# Natural Phenolic Antioxidants As a Source of Biocompatibilizers for Immiscible Polymer Blends

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S *Supporting Information*

ABSTRACT: Antioxidants are widely used in the plastic industry to protect polymers during their processing. In this work, the antioxidant effect of a series of biobased phenolic compounds has been investigated onto a polymer widely used in the industry: poly(acrylonitrile-butadiene-styrene) (ABS). The antioxidant properties were assessed by measuring the oxidation induction time (OIT). The antioxidant efficiency was directly linked to the number of mesomeric forms of the biophenols. In particular, with 5 wt % of gallic acid, which has 10 mesomeric forms, a very low value of the enthalpy of oxidation (ΔH_{ox}) was measured (70 J/g), while ΔH_{ox} of ABS is measured to be 270.4 J/g. With phloretic, ferulic, or coumaric acid (4−5 mesomeric forms), an intermediate stage is reached, slightly decreasing ΔH_{ox} to 200 J/g. Cinnamic acid, which does not have a phenolic structure, acts as a pro-oxidant of ABS. In addition, the effect of the biophenols to act as compatibilizer of immiscible blends of 30 wt % ABS and 70 wt % polylactide (PLA) was studied. In between 4 and 6 mesomeric forms lead to an efficient compatibilization, according to dynamic mechanical analysis (DMA) and morphological analyses by scanning electron microscopy (SEM). This work shows that a double reaction occurs between the propionic side chain of the biophenolic acids and PLA, on one hand, and between the phenolic part of the biophenols and ABS on the other hand. Interestingly, selected biobased compounds proved to be efficient not only as antioxidants but also as reactive compatibilizing agents in ABS/PLA blends during extrusion processing.

KEYWORDS: *Antioxidant, Biophenol, Compatibilization, Polylactide, ABS*

Efficiency of natural phenolic antioxidants to compatibilize PLA/ABS blends
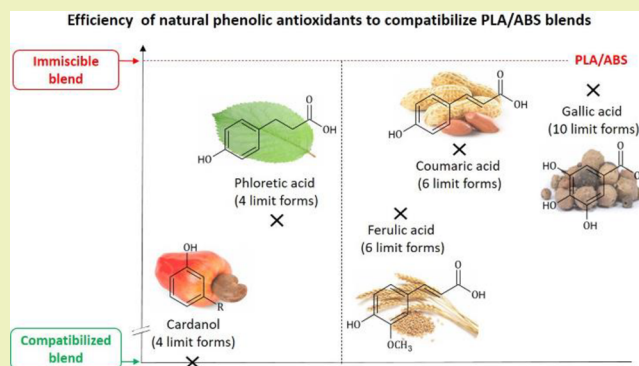
INTRODUCTION

Antioxidants are widely used in the plastics industry, for instance, aiming at protecting polymers during their processing by extrusion.[1] Polymer oxidation occurs when it is exposed to an aggressive environment under heating in the presence of oxygen. In these conditions, free radicals are generated, leading to chain scission reactions, cross-linking, or the autocatalysis of oxidation reactions.[2]

Antioxidants efficiency depends on their solubility in polymers, as well as their distribution/dispersion, their mechanism of radical scavenging, and their thermal stability.[3−5] Hindered phenolic antioxidants are commonly used to trap free radicals to prevent polymer oxidation during their melt processing. Once the labile hydrogen atom of the phenolic group has been removed due to free radical trapping, it is stabilized due to the delocalization of the free electron within the aromatic ring, and depending on its rate of substitution, many limit forms exist.[6−8]

This kind of antioxidant is widely found in nature and in particular is issued or derived from the biomass.[9,10] For instance, vanillic and syringic acids can be obtained from the chemical modification of benzoic acid while coumaric, ferulic, and synapic acids are obtained from cinnamic acid.[11] The antioxidant properties of these compounds rely on the stabilization of trapped free radicals due to their mesomeric resonance. The efficiency of their property is directly linked to their chemical structure, in particular to the substitution of the aromatic ring in ortho and para positions, and to their steric hindrance.[6,12]

The antioxidant properties of these biobased phenols are well-known and documented,[13] but their use for the thermal stabilization or to prevent the thermo-oxidation of polymers during their processing has been barely reported. However, the work reported by the group of Torkelson in 2015 has evidenced the suitability of this approach by showing the enhancement of the thermal stability of low-density polyethylene blended with antioxidants from agro-wastes.[10] For several decades, traditional and well-known synthetic antioxidants like Inorganox 1010 or Ultranox 626 have flooded the market of polymer stabilizers, even if they are known to wreak

havoc on human health, and may migrate to the surface of polymeric materials. Food packaging is then directly impacted by these chemicals, and their substitution with safer phenols issued from renewable resources is relevant. On the opposite hand, many biophenols are considered as rather low-value compounds from wastes of agriculture or paper industry, with a great impact on human health, and could be better valorized.

In this work, attention is paid to the determination of the antioxidant properties of a series of biophenols from a polymer-processing point of view, i.e., by determining their efficiency to reduce the oxidation enthalpy of poly-(acrylonitrile-butadiene-styrene) (ABS). Several biophenols have been selected depending on their chemical structure (reported in Scheme 1). Coumaric and phloretic acids have

Scheme 1. Chemical Structure of the Biophenols Used As ABS Antioxidant
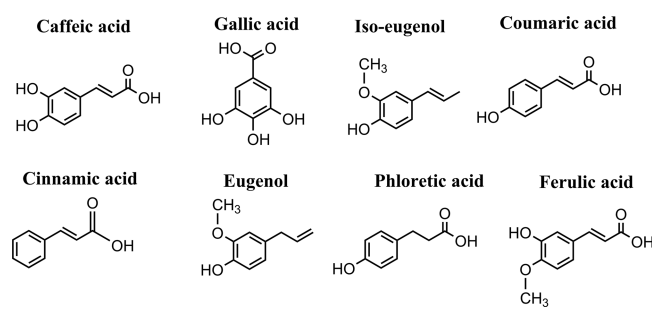
been considered initially due to their abundance and suitable chemical structure. Caffeic and ferulic acids have been chosen to determine the effect of the conjugated double bond of the propionic group in para position. Eugenol and iso-eugenol have been considered to explain the effect of the carboxylic group as well as the position of the double bond on the side chain. Cinnamic acid has been selected for sake of comparison, as it does not bear any hydroxyl group. Finally, gallic acid has been used because of its hindered chemical structure with hydroxyl groups on the aromatic ring.

Caffeic, gallic, cinnamic, coumaric, and ferulic acids are present in relatively large quantities in vegetables like peanuts, tomatoes, fennel, coffee, or artichokes (between 500 mg/kg to several g/kg).[13] As main components of lignocellulose, they are commercially produced mainly by chemical or enzymatic transformation of corn, sugar cane, and other agricultural bagasse. The main source of eugenol is the essential oil especially of clove oil, with an annual worldwide production of ~4 000 tons.[14] Iso-eugenol can be synthesized from eugenol. Phloretic acid is commonly produced by chemical or enzymatic treatment of phloretin, present in apple tree leaves.[15,16]

These natural phenolic antioxidants were all tested to limit the thermal oxidation of ABS and compared to a traditional antioxidant (Ultranox 626). In parallel, we have considered the use of these biophenols as compatibilizers of ABS/PLA immiscible blends. Indeed, the ability of cardanol, a biophenol issued from the cashew nutshell industry, to compatibilize immiscible blends of ABS with PLA has been recently reported.[17] The compatibilization mechanism relies upon the antioxidant properties of cardanol. Similarly, the ability of the studied biophenols (Scheme 1) to compatibilize ABS/PLA immiscible blends processed by extrusion was investigated.

■ EXPERIMENTAL SECTION

Materials. Polylactide (PLA, reference Ingeo 4043D) was supplied by NatureWorks (Minnetonka, MN, U.S.A.) and contained 4.2 mol % D-isomeric units. Poly(acrylonitrile-butadiene-styrene) terpolymer (ABS, Terluran HI-10), injection molding and extrusion grade, was purchased from Styrolution (Frankfurt, Germany). Cardanol (Ultra-Lite2023) was kindly supplied by Cardolite Chemical Zhuhai Ltd. (Zhuhai, Guangdong, China). All chemicals were used as received. Biobased phenolic antioxidants, i.e., coumaric acid, phloretic acid, ferulic acid, caffeic acid, eugenol, iso-eugenol, cinnamic acid, gallic acid, and methyl 3-(4-hydroxyphenyl)propionate, were supplied by Sigma-Aldrich (St. Louis, U.S.A.). Ultranox was supplied by Addivant (Danbury, U.S.A.).

Processing. *Reactive Extrusion.* Extrusions were performed using a twin-screw DSM XPlore 15 mL microcompounder (Geleen, The Netherlands) at 190 °C under a nitrogen purge flow to avoid any oxygen presence in the extruder barrel. The screw speed was set to 100 rpm, while the overall residence time was 5 min. A total of 10 g per batch was introduced into the microcompounder. Prior to processing, PLA and ABS pellets were dried at 50 °C under reduced pressure for 24 h. PLA and ABS were introduced, melted, and blended in the microcompounder with ratios of 70 and 30 wt % respectively. Other chemicals were introduced simultaneously with polymers at the given ratio.

Injection Molding. The extruded strands were pelletized and molded using an injection-molding machine (Haake MiniJet Thermo Scientific). The cylinder temperature was set to 190 °C, and the mold temperature was set at 65 °C. Pellets were poured in the cylinder, melted for 5 min, and injected at a pressure of 700 bar. For DMA measurements, the mold and Haake MiniJet 60 mm × 10 mm × 3 mm (reference 557-2296) were used. Samples were annealed at 100 °C for 1 h.

For OIT measurements, the samples were prepared by solvent mixing in $CHCl_3$ and dried at room temperature overnight and under reduced pressure for 4 h.

Characterizations. *Scanning electron microscopy.* The microstructure of PLA/ABS blends was studied by means of a pressure-controlled scanning electron microscope model Quanta FEG 200 from FEI (Eindhoven, The Netherlands). The samples were soaked in butanone for 3 days under stirring to selectively remove ABS domains, dried under vacuum for 48 h at 50 °C, and cryo-fractured after immersion in liquid nitrogen. The obtained surfaces were observed at different magnifications (2 500×, 5 000×, and 10 000×) with the large-field detector (LFD) at a pressure of 150 Pa with an accelerating voltage ≤5 kV in order to avoid any sample degradation.

Dynamic Mechanical Analysis. The viscoelastic properties of the blends were assessed by using a Netzsch DMA 42 C equipment (Selb, Germany). Samples were sized (60 mm × 10 mm × 3 mm) by injection molding. Samples were tested in a 3-point bending mode in the temperature range from −120 to 140 °C with a heating rate of 3 °C/min, with a loading amplitude of 20 μm and a dynamic force of 6 N at 5 Hz.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) thermograms were recorded by means of a Netzsch DSC 204 F1 Phoenix apparatus operating in inert atmosphere (nitrogen) with a succession of linear heating/cooling/heating ramps from 0 to 190 °C/190 to 0 °C/0 to 190 °C at a 10 °C/min rate.

Antioxidant properties were assessed by determining the oxidation induction time (t_{ox}), the oxidation enthalpy (ΔH_{ox}), and the most important oxidation time (t_{max}) using the OIT method. The first time, samples were heated at 220 °C under an inert atmosphere (nitrogen) and then maintained for 5 min in these conditions (isotherm). For the second time, samples were exposed to an oxidative atmosphere by switching from nitrogen to oxygen.

Solvent Extractions in Methanol. Solvent extractions were carried out in methanol for 24 h to quantify the grafting efficiency of compatibilizers during extrusion. Recovered solid fractions were dried during 8 h at 50 °C under vacuum to remove residual methanol. Each extraction was repeated in quadruplicate.

■ RESULTS AND DISCUSSION

Evaluation of the Antioxidant Properties of the Biophenolic Compounds. Figure 1 represents the evolution
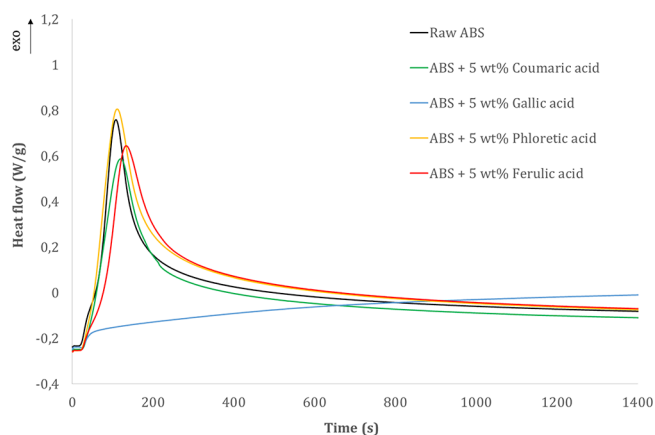
Figure 1. OIT measurements of raw ABS and its mixture with 5 wt % of various phenolic acids.

of the heat capacity of neat ABS and its blend with coumaric, ferulic, gallic, or phloretic acids. The experimental curves of each compound (i.e., with the other biophenols) have not been reported on Figure 1 to help the readiness. However, they can be consulted in the Supporting Information (Figure S1), and the data are gathered in Table 1.

Table 1. Summary of OIT Measurements for ABS Mixed with 5 wt % of Different Phenolic Compounds

| composition	t_{ox} (s)	t_{max} (s)	ΔH_{ox} (J/g)	no. of mesomeric forms
raw ABS	22	108	270.4	n.a.
ABS + 5 wt % eugenol	33	86	326.6	4
ABS + 5 wt % ferulic acid	24	133	274.5	6
ABS + 5 wt % phloretic acid	25	111	269.1	4
ABS + 5 wt % cinnamic acid	24	47	259.2	4[a]
ABS + 5 wt % coumaric acid	29	113	236.2	6
ABS + 5 wt % cardanol	22	168	236.6	4
ABS + 5 wt % iso-eugenol	23	256	207.4	5
ABS + 5 wt % gallic acid	26	54	71.4	10
ABS + 5 wt % caffeic acid	24	132	41.0	10
ABS + 0.5 wt % Ultranox 626	33	102	95.6	

[a]Cinnamic acid has 4 mesomeric forms but is not a phenolic compound.

ABS is a polymer widely processed in industry. According to OIT characterization, it appears essential to use an antioxidant during melt processing to prevent its degradation as much as possible, as indicated by its high enthalpy of oxidation (270.4 J/g) and short time of inductive oxidation (22 s at 220 °C).

ABS is composed of chemical groups expected to overcome oxidation reactions upon heating in the presence of oxygen.[18] Indeed, upon some specific conditions, the butadiene-derived repeating monomer units (double bonds) can react with oxygen, leading to the generation of allylic hydroperoxides.[19,20]

Scheme 2 illustrates the corresponding degradation mechanism. A possible oxidation mechanism would imply the

Scheme 2. Schematic Representation of the Oxidation of the Butadiene Units of ABS
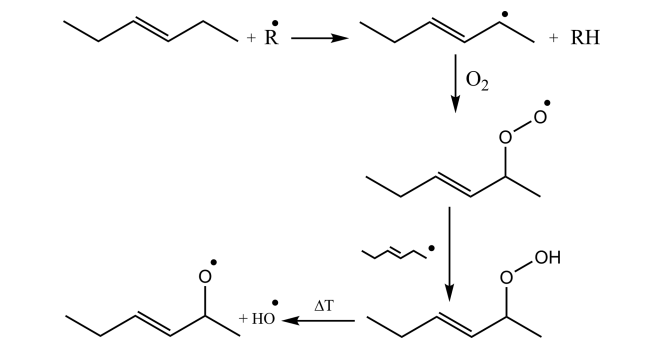
abstraction of the labile hydrogen atom in α position of the double bond, leading to the formation of an alkyl radical able to react with oxygen and to form an alkyl peroxyde radical (POO·). Its reaction with the butadiene unit of ABS to form hydroperoxide is widely possible. Upon heating, hydroperoxides are expected to decompose to form two new alkoxyl and hydroxyl free radicals, catalyzing the oxidation reaction.[20−22]

ABS has been mixed with 5 wt % of each phenolic compound to characterize their antioxidant efficiency by OIT. For the sake of reference, Ultranox 626, a widely used antioxidant in the polymer industry, has been mixed with ABS, and the mixture similarly has been characterized by OIT. When Ultranox 626 is used, the oxidation enthalpy ΔH_{ox} of ABS decreases from 270.4 to 96 J/g, evidencing the ability of this antioxidant to reduce the thermal oxidation of ABS by trapping free radicals. t_{ox} is also affected (shifting from 22 to 33 s), indicating that the degradation of ABS is delayed.

As expected, each selected biophenolic compound also has the ability to trap free radicals, as evidenced by its impact on the ΔH_{ox} of ABS as well as the evolution of t_{ox}. Their efficiency is related to their chemical structure, and particularly to the number of mesomeric forms they possess. The comparison of ΔH_{ox} of ABS in the presence of the different phenolic compounds is depicted in Figure 2.
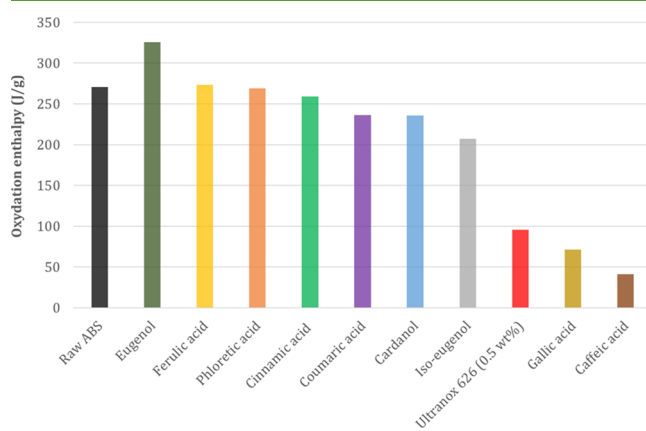

Figure 2. Evolution of the oxidation enthalpy of ABS with various biophenols (5 wt %).

With cinnamic acid, the maximum of oxidation peak is quickly reached (t_{max} = 47 s) with quite a high ΔH_{ox} (259.2 J/g), indicating it is behaving like a pro-oxidant of ABS. Coumaric, phloretic, and ferulic acids have a similar antioxidant behavior, characterized by a peak of maximum oxidation similar to ABS (108 s). Phloretic acid has a weak effect onto ABS ΔH_{ox}, probably due to its low number of mesomeric forms. The other two biophenols (i.e., ferulic and coumaric acids) delay the oxidation of ABS (from 108 to 133 or 113 s with ferulic or coumaric acids, respectively), but the impact on ABS ΔH_{ox} is low with coumaric acid (as ΔH_{ox} decreases from 270.4 to 236.6 J/g) to similar with ferulic acid (in this case, ΔH_{ox} = 273 J/g). In addition, it is interesting to note that, whatever the natural phenols used, t_{ox} increases to a higher time, reaching 33 s in the case when eugenol is used, similarly to Ultranox 626.

On the opposite hand, gallic and caffeic acids have a strong impact on the oxidation of ABS, as evidenced by the strong reduction of ΔH_{ox} from 270.4 to 71 and 41 J/g with gallic and caffeic acids, respectively, which appear to be very efficient antioxidants for ABS.

Eugenol and iso-eugenol were considered in this study to understand the effect of the carboxyl groups of the other biophenols on the oxidation of ABS. Interestingly, iso-eugenol strongly delays the oxidation of ABS as indicated by the shift of t_{max} from 108 to 256 s, while eugenol appears to catalyze the oxidation as t_{max} is reached after 86 s. In addition, ΔH_{ox} follows the same trend: when eugenol is used, it increases from 270.4 to 320 J/g, while it decreases to 207 J/g with iso-eugenol. These results clearly indicate that the conjugation of the double bond of the side chain has a strong effect on the stabilization of free radicals by mesomeric effect, as illustrated on Scheme 3 for coumaric acid. Finally, Scheme 4 sorts them by efficiency to reduce ABS ΔH_{ox}.

Scheme 3. Illustration of the Mesomeric Forms of Coumaric Acid
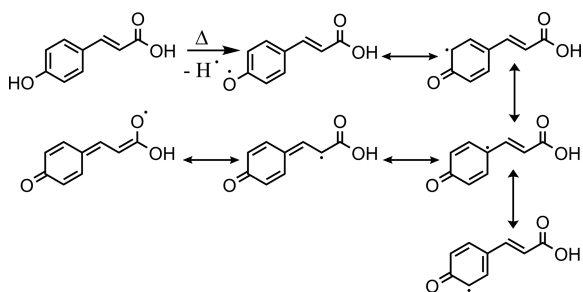
In conclusion, the number of mesomeric forms of the biophenols hereby studied is the main parameter affecting the thermo-oxidation of ABS. The conjugation of a double bond in the para position seems to have a strong impact on the antioxidant properties of these biophenols in addition to the number of mesomeric forms. In addition, by comparing the results obtained with iso-eugenol and ferulic acid, it can be concluded that the carboxylic group triggers the thermal degradation of ABS.

Gallic and caffeic acids are the two phenolic acids that are preventing the most the degradation of ABS, even better than Ultranox 626. However, they are introduced at a higher extent than the synthetic antioxidant, and their use instead of synthetic antioxidants would make sense in specific applica- tions, for instance, as food packaging. Indeed, synthetic antioxidants are known to migrate to plastic surface and to contaminate the food they protect. In this case, the use of biophenols may be justified, in spite of the possible increase of the cost due to their higher content compared to synthetic antioxidants. To this aim, ABS should be used in combination with another polymer used in this field of application.

Outstanding impact resistance, high mechanical strength, good chemical resistance, and ease of extrusion and molding are characteristics that makes poly(acrylonitrile-butadiene-styrene) (ABS) widely used as a toughening agent for many engineering plastics such as polycarbonate (PC)[23] or polyamide (PA).[24] In particular, ABS has been reported to be a good candidate to toughen PLA, which is widely considered for its use in packaging applications.[25−31]

In a recent study, we evidenced that cardanol, another biophenol issued from the cashew nutshell industry, was able to compatibilize immiscible blends of ABS and PLA.[17] The compatibilization mechanism relies on the antioxidant proper- ties of cardanol toward ABS, where cardanol was assumed to graft onto ABS via its phenolic ring. In the following section, we investigate the potential of the previously tested antioxidants to compatibilize immiscible blends of PLA and ABS.

Investigation of the Relationship between the Antioxidant Properties of Biophenols and Their Efficiency to Compatibilize PLA/ABS Immiscible Blends.

In a first step, the thermal stability of each biophenol has been evaluated by thermogravimetric analysis (TGA) to check their thermal stability in the condition of extrusion. Eugenol, iso-eugenol, and both cinnamic and caffeic acids have a thermal degradation temperature below the extrusion temperature (190 °C), meaning they cannot be employed during the extrusion process. The corresponding TGA data can be consulted in the Supporting Information (Figure S2).

The other biophenols (i.e., phloretic, gallic, coumaric, and ferulic acids) were mixed with PLA and ABS by reactive extrusion at 190 °C. The blends were prepared with 70 wt % of PLA and 30 wt % of ABS, as previously reported.[17] Five wt % of biophenols was added to the blends.
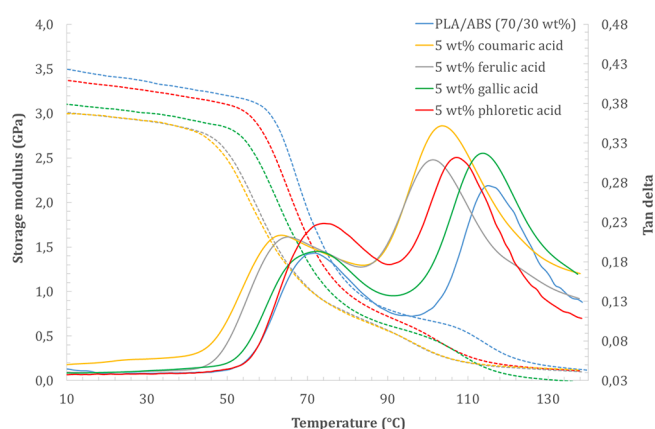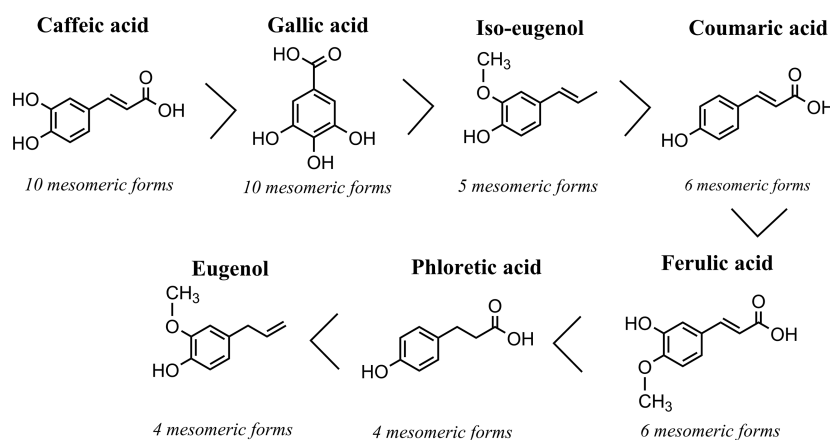
PLA and ABS are immiscible, and their blends have two distinct relaxation temperatures (Tα), i.e., 74.6 °C for PLA and 119.6 °C for ABS. Dynamic mechanical analysis (DMA) characterizations of the blends are reported in Figure 3, and the values of Tα of PLA and ABS, as well as the storage modulus of the blends with or without the addition of the biophenols, are gathered in Table 2.

Three distinct behaviors can be determined from the thermo-mechanical characterizations.

(a) Gallic acid has been shown to be the most efficient antioxidant due to the very significant decrease of the oxidation enthalpy of ABS when they are mixed together. Surprisingly, its effect on the compatibilization of PLA and ABS is almost not detected as the Tα of the two polymers remain similar (from 74.6 to 72.9 °C for PLA, and from 119.6 to 114.7 °C for ABS), as well as ΔTα (from 45.0 to 41.8 °C). This result is all the more surprising that it was reasonable to expect a highly compatibilized blend as the compatibilization mechanism relies upon the antioxidant properties of the phenol used. In this case, it seems the efficiency of gallic acid to trap free radicals is so strong it impedes the compatibilization process.

(b) When coumaric and ferulic acids, which both exhibit 6 mesomeric forms, are used, a significant compatibilization can

Scheme 4. Classification of the Biophenolic Compounds Depending on Their Antioxidant Efficiency, According To OIT Measurements

Caffeic acid — *10 mesomeric forms*

Gallic acid — *10 mesomeric forms*

Iso-eugenol — *5 mesomeric forms*

Coumaric acid — *6 mesomeric forms*

Eugenol — *4 mesomeric forms*

Phloretic acid — *4 mesomeric forms*

Ferulic acid — *6 mesomeric forms*

Figure 3. Evolution of the thermo-mechanical properties of PLA/ABS blends (70/30 wt %) with or without 5 wt % of biophenolic compounds as a function of temperature.

Table 2. Summary of the Thermo-mechanical Properties of PLA/ABS Blends (70/30 wt %) with or without Biophenolic Compounds

composition	Tα PLA (°C)	Tα ABS (°C)	ΔTα (°C)	storage modulus at 20 °C (GPa)
PLA/ABS (70/30 wt %)	74.6	119.6	45.0	3.4
PLA/ABS + 5 wt % phloretic acid	73.4	108.1	34.7	3.3
PLA/ABS + 5 wt % gallic acid	72.9	114.7	41.8	3.1
PLA/ABS + 5 wt % ferulic acid	65.2	101.4	36.2	3.0
PLA/ABS + 5 wt % coumaric acid	63.5	103.6	40.1	3.0

be appreciated. The introduction of 5 wt % of each of them leads to a decrease of the Tα for both PLA and ABS (from 74.6 to 63.5 or 65.2 °C and from 119.6 to 103.6 and 101.4 °C for coumaric and ferulic acids, respectively). In both cases, the storage modulus slightly decreases from 3.4 to 3.0 GPa. These two biophenolic compounds have a similar effect on PLA/ABS blends, with a higher efficiency when ferulic acid is used, as indicated by the decrease of ΔTα (36.2 °C).

(c) Despite phloretic acid being the less-efficient antioxidant according to OIT measurements with its four mesomeric forms, it leads to a decrease of ABS Tα from 119.6 to 109.8 °C, while PLA Tα remains similar (73.4 °C instead of 74.6 °C for neat PLA). Surprisingly, the addition of the phenolic compound does not lead to a decrease of PLA Tα. Indeed, SEC measurements were performed to follow the evolution of the molecular structure of extruded PLA in the presence of the phenolic acids used. Results are reported in Table 3, and it can

Table 3. Summary of SEC Measurements on PLA Extruded with or without 5 wt % of Biophenolic Compounds

composition	M_n (kg/mol)	M_w (kg/mol)	polydispersity Đ (M_w/M_n)
ePLA	106.7	219.6	2.1
PLA + 5 wt % phloretic acid	39.0	106.3	2.7
PLA + 5 wt % gallic acid	36.1	95.3	2.6
PLA + 5 wt % coumaric acid	33.5	84.7	2.5
PLA + 5 wt % ferulic acid	34.7	95.3	2.7

be observed that a clear decrease of both M_n and M_w occurs during the extrusion in the presence of these phenolic compounds. The conditions are ideal to trigger PLA chains scission during the process, explaining both the decrease of the molecular weight of PLA and the decrease of its Tα. However, when phloretic acid is used, both M_n and M_w decreased (M_n from 106.7 to 39.0 kg/mol and M_w from 219.6 to 106.3 kg/ mol), but PLA Tα remains similar, while ABS Tα is strongly affected, shifting from 119.6 to 108.1 °C. These observations will be discussed in more detail hereafter.

Morphological analyses were performed to assess the evolution of the microstructure of the blends, depending on the biophenolic compound used. Micrographs of cryo-fractured surfaces for which the ABS phase has been removed with butanone are reported in Figure 4.

When 5 wt % of gallic acid is added to PLA/ABS blends (Figure 4e), the size of ABS nodules remains similar to that for PLA/ABS blends (Figure 4a), confirming DMA character-ization and the conclusion that this acid does not promote the compatibility of the two immiscible polymers. With phloretic (Figure 4d) and ferulic acids (Figure 4c), the average size of
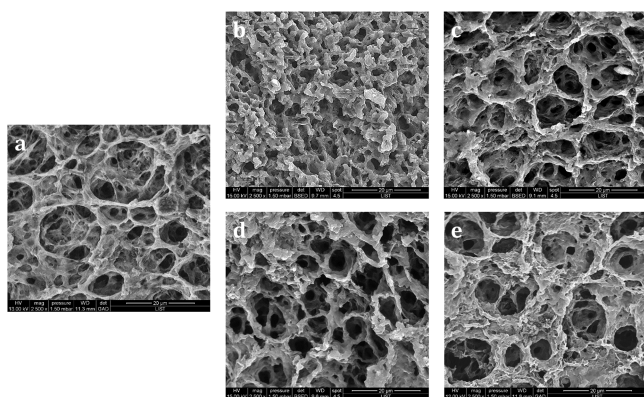
Figure 4. SEM micrographs of PLA/ABS blends (70/30 wt %) without (a) and with 5 wt % of coumaric (b), ferulic (c), phloretic (d), or gallic (e) acids.

ABS nodules slightly decreases, leading to the same conclusions as from DMA characterizations, i.e., a slight compatibilization is observed. It is worthy to note that these two phenolic compounds also lead to a reduction of the PLA molecular weight as attested by SEC measurements (Table 3, entries 2 and 5).

Surprisingly, when coumaric acid is used (Figure 4b), a more significant decrease of the size of ABS nodules is observed (from several micrometers to some hundreds of nanometers), reflecting a possible compatibilizing effect of the phenolic compound reached by an equilibrium between the different phenomena occurring during the reactive mixing, i.e., PLA chains cleavage, free radicals trapping, plasticization, and/or chemical reactions with PLA and/or ABS.

In conclusion, and based on the evolution of the $\Delta T\alpha$, phloretic acid is the most efficient compatibilizer compared to the other biophenolic compounds tested in this study (Scheme 5), in spite of its molecular weight reduction. It appears that the antioxidant efficiency of the biophenols needs to be moderate, as attested by the comparison of the effect of phloretic and coumaric acids. Indeed, the only structural difference between these two biophenols is the presence of a conjugated double bond for the latter one, leading to a higher number of mesomeric forms and, thus, to a higher free radical trapping efficiency. With these results, it is clear that a balance has to coexist between the ability to trap radicals and the stability of the mesomeric form of the biophenol.

These results shed light on the mechanism of compatibilization occurring during the extrusion. In particular, it could be assumed that phenolic acids react first with PLA. Indeed, when phenolic acids with double bonds on the propionic side chain are used (e.g., coumaric and ferulic acids), the mesomeric effects of the structure are reinforced, as they are not destabilized by the carboxylic group. Their radical-scavenging

ability is higher than that for phloretic acid. However, as a high antioxidant efficiency is not suitable for the compatibilization of PLA/ABS blends, it results that phloretic acid behaves as a more efficient compatibilizer than ferulic and coumaric acids, due to the absence of a conjugated double bond on the propionic side chain.

Finally, to avoid any possible reaction with the carboxylic acid and/or acid-catalyzed hydrolysis of PLA during reactive mixing, the methylation, we decided to investigate the effect of methylating the −COOH group of phloretic acid on its compatibilization efficiency.

Study on the Effect of the Methylation of Phloretic Acid on the Compatibilization of PLA/ABS Blends. The methyl ester of phloretic acid (m-phlo) was blended with PLA following the same extrusion conditions as for the previously reported blends. In Table 4 are reported M_n, M_w, and Đ of PLA after extrusion in the presence of either m-phlo or phloretic acid.

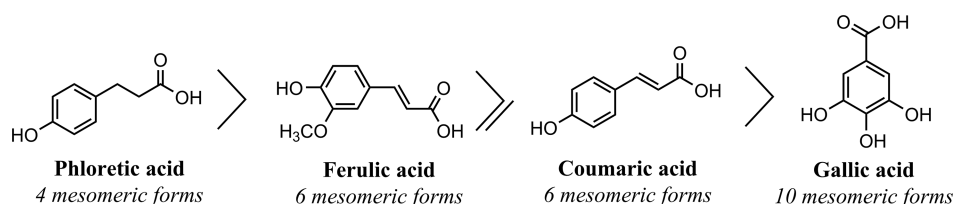**Table 4. Summary of SEC Measurements of Extruded PLA (ePLA), with 5 wt % Phloretic Acid and 5 wt % Methyl Phloretate**

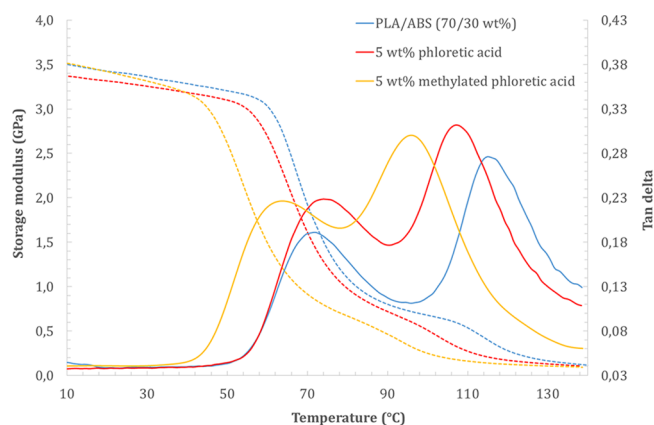| composition	M_n (kg/mol)	M_w (kg/mol)	polydispersity Đ (M_w/M_n)
ePLA	106.7	219.6	2.1
5 wt % phloretic acid	39.0	106.3	2.7
5 wt % m-phlo	109.4	217.3	2.0

Clearly, it appears that the decrease of the molecular weight when phloretic acid is used is well-linked to the presence of the carboxyl group. Indeed when m-phlo is employed, M_w, M_n, and Đ remain similar (Table 4, entry 3).

The thermo-mechanical properties of the blends were characterized by DMA and are reported in Figure 5 and Table 5. Blends prepared with 5 wt % phloretic acid are also reported for the sake of comparison.

Interestingly, the results issued from the use of methylated phloretic acid confirm the previous assumption. A better compatibilization is reached, as attested by the decrease of $\Delta T\alpha$ from 45.0 to 32.1 °C, while $\Delta T\alpha$ reaches 34.7 °C when phloretic acid is used. Storage modulus at 20 °C is not impacted by the use of m-phlo. The shift of PLA and ABS Tα to lower temperatures is the result of an outstanding plasticizing effect, probably due to changes in the polarity of the alkyl side chain compared to phloretic acid, promoting its interaction with the polymers chains. This plasticizing effect could also be the result of the higher volume occupied by m-phlo compared to phloretic acid, as it has also been reported with poly(acrylic acid) ester plasticizing polyvinyl acetate (PVAc) and polyvinyl methyl ether (PVME).[32]

Scheme 5. Classification of the Biophenolic Compounds Depending on Their Compatibilization Efficiency on PLA/ABS Blends

Phloretic acid
4 mesomeric forms

Ferulic acid
6 mesomeric forms

Coumaric acid
*6 mesomeric forms*

Gallic acid
10 mesomeric forms

Figure 5. Evolution of the thermo-mechanical properties of raw PLA/ABS blends (70/30 wt %) or with 5 wt % phloretic acid or 5 wt % m-phlo.

Table 5. Summary of the Thermo-mechanical Properties of Raw PLA/ABS Blends (70/30 wt %) or with 5 wt % Phloretic Acid or 5 wt % m-phlo

composition	$T\alpha$ PLA (°C)	$T\alpha$ ABS (°C)	$\Delta T\alpha$ (°C)	storage modules at 20 °C (GPa)
PLA/ABS (70/30 wt %)	74.6	119.6	45.0	3.4
5 wt % phloretic acid	73.4	108.1	34.7	3.3
5 wt % m-phlo	63.8	95.9	32.1	3.4

Morphological analyses were performed by SEM on cryo-fractured samples, and the micrographs are reported in Figure 6. The micrographs clearly show that phloretic acid
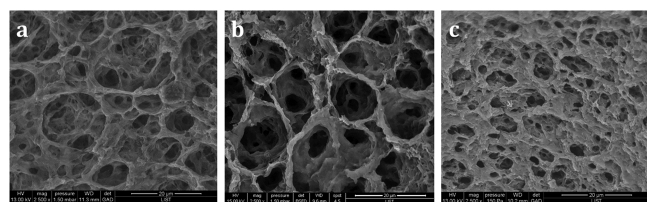
Figure 6. SEM micrographs of raw PLA/ABS blends (70/30 wt %) (a) and with 5 wt % of phloretic (b) or m-phlo (c).

methylation helps the compatibilization of PLA and ABS, as attested by the decrease of the average size of ABS nodules within the PLA matrix (Figure 6c), confirming the DMA results. Substitution of the carboxylic group toward methylated groups clearly prevents the reduction of PLA molecular weight during melt blending, while a significant plasticizing effect is observed for both PLA and ABS.

As a conclusion, these results shed more light on the mechanism occurring while using phloretic acid. The results could be a combination of two mechanisms: free radical grafting onto the phenolic part of phloretic acid, as previously reported on cardanol,[17] and a reaction of phloretic acid carboxylic group with PLA via esterification reaction. Scheme 6 tentatively depicts the compatibilization mechanism.

■ CONCLUSION

In this work the antioxidant effect of a series of biobased phenolic compounds has been investigated on commercially available poly(acrylonitrile-butadiene-styrene). The antioxidant properties were assessed by measuring the oxidation induction time (OIT) by DSC. As expected, the antioxidant efficiency of the biophenols was directly linked to their number of mesomeric forms. In particular, with 5 wt % of gallic acid, which has 10 mesomeric forms, a very low value of the enthalpy of oxidation ΔH_{ox} was measured (ca. 70 J/g), while ΔH_{ox} of ABS is measured to be 270.4 J/g. With phloretic, ferulic, or coumaric acids (4−5 mesomeric forms), an intermediate stage is reached, slightly decreasing ΔH_{ox} to 200 J/g. Finally, cinnamic acid, which has 4 mesomeric forms but does not scavenge free radical, acts as a pro-oxidant of ABS.

The comparison of the effect of eugenol and iso-eugenol gives a clear answer about the effect of the stabilization of free radicals by mesomeric effects. Indeed, their molecular structure differs by the position of a double bond on the side chain in the para position. For eugenol, the double bond is located in position 3 of the side chain, while it is conjugated to the aromatic ring for iso-eugenol. For this latter one, an outstanding antioxidant effect is observed, due to the additional number of mesomeric forms that trap free radicals, while eugenol slightly reduces and delays the oxidation of ABS. By comparing the effects of iso-eugenol and coumaric acid, it appears that the carboxylic group triggers slightly the oxidation of ABS.

In a second step we studied the effect of the biophenols with a suitable thermal stability (i.e., ferulic, phloretic, and coumaric acids) to act as compatibilizers of immiscible blends of 30 wt % ABS and 70 wt % PLA. It was evidenced that a moderate antioxidant efficiency, i.e., a medium number of mesomeric forms in between 4 and 6, led to the most efficient compatibilization, according to DMA and morphological analyses by SEM. It was necessary for the antioxidant to be just able to trap free radicals without stabilizing them too much, allowing their reaction with ABS during the extrusion process. As expected, a reaction also occurs between the propionic side chain of the biophenolic acids and PLA. SEC measurements on PLA/biophenolic acids were performed, evidencing a reduction of the polyester chain length. Finally, by comparing the results between the use of phloretic acid and its methylated form (to avoid PLA chain cleavage via acid-catalyzed hydrolysis), it was shown that the $T\alpha$ of PLA was not shifted even if its molecular weight decreased. However, the $T\alpha$ of ABS was reduced to 60 °C, leading to the assumption of a mutual reaction of phloretic acid between PLA and ABS during the extrusion.

Scheme 6. Schematic Representation of the Possible Grafting of Phloretic Acid onto ABS and PLA
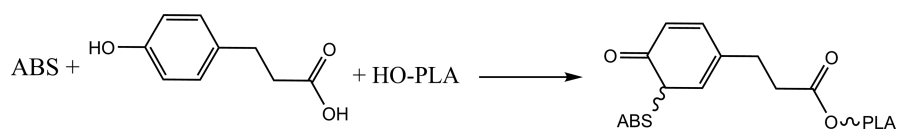
■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssusche-meng.8b02999.

> OIT measurements of raw ABS and its mixture with 5 wt % of various phenolic acids, and evolution of the weight loss of the different biophenolic compounds depending on the temperature (PDF)

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■ ABBREVIATIONS

PLA, polylactide; ABS, poly(acrylonitrile-butadiene-styrene); ΔH_{ox}, enthalpy of oxidation; t_{max}, most important oxidation time; t_{ox}, oxidation induction time; DMA, dynamic mechanical analysis; SEM, scanning electron microscopy; DSC, differential scanning calorimetry; OIT, oxidation induction time; SEC, size-exclusion chromatography

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