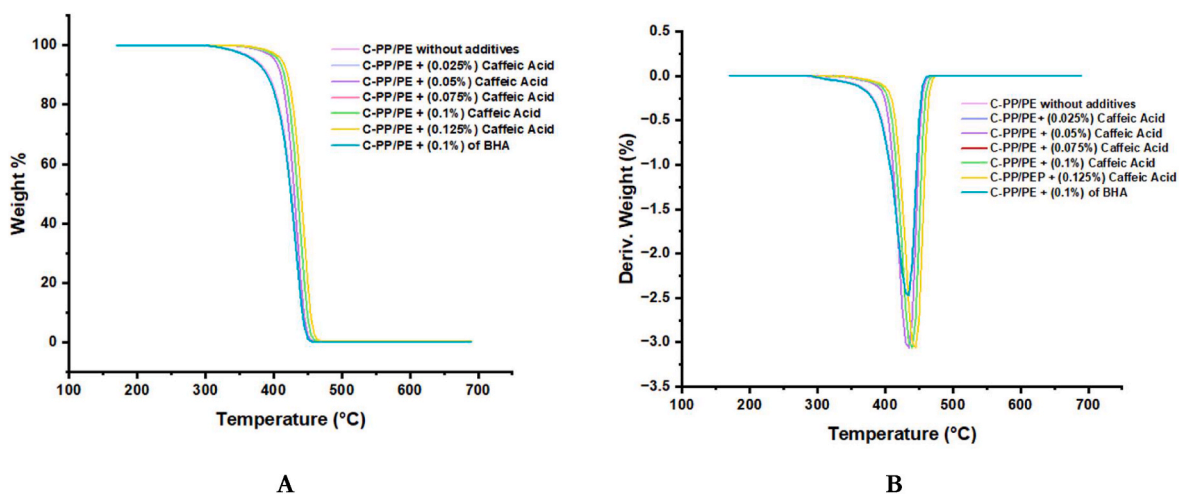


Fig. 11. Thermal degradation of the copolymer blended with different concentrations of caffeic acid. A: TGA; B: DTG.

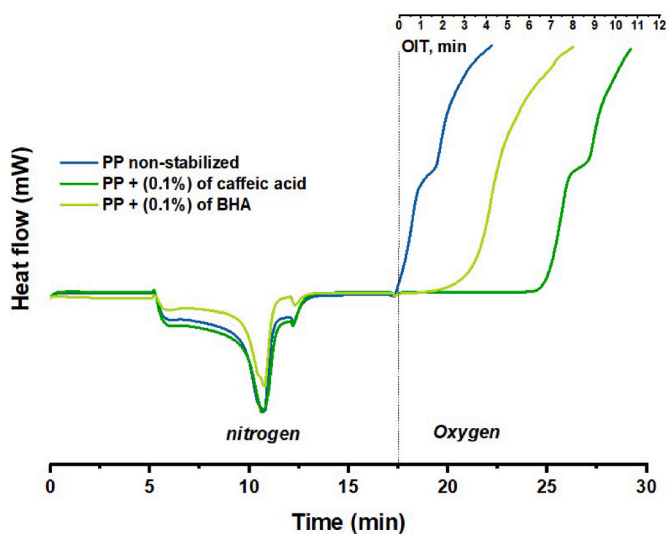


Fig. 12. Curves from isothermal DSC testing conducted at $200\text{ }^{\circ}\text{C}$ for PP-based films, and heat flux measured across temperature ranges.

activation energies of the degradation process of the PP/PE copolymer varied between 166.06 and $293.31\text{ kJ mol}^{-1}$ following the Horowitz method, while in the Coats method, they ranged from 128 to 235 kJ mol^{-1} . We observed that the untreated C-PP/PE samples show a value of $176.18\text{ kJ mol}^{-1}$, suggesting lower thermal stability than samples treated with CAF at different concentrations. As the concentration of

caffeic acid in the C-PP/PE samples increases, the obtained value also increases, indicating an improvement in thermal stability. For example, the sample with 0.125% caffeic acid shows the highest value of $293.31\text{ kJ mol}^{-1}$, suggesting more excellent resistance to thermal degradation.

On the other hand, the PP sample treated with 0.1% BHA shows a value of $166.06\text{ kJ mol}^{-1}$, indicating comparatively lower thermal stability compared to C-PP/PE samples treated with caffeic acid. The relationship between high activation energy and polymer stability lies in the fact that high activation energy may indicate that polymer decomposition is a more complex process and requires more energy to occur. Suppose much energy is needed for the polymer decomposition to begin. In that case, it is less likely that the polymer will quickly decompose at average temperatures or under conditions of use. Therefore, a polymer with high activation energy tends to be more stable and resistant to chemical and thermal degradation compared to those with low activation energy.

3.7.5. Trend between CAF concentrations and activation energy

When we increase the parts per million (ppm) of CAF in the polymer, we observe an increase in the activation energy required for its thermal degradation (Fig. 13A). This phenomenon indicates greater resistance of the polymer to thermal degradation as the concentration of CAF increases. This increase in E_a suggests that the presence of CAF in the polymer is strengthening its structure and protecting it against thermal degradation. CAF, acting as an antioxidant, is likely neutralizing free radicals and preventing them from initiating oxidation reactions in the polymer. As a result, more energy is required for thermal degradation to occur, indicating greater stability of the polymer. This finding has significant implications in various industrial applications. For example, if we are considering the use of this polymer in applications involving high

Table 8

Activation energies of C-PP/PE and their mixtures with CAF using the Horowitz and Coats method.

Methods	Samples						
	C-PP/PE non-stabilized	C-PP/PE + (0.025) of Caffeic Acid	C-PP/PE + (0.05) of Caffeic Acid	C-PP/PE + (0.075) of Caffeic Acid	C-PP/PE + (0.1) of Caffeic Acid	C-PP/PE + (0.125) of Caffeic Acid	PP + (0.1) of BHA
Horowitz	176.18	185.19	205.19	225.23	273.16	293.31	166.06
Coats	128	155	195	205	217	235	130

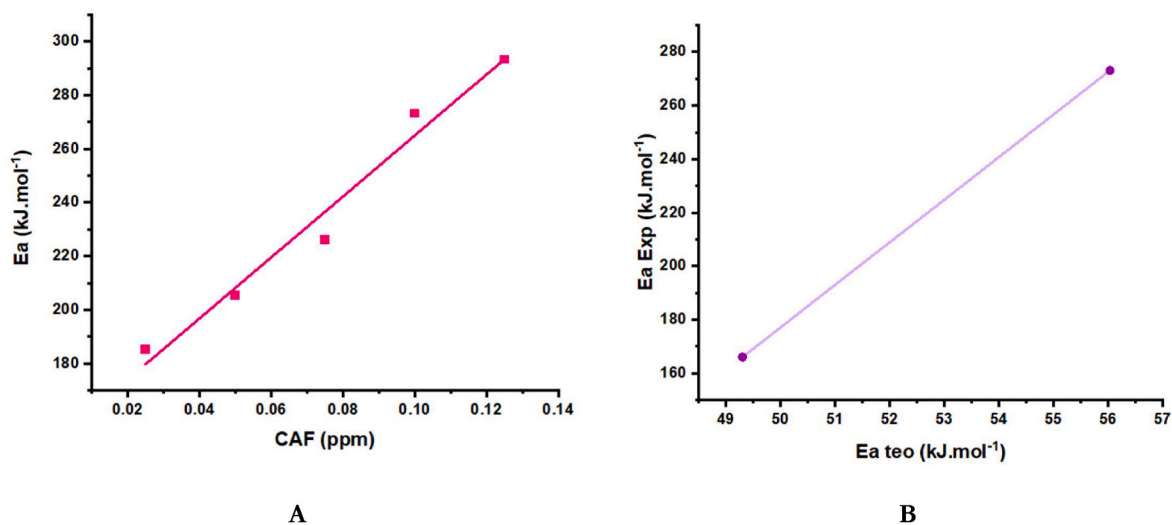


Fig. 13. A) CAF concentrations Vs activation energy following the Horowitz model; B) activation energy following the Horowitz model Vs theoretical activation energy.

temperatures or thermal processing conditions, the incorporation of CAF as an antioxidant could significantly improve the thermal resistance of the material, prolonging its lifespan and enhancing its performance in service. Additionally, this analysis supports the feasibility and efficacy of using CAF as an antioxidant in polymers, providing a solid scientific basis for the formulation and design of materials with improved thermal resistance and oxidative stability.

Now, when comparing the theoretical activation energies, we see that CAF has a slightly higher theoretical activation energy than BHA. However, upon observing the experimental activation energies, we notice that CAF has a much higher experimental activation energy than BHA. This significant difference in experimental activation energies could indicate that CAF is a more effective antioxidant than BHA. Although CAF has a slightly higher theoretical activation energy, its ability to neutralize radicals under experimental conditions seems to be much better than that of BHA, as suggested by the higher experimental activation energy. This could be attributed to various reasons, such as molecular structure and the ability to capture radicals more efficiently (Fig. 13B).

4. Discussion

This study investigated the precision of various theoretical approaches in forecasting the bond dissociation enthalpy (BDE) for antioxidant compounds such as CAF, BHA, and BHT. The results showed that the B3LYP method and the 6-311+G(d) basis set produced significant discrepancies, with differences exceeding 19 kJ/mol for caffeic acid and over 22 kJ/mol for BHA and BHT compared to experimental values. In contrast, the M06/6-311++G(d,p) and M06/6-311+G(d,p) methods demonstrated a better approximation, reducing the differences to less than 2.1 kJ/mol for BHA and BHT. A comparative examination of the findings derived from this study with those of previous research [69,70], illustrates a higher level of precision in the calculations conducted within this study. While previous studies showed significant

discrepancies between theoretical values and experimental values, with differences of over 7.5 kJ/mol in some cases, the results obtained in this study demonstrated a minimal difference of less than 2.1 kJ/mol for the compounds BHA and BHT. This substantial difference suggests greater accuracy in the calculations performed in this study, reinforcing the reliability of the theoretical methods used. Additionally, the consistency of the results with previous research, such as that of Rodrigo A. Mendes and his team, confirms the robustness of the findings presented here and highlights the significant contribution of this study to the field of predicting antioxidant properties of compounds relevant to various industries.

In this study, BDE, IP, PA, PDE, and ETE calculations were performed for three phenolic antioxidants, CAF, BHA, and BHT, using DFT. These calculations were used to evaluate these compounds' free radical scavenging activity. The antioxidant activity of phenolic compounds is associated with the ability of hydroxyl groups to donate protons, which primarily depends on the O-H bond BDE. Comparing the BDEs of phenolic hydroxyl groups at different positions, the antioxidant activity was proposed to follow the sequence CAF > BHT > BHA. Furthermore, other parameters such as PDE, PA, IP and ETE were examined to evaluate the antioxidant activity of polyphenols in different solvents. Computational kinetic results show that the hydrogen atom transfer (HAT) abstraction rate constants were significantly different among butylated hydroxyanisole (BHA), caffeic acid (CAF), and butylated hydroxytoluene (BHT). CAF exhibited the highest rate constant, with $k = 1.05 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, followed by BHA with $k = 1.17 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, and finally BHT with $k = 4.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, which was the lowest. This suggests that, in terms of antioxidant activity measured by hydrogen atom abstraction, CAF has a clear advantage over BHA and BHT.

Experimental studies validate these theoretical predictions, as a gradual decrease in MFI was found as the concentration of CAF in the copolymer increased, suggesting a continuous improvement in the thermal stability of C-PP/PE with increasing natural antioxidants. These findings are consistent with the theoretical prediction that CAF could

enhance the thermal properties of the copolymer, supporting the feasibility of using natural antioxidants such as CAF for this purpose. Therefore, the experimental data validate the theoretical part of the study and provide further confirmation of the efficacy of natural antioxidants in improving the properties of polymeric materials.

5. Conclusion

In summary, this study compared the impact of caffeic acid (CAF), a natural antioxidant, with two synthetic antioxidants, BHA and BHT, on the thermal stability of propylene/ethylene copolymer (C-PP/PE). Theoretical calculations revealed that CAF had the lowest phenolic hydroxyl bond dissociation enthalpy (BDE), indicating a greater antioxidant capacity. Specifically, the BDE values were 325.6 kJ mol⁻¹ for CAF, 328.2 kJ mol⁻¹ for BHA, and 341.3 kJ mol⁻¹ for BHT. Additionally, BHA exhibited the lowest transition state energy (TS) (49.29 kJ mol⁻¹), followed by CAF (57.61 kJ mol⁻¹), and then BHT (75.57 kJ mol⁻¹). With the highest hydrogen abstraction rate, CAF had a rate constant (k) of 1.05 × 10⁵ M⁻¹ s⁻¹, while BHA had 1.17 × 10⁴ M⁻¹ s⁻¹, and BHT had 4.2 × 10³ M⁻¹ s⁻¹. These results support CAF's effectiveness as a potentially more active antioxidant. In the experimental part, C-PP/PE with BHA exhibited a lower melt flow index (MFI) of 8.51, indicating greater thermal stability. Conversely, samples containing natural caffeic acid extracts showed a gradual decrease in MFI with increasing CAF concentration, with MFI values of 9.4, 8.82, 7.59, 6.44, and 5.98 for concentrations of 0.025, 0.05, 0.075, 0.1, and 0.125 ppm, respectively, suggesting continuous improvement in C-PP/PE thermal stability with higher concentrations of the natural antioxidant. These findings support the feasibility of using natural antioxidants like CAF to enhance the thermal properties of copolymers.

Author statement

Conceptualization, JH-F and JL-M.; data curation, JH-F. and KO-P.; formal analysis, JH-F. and KO-P.; acquisition financing, JL-M.; research, JH-F., KO-P. and JL-M.; methodology JH-F., KO-P. and JL-M.; resources, JL-M.; software, supervision, JH-F. and KO-P.; validation, JH-F. and KO-P.; visualization, JH-F. and KO-P.; writing: original draft, JH-F. and KO-P.; writing, review and editing, JH-F. and KO-P. All authors have read and accepted the published version of the manuscript.

Declaration of competing interest

Authors declare no COI.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.crgsc.2024.100422>.

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