

High-performance sustainable active packaging from poly(hexamethylene furanoate) and bark extracts

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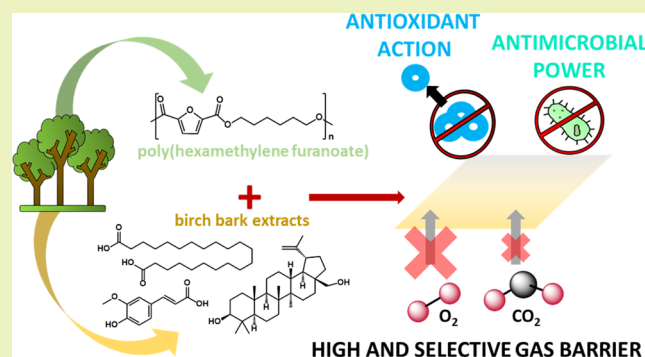
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ABSTRACT: The development of sustainable high-performance polymeric formulations, possibly showing multifunctional characteristics, is of key importance to produce materials in line with the circular economy agenda. This work focuses on the preparation of fully biomass-derived blends from furan-based polyester and natural extracts to yield an innovative packaging system. Terpenoids and suberin monomers are isolated from largely available waste biomass, namely, birch bark, through simple and straightforward methodologies and mixed with poly(hexamethylene furanoate) (PHF). The physicochemical properties of the blends evidence a modulation of the surface hydrophobicity together with a significant increase in flexibility and toughness owing to the dual function exerted by the extracts, which act both as plasticizing agents and cross-linking molecules due to the formation of weak interactions, such as hydrogen bonding, with the macromolecular chains of PHF. The evaluation of the functional properties highlights that the excellent gas barrier characteristics of PHF are not just preserved; rather, a substantial increase of the CO₂/O₂ permselectivity ratio is measured because of the presence of an increased concentration of disclinations that favor the diffusion of CO₂. Lastly, the addition of natural extracts allows for the implementation of antioxidant and antibacterial features otherwise absent in the pristine polymer.

KEYWORDS: poly(hexamethylene furanoate), suberin, bark extractives, antioxidant activity, antimicrobial activity, sustainable packaging, active packaging, biobased polymers



INTRODUCTION

The concept of circular economy aims at maximizing the lifecycle of a product while reducing both waste and the consumption of virgin sources. Thus, the effective implementation of green chemistry principles and circular economy practices cannot escape from developing sustainable materials that can successfully substitute traditional ones.¹ This, of course, without compromising the performances, rather implementing additional valuable features to yield multifunctional products. Among others, the plastic sector urgently needs alternatives because of the huge amount of waste that accumulates in the terrestrial and marine environment in the form of macro- and microplastics.² Especially in the case of food packaging, where recycling is not always a viable solution due to, for example, contamination with organic matter or the use of high-barrier multilayer films, the intrinsic short life span of this application represents a serious issue in terms of waste management and littering.³ Therefore, high-performance biobased and biodegradable plastics are of great interest, and much work is being carried out on this topic from academic and industrial researchers.

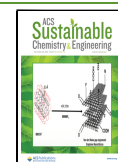
In this framework, polyesters based on 2,5-furandicarboxylic acid (FDCA) attracted considerable attention due their peculiar features that make them excellent candidates as packaging materials.⁴ FDCA, listed among the top 12 biobased chemicals by the Department of Energy of the United States, is indeed obtained from biomass, specifically from cellulose or hemicellulose-derived sugars, i.e., fructose or xylose.⁵ The development of FDCA-based polyesters is a hot topic because these polymers display, in addition to high melting temperature and thermal stability, proven biodegradability^{6,7} and outstanding gas barrier properties. These are due to the presence of 1D/2D ordered domains, arising from hydrogen bonds as well as π - π interactions, generally defined as the mesophase, which are very efficient in hampering the diffusion of the gas molecules through the polymer matrix.^{8–10} The

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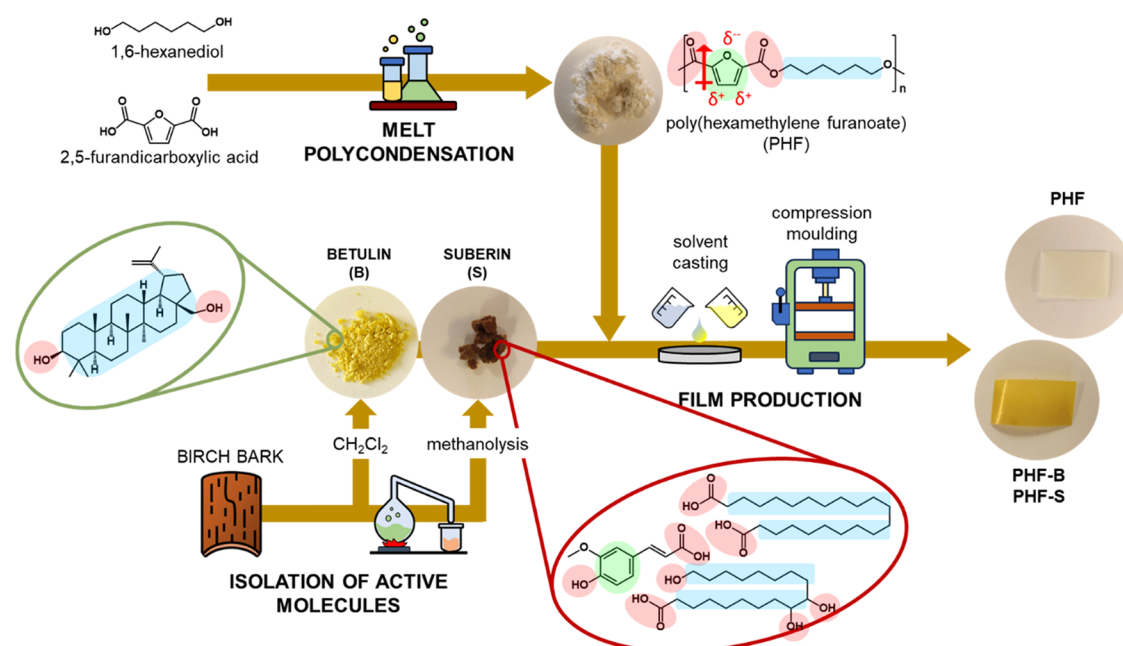


Figure 1. Scheme of the workflow leading to the production of the PHF-based films containing bark extracts. The chemical structure of betulin, representative suberin components, and poly(hexamethylene furanoate) is reported, and the functional groups responsible for the interactions among the blend components are highlighted (polar: red, apolar: blue, aromatic: green). The dipole moment on furan is also shown.

most known member of FDCA-based polyesters is poly(ethylene-2,5-furanoate) (PEF), which demonstrated superior mechanical and permeability performances than poly(ethylene terephthalate) (PET), but other polyesters containing longer diol subunits have also been synthesized and characterized, all showing very interesting properties both in terms of outstanding gas barrier capability and tunable mechanical response, making them suitable for rigid as well as flexible packaging.¹¹ Among those, poly(hexamethylene-2,5-furanoate) (PHF) is a quite stiff material, mainly owing to its high degree of crystallinity. It shows glass transition below ambient temperature (in the range of 7–18 °C)¹² and melting temperature of about 140–145 °C,¹² both lower than other furanoate polymers,^{13,14} allowing its processing under milder conditions. Despite all of the abovementioned features that make FDCA-based polyesters the most promising class of bioplastics, they still lack “active” properties that would not only allow physical protection of the enveloped food but also prolong the shelf life of the product by counteracting spoiling due to oxidation and biological activity. To this purpose, various additives can be introduced in the packaging formulation.^{15,16} However, traditional compounds present two major drawbacks: (i) they are usually of synthetic origin, and (ii) the microbial strains have developed high resistance to these molecules, which considerably decreases their efficacy. Natural active compounds may offer a valid alternative, especially if they can be extracted from waste biomass, thus generating upcycling pathways that are in line with circular economy objectives. In this respect, bark represents a potential resource. Bark is produced in large amounts (more than 50 Mt/y only in North America) mainly as a byproduct of the pulp industries and it is usually landfilled or burned.¹⁷ In addition to cellulose, hemicellulose, and polyphenols (tannins and lignins), for which established and emerging exploitation routes are known, bark is rich in other valuable compounds, i.e., triterpenoids and suberin, whose high potential is much

less explored. Suberin constitutes up to 50% of the cork mass and is an aliphatic–aromatic cross-linked polyester composed of long-chain ω -hydroxyacids, α,ω -dicarboxylic acids, aromatics such as ferulic and vanillic acids, and glycerol.¹⁸ Due to its complex nature, for the extraction of suberin, at least a partial depolymerization to cleave the ester bonds, usually carried out by hydrolysis or methanolysis, is needed.¹⁸ On the other hand, triterpenoids are a mixture of various compounds, betulin and betulinic acid being the most abundant, although the composition may vary depending on the plant and the extraction procedure.^{17,19} Both suberin components and triterpenoids have shown bactericidal, antiviral, and anti-inflammatory activities.^{20,21}

Early literature reports deal with the use of cork to modify and implement the physicochemical characteristics of polypropylene and polyethylene,^{22–24} in a few cases with the addition of suberin as a filler–matrix compatibilizer,²³ of ethanol-soluble cork extracts²⁵ to provide antioxidant capacity, and of betulin to generate antimicrobial resistance.²⁶ As to biopolymeric matrices, terpenoids such as limonene, thymol, eugenol, and geranyl esters have been inserted in polyhydroxybutyrate^{27–29} and polylactide^{30,31} formulations with the aim of modulating their properties and introducing active features. Nevertheless, to the best of our knowledge, only one work employed a commercial birch bark extract mainly composed of betulin to prepare PLA-based composite fibers for wound healing purposes.³²

In light of this information, and owing to the above-described intriguing properties of betulin and suberin, this contribution proposes: (i) an interesting upcycling pathway for largely available biomass residues, i.e., birch bark, and (ii) a systematic investigation on the effects of the introduction of either betulin or suberin on the physicochemical characteristics of high-performance furan-based polyesters. The combination of such a polymer matrix with bark extracts is aimed at broadening the already wide and diverse properties of this class

of materials by introducing active features without compromising their peculiar features, i.e., their outstanding gas barrier behavior. The overall purpose of the work is the development of a fully biomass-derived high-performance packaging system.

Among furanoate polyesters, the choice fell on the polymer with a low processing temperature, poly(hexamethylene furanoate), PHF, to reduce the risk of filler degradation. Moreover, PHF was supposed to show good compatibility with the birch bark extracts since it contains polar (ester groups) and apolar moieties (PE-like segment of the glycol subunit) as well as aromatic rings, also present in the extracts (Figure 1).

EXPERIMENTAL SECTION

Synthesis of Poly(hexamethylene furanoate). Poly-(hexamethylene furanoate) (PHF) was synthesized by a two-step solvent-free polycondensation. In detail, DMF (0.106 mol) and HD (0.195 mol) were charged in a 250 mL glass reactor, together with the catalysts TBT and TIP (200 ppm each). The apparatus, coupled to a condenser cooled by liquid nitrogen, was immersed in a silicon oil bath, and the reaction mixture was kept under constant stirring (100 rpm) by an overhead stirrer. The first step was carried out at 190 °C under a nitrogen flow (20 mL/min). Once 90% of theoretical methanol was collected (after about 90 min), the pressure was progressively reduced to 0.06 mbar and the temperature was raised to 230 °C. During this stage, which lasted for about 150 min, the excess of hexanediol was distilled off, while the viscosity of the polymeric mass increased, as well as the torque value. When a constant value of torque was reached, the polymer was discharged from the reactor.

Isolation of Extractives and Suberin. Triterpenoids and suberin were isolated from silver birch (*Betula pendula*) bark. Specifically, to obtain the triterpenoids, 5 g of pulverized bark was extracted with dichloromethane (50 mg/mL) for 12 h using a Soxhlet apparatus. Subsequently, the solution was cooled to room temperature and anhydriated with sodium sulfate. After filtration, the solvent was evaporated under reduced pressure to yield a yellowish powder.

Suberin was obtained by methanolysis. Briefly, the dewaxed bark powder was dispersed in 3% m/v sodium methoxide in methanol (6 mg/mL) and refluxed for 4 h. After cooling to room temperature, the reaction mixture was filtered and the precipitate was refluxed with 250 mL of fresh methanol for an additional 1 h. The reaction mixture was subsequently filtered, and the permeates obtained from the two steps were combined and acidified to pH 5 with 2 M HCl, yielding a yellow dispersion. The supernatant was evaporated under reduced pressure at 50 °C and the obtained precipitate was dispersed in 200 mL of water and extracted with chloroform (3×). The organic phase was anhydriated with sodium sulfate and filtered. The obtained solution was finally evaporated under reduced pressure at 40 °C to yield a brownish wax-like product.

Preparation of Blend Films. Blends containing different amounts of filler were prepared by dissolving both PHF and the extract (either triterpenoids or depolymerized suberin) in chloroform under magnetic stirring at room temperature. To avoid possible detrimental effects on the characteristics of PHF due to high additive concentrations, 5 and 10 wt % loadings were selected. Specifically, PHF was let dissolve overnight, and then the filler was added and let dissolve for an additional 2 h. The resulting solutions were poured into Petri dishes, and the solvent was evaporated at room temperature for at least 24 h. Successively, films were obtained by compression molding using a Carver C12 laboratory press. Each blend was heated to 170 °C and kept under a pressure of 5 ton/m² for 2 min before pressure release and cooling. The films were then stored at room temperature for 2 weeks prior to further characterization.

Blend films are named PHF-Bx and PHF-Sx, where x represents the wt % of the filler, while B and S stand for triterpenoids (betulin) and depolymerized suberin, respectively.

Thermal Characterization. Differential scanning calorimetry (DSC) was performed using a PerkinElmer DSC6 calibrated with indium and cyclohexane standards. Scans were performed by heating

5 mg of the sample from −40 to 180 °C at 20 °C/min (I scan). Then, the samples were cooled to −40 °C at 100 °C/min, and after an isotherm of 15 min, a second heating scan was performed (II scan) under the same conditions of the I scan. The glass-transition temperature (T_g) was taken as the midpoint of the baseline deviation associated with glass-to-rubber transition, while the relative heat capacity (Δc_p) was determined as the total height of the step associated with glass transition. Melting (T_m) and crystallization (T_{cc}) temperatures were determined as the peak maximum and minimum of the endothermic and exothermic transitions, respectively. The corresponding heat of fusion (ΔH_m) and heat of crystallization (ΔH_{cc}) were obtained from the total areas of the endothermic and exothermic phenomena, respectively.

Mechanical Characterization. Stress–strain tests were performed on rectangular film specimens (5 × 50 mm²) by means of an Instron 5966 testing machine equipped with a transducer-coupled 1 kN load cell. The measurements were carried out at room temperature at a stretching rate of 10 mm/min. The elastic modulus (E) was calculated from the initial linear segment of the tensile curve. Stress (σ_y) and elongation (ϵ_y) at yielding, and stress (σ_b) and elongation (ϵ_b) at break were also determined. At least six specimens for each sample were tested.

Gas Barrier Properties. The oxygen and carbon dioxide barrier behavior of the blend films was evaluated by a manometric method using a Permeance Testing Device type GDP-C (Brügger Feinmechanik GmbH), according to ASTM 1434-82, DIN 53 536, and ISO/DIS 15 105-1 protocols. In detail, after a preliminary high-vacuum desorption from the lower analysis chamber, the upper one was filled with gas (either oxygen or carbon dioxide) at ambient pressure. A pressure transducer, set in the lower chamber, recorded the increase of gas pressure over time. Before the analysis, film thickness was measured on different points of the polymeric surface by a digital micrometer (MarCator type 1086, Mahr GmbH, Esslingen, Germany). The reported results represent the mean thickness of three tests carried out at 10 different points on the film surface. Permeability measurements were then performed using food-grade gases (gas stream of 100 cm³/min) at 23 °C and 0% RH on circular specimens (110 mm diameter). The measurements were carried out in triplicate, and the result is reported as the mean value of the gas transmission rate (GTR, in cm³·cm·m^{−2}·d^{−1}·atm^{−1}).

Antioxidant Activity. The antioxidant activity was determined by evaluating the free-radical scavenging effect on 1,1-diphenyl-2-picrylhydrazyl (DPPH). The test was performed both on the extracts and on PHF and the blend films. As for the free extracts, a known aliquot (50 μL) of an ethanol solution was mixed with 1450 μL of a 6 × 10^{−5} M ethanol solution of DPPH to obtain eight different concentrations in the range of 0.01–1 mg mL^{−1}. The mixture was thoroughly shaken for 30 min at 25 °C in the dark, and the absorbance was measured at 517 nm with a Shimadzu UV-1800 Spectrophotometer against a blank. Each test was carried out in triplicate. The results are expressed as the percentage of inhibition of the DPPH radical, calculated according to the following equation

$$\text{DPPH}_{\text{radical scavenging}} (\%) = \left(1 - \frac{A_s}{A_c} \right) \times 100 \quad (1)$$

where A_s is the absorbance of the sample and A_c is the absorbance of the DPPH solution without the extract. By plotting the percentage of inhibition against the extract concentration, the IC₅₀ value, that is, the concentration inhibiting 50% of the radical activity, can be calculated.

The antioxidant activity of PHF and blend films was evaluated as follows. About 150 mg of a rectangular film specimen was soaked in a vial containing 5 mL of ethanol and placed in an orbital shaker at 150 rpm and 20 °C for specific time intervals (24, 48, and 168 h). At the end of the incubation, 1450 μL of the solution was withdrawn and mixed with 50 μL of a DPPH ethanol solution to reach a final concentration of 6 × 10^{−5} M. The analysis was carried out as described above to yield the DPPH inhibition percentage. Each test was carried out in triplicate.

Table 1. Thermal (TGA and DSC) and Surface Wettability (WCA) Data of PHF and Blend Films

	WCA (deg)	T_{onset} (°C)	T_{max} (°C)	DSC I scan				DSC II scan					
				T_1 (°C)	ΔH_1 (J/g)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	Δc_p (J/g °C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)
PHF	99 ± 1	374	394	46	7.9	143	41	16	0.178			143	36
PHF-B5	95 ± 2	361	384	51	1.5	143	29	17	0.268			143	27
PHF-B10	84 ± 5	365	389	50	0.8	142	30	16	0.264	66	3	142	30
PHF-S5	93 ± 2	361	390	52	1.9	143	29	15	0.257			143	29
PHF-S10	76 ± 2	365	392	51	4.7	143	32	14	0.272			143	32

Antibacterial Activity. The antimicrobial activity of PHF and the blend films was determined in accordance with the ISO 22196:2011 standard protocol. The inocula of bacterial strains were prepared from fresh overnight culture in LB broth. Final concentrations of 1×10^6 CFU·mL⁻¹ for *Escherichia coli* and 1×10^5 CFU·mL⁻¹ for *Staphylococcus aureus* were used for the test. Samples were sterilized by UV irradiation (30 min on each side). 300 μ L of the cell suspension was placed between the sample film (3×5 cm²) and a sterilized LDPE sheet and incubated in sterile Petri dishes at 37 °C in upward 90% humidity for 24 h. Negative (no bacterial inoculum) and positive (PHF film) controls were incubated under the same conditions. Afterward, a specific amount of fresh LB broth (3 mL for *E. coli* and 6 mL for *S. aureus*) was added to each Petri dish for the detachment and resuspension of the bacteria, and the Petri dishes were shaken at 250 rpm for 180 s. 7-fold and 9-fold dilutions were then made for *E. coli* and *S. aureus*, respectively, and the samples were cultured on an LB agar plate. Plates were incubated at 37 °C for 24 h and the number of colony-forming units (CFU) was finally determined.

The antibacterial activity is expressed as follows³³

$$\text{antibacterial activity (\%)} = 100 \times \left[\frac{(\text{CFU}_{\text{control}} - \text{CFU}_{\text{sample}})}{\text{CFU}_{\text{control}}} \right] \quad (2)$$

RESULTS AND DISCUSSION

Molecular Characterization of PHF and the Blend Components. The chemical structure and average molecular weight and D of PHF, synthesized by melt polycondensation, were determined by ¹H NMR and GPC measurements, respectively. The ¹H NMR spectrum is reported in Figure S1 and confirms the expected structure. The number-average molecular weight and PDI are respectively equal to 31 800 g/mol and 2.0, in agreement with the literature data,^{11,13} thus confirming a good control over the polycondensation reaction.

As to the treatment of birch bark, the two-step extraction process led to the isolation of a yellowish powder (yield 20%) after treatment with dichloromethane and of a waxy brownish solid (yield 59%) after the methanolysis process. Specifically, the use of dichloromethane allowed to isolate a mixture of triterpenoids mainly composed of betulin, with minor amounts of α -amyrin and lupenone, similar to previous reports.^{19,34} On the other hand, by methanolysis, suberin was depolymerized permitting the obtainment of its constituent monomers. Specifically, GC-MS characterization highlighted the presence of α, ω -dicarboxylic acids (9,10-dihydroxyoctadecanedioic acid, docosanedioic acid, and eicosanedioic acid), ω -hydroxyfatty acids (10,16-dihydroxyhexadecanedioic acid, 18-hydroxy-9-octadecenoic acid, 9,10,18-trihydroxyoctadecanoic acid, 22-hydroxydocosanoic acid, and 18-hydroxy-9,12-octadecanedioic acid), carboxylic acids (linoleic and icosanoic acid), and aromatic acids (*trans*-ferulic acid). With respect to the literature data, a comparable amount of suberin has been extracted in the present study.^{35,36} Its composition is

consistent with previous reports, although in this case also unsaturated acids, whose presence has been only seldomly reported,¹⁸ have been detected.

Production of Blends and Morphological Characterization. The production of the blend films was carried out by a two-step process involving: (i) the dissolution of PHF and the selected additive (either B or S) in chloroform followed by solvent evaporation to form the film and (ii) a compression molding step of the film obtained in step 1. This procedure allowed to reach an even dispersion of the filler in the polymer matrix and the formation of smooth and regular free-standing films of uniform thickness, in the range 100–150 μ m (Figure 1).

The morphology of the cross section of the blends has been studied by SEM analysis to verify and confirm the compatibility between PHF and the fillers. The cross-sectional images of the produced blends show in all cases a quite homogeneous fracture surface and no clear separation between the filler and the homopolymer, suggesting a high compatibility between the two phases (Figure S2). The absence of visible macrodomains of either component allows assessing that the two phases are efficiently mixed.

Thermal Properties and Surface Wettability. PHF and blend films were subjected to calorimetric studies to verify any possible effect of the nature and amount of the additive on the thermal behavior of the homopolymer. Furthermore, the thermal stability of both extracts has been confirmed both by isothermal TGA analysis carried out at 170 °C for 1 h and by dynamic temperature scan, which allowed to calculate a T_{onset} equal to 257 and 339 °C for suberin and betulin, respectively (Figure S3). Thermogravimetric analysis did not highlight any significant modifications with respect to PHF (Figure S3 and Table 1), with the blends being in all cases stable up to 360 °C, indicating that the high thermal stability of the furan-based polyester was preserved.

It must be pointed out that an additional weight loss step at about 100 °C, equal to 5–7% of the sample weight, appeared in the blend films with respect to the PHF homopolymer. The observed phenomenon most likely indicates the evaporation of absorbed water, suggesting that the introduction of the bark extracts may have caused an increase of hydrophilicity. To verify this hypothesis, water contact angle measurements have been carried out on the film surface (Table 1).

The analysis demonstrated that by adding the extracts, the surface properties of PHF can be nicely modulated from hydrophobic (99° for neat PHF) to hydrophilic (PHF-B10 and PHF-S10). The results can be explained based on the chemical nature of the extracts introduced in the blend formulations, the presence of polar hydroxyl and carboxylic groups being the cause of the lowering of the water contact angle. More specifically, it can be hypothesized that the compounds, especially as regards fatty acids and hydroxyl fatty acids,

reorganize their chains to expose the polar functional groups on the surface of the polymer upon contact with water molecules, while leaving the methylene chains buried inside the polymer matrix, thus enhancing the overall surface hydrophilicity, as previously reported for similar systems.³⁷

As to the DSC analysis, the curves of the first and second scan of the films are respectively reported in Figure 2A,B, while data are collected in Table 1.

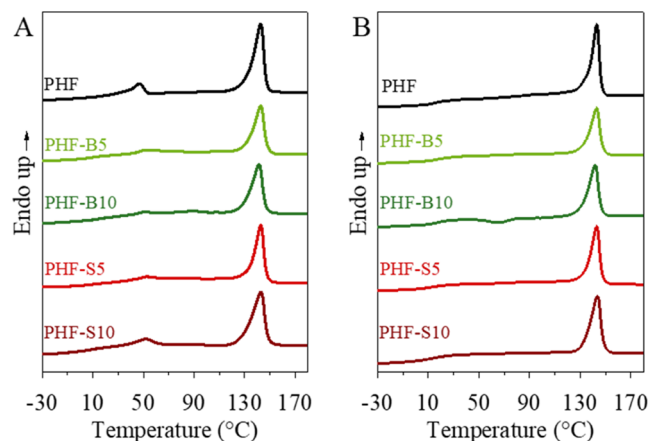


Figure 2. First (A) and second (B) DSC scans of PHF and blend films.

The first scan of PHF displays the typical behavior of semicrystalline materials, showing two endothermic peaks, the first one of low intensity at 46 °C and the second, at 143 °C, much more intense. The two phenomena can be respectively attributed to the isotropization of the mesophase, characterized by a low degree of order (one- or two-dimensional) and responsible for the exceptional gas barrier properties of furan-based polyesters,¹¹ and to the melting of the crystalline domains.

The introduction of the two extracts into the PHF matrix does not significantly modify the DSC curves, as both melting peaks are still visible. Further, the first endotherm widens and decreases in intensity slightly moving toward the high temperature. With regard to the main peak, except for PHF-B10, the T_m value is unchanged, indicating that the crystalline phase is of pure PHF. However, a lowering of the ΔH_m , of about 20–30% with respect to neat PHF, has been recorded for the blends. If this effect had been only ascribable to the lower amount of PHF in the formulation, the ΔH_m would have been equal to 39 and 37 J/mol for the blends containing 5 and 10% extracts, respectively. However, the variation is much more consistent, and thus it can be inferred that the introduction of the extracts partially hampers the regular packing of the PHF chains, resulting in a reduced amount of crystalline domains. The second heating scan was carried out after fast cooling from the melt. In all samples, the peak relative to the melting of the crystalline domains is still present, implying that the cooling treatment could not suppress the formation of the PHF crystallites, while the peak of the mesophase is not visible, most probably due to the slower kinetics of formation of these domains. Additionally, PHF-B10 displays a small exothermic peak centered at 66 °C, which can be attributed to crystallization phenomena and suggests a slower crystallization kinetics, in accordance with the slight lowering of the T_m value detected in the first scan. However,

the recorded ΔH_{cc} is much smaller than the ΔH_m , indicating that the crystalline domains of PHF could still develop during the rapid cooling treatment. As for the glass transition, an endothermic deviation of the baseline is visible for all samples. Specifically, the T_g of PHF is equal to 16 °C, and thus a mobile amorphous phase can be considered. In general, the presence of extractives did not alter the T_g value. Again, PHF-B samples show a different response, i.e., a lowering of the T_g , proportional to the filler content, possibly due to a plasticizing action as well as crystallization hampering accomplished by the filler. Concomitantly, Δc_p increased because of a higher amount of the amorphous phase. A more evident decrease of the T_g was recorded for the suberin-containing films, likely ascribable to the aliphatic PE-like moieties.

The DSC results confirm good polymer-additive compatibility. As reported,³⁸ the presence of the oxygen atom in the furan ring reduces the aromaticity degree and contextually enhances the polar character of the diacid moiety. Moreover, H-bond-like interactions can take place between the furan subunit and filler functional groups, increasing the compatibility between the two components.

Mechanical Characterization. Tensile tests were performed to evaluate the mechanical behavior of the prepared films. The resulting stress–strain curves are reported in Figure 3A, while the numeric values are collected in Table 2.

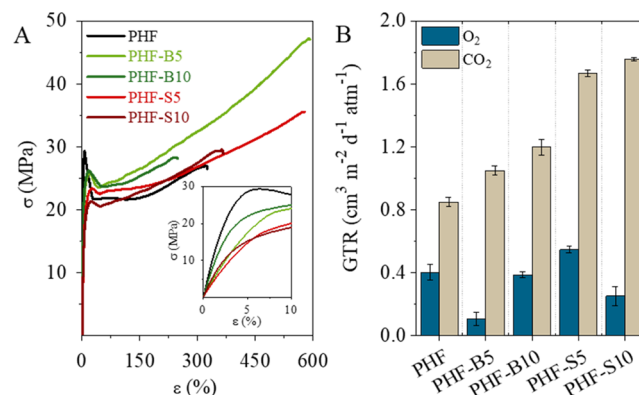


Figure 3. (A) Stress–strain curves, (inset) an enlargement of the first segment of the curve. (B) Gas transmission rate of PHF and the blend films.

Table 2. Mechanical Characterization Data from Tensile Tests on PHF and Blend Films

	E (MPa)	σ_y (MPa)	ϵ_y (%)	σ_b (MPa)	ϵ_b (%)
PHF	1170 ± 160	29 ± 2	8 ± 1	28 ± 4	327 ± 80
PHF-B5	648 ± 49	26 ± 2	18 ± 1	42 ± 7	543 ± 64
PHF-B10	750 ± 40	27 ± 2	18 ± 2	27 ± 2	272 ± 23
PHF-S5	538 ± 67	23 ± 2	27 ± 3	35 ± 3	500 ± 70
PHF-S10	531 ± 36	21 ± 2	29 ± 3	27 ± 2	340 ± 35

Different factors affect the mechanical properties of polymers, very important being the chain flexibility and degree of crystallinity. In all of the samples under study, the typical behavior of thermoplastic materials can be observed, including the presence of the yield phenomenon, although less evident in the blends with respect to PHF. Furthermore, as to PHF, the high degree of crystallinity results in E values greater than 1 GPa. The addition of the extracts leads to a decrease in the

elastic modulus, therefore, exerting a plasticizing action. Further, the effect caused by the presence of suberin monomers is more significant than that of betulin, as the elastic modulus of PHF was more than halved in the case of PHF-S5 and PHF-S10, in agreement with T_g data. As to the elongation at break, all materials display values higher than 250%, yet the PHF-B5 and PHF-S5 reaching ϵ_b above 500%, thus significantly improved with respect to PHF. Furthermore, the stress at break of the blends is at least comparable with that of PHF, with a significant improvement for PHF-B5.

In terms of toughness, better results have been achieved when a lower amount of filler was added to the formulation, i.e., for PHF-B5 and PHF-S5, while PHF-B10 and PHF-S10 showed similar behavior to PHF.

Overall, it can be concluded that the good mechanical performances of the blends imply high compatibility between the polymer matrix and the additives. However, to better explain the obtained results, two counteracting effects can be considered.

On the one hand, the chemical functionalities of the extracts, especially hydroxyl and carboxylic moieties (Figure 1), allowed for the formation of intermolecular interactions, e.g., hydrogen bonds, with the polymer matrix, thus acting as cross-linking points, in turn resulting in higher toughness. On the other hand, an increased amount of the filler may have introduced a greater concentration of defects in the PHF domains, thus weakening the tensile properties with respect to the blends containing a lower amount of extracts.

Gas Barrier Properties. With the aim of employing the composite materials under study for packaging applications, the determination of functional characteristics, such as gas transmission rate and antioxidant and antimicrobial activity, is of utmost importance to prolong the product life. For this purpose, the barrier properties of the PHF and blend films have been studied in terms of permeability to oxygen and carbon dioxide measured at 23 °C (Figure 3B and Table S1).

Furan-based polyesters display an outstanding gas barrier ability. This behavior is due to the presence of mesophase, i.e., 1D and 2D ordered domains that have a great ability to hamper the diffusion of gas molecules through the polymeric matrix. The performances of PHF are slightly inferior to those of other furan-based polymers because of the higher degree of crystallinity, which in turn may result in a lower fraction of mesophase and lead to a higher amount of disclinations, that is defects at the interface between different phases.¹¹ Nevertheless, PHF displays considerably better gas barrier features than other polymers commonly employed for packaging purposes, such as polyolefins, and similar to those of PET.^{39,40}

The excellent characteristics of PHF are preserved after the addition of biobased additives to the formulation. In detail, the oxygen permeability does not significantly vary with respect to pristine PHF, while the CO_2 -TR values appear in all cases greater than PHF, up to a factor of 2 for PHF-S10, causing a significant enhancement of the permselectivity ratio (Table S1), i.e., the ratio between carbon dioxide and oxygen permeability, from 2.1 (PHF) up to 11.9 (PHF-B5). The results obtained are particularly relevant considering that the presence of additives is supposed to increase the concentration of disclinations, and thus the high compatibility between the macromolecular chains of PHF and the bark extracts is confirmed. Nonetheless, some differences can be highlighted between the blends containing betulin and depolymerized suberin. Specifically, PHF-B samples displayed a lower CO_2

permeability than PHF-S ones. Thus, betulin seems to generate overall a higher concentration of interactions with the polymer matrix as compared to the depolymerized suberin. By reducing the mobility of the macromolecular chains, this additive exerts a greater activity in hampering the diffusion of the gas molecules through the film with respect to the suberin constituents.

Antioxidant Activity. The antioxidant activity of the free additives (Figure S4), PHF, and blend films (Figure 4A) was measured by evaluating the scavenging ability against DPPH radicals.

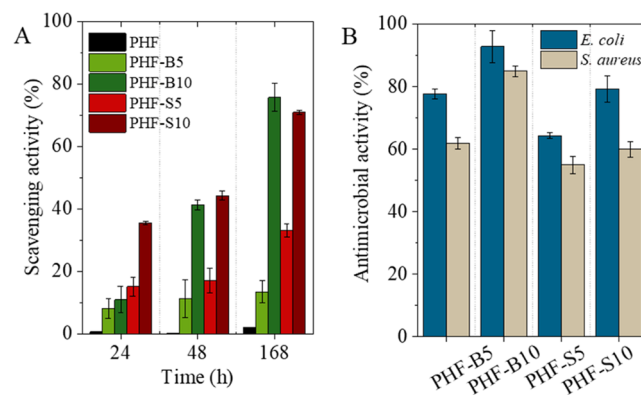


Figure 4. Antioxidant (A) and antibacterial (B) activities of PHF and the blend films.

As for the bark extracts, both displayed good antioxidant ability also at low concentrations, more evident for betulin than depolymerized suberin, the IC_{50} values being respectively equal to 0.16 ± 0.01 and 0.48 ± 0.09 mg mL^{-1} . These results are closely related to the chemical compositions of the two extracts. In particular, betulin is a well-known antioxidant molecule.^{41,42} On the other hand, the antioxidant characteristics of depolymerized suberin are mainly linked to ferulic acid and unsaturated fatty acids.^{43,44}

To measure the behavior of the blends, films were incubated in ethanol and, at predetermined time intervals, an aliquot of the supernatant was withdrawn to evaluate the antioxidant activity generated by the diffusion of the active species in the solution. The experiment was carried out up to 168 h as no differences in the radical scavenging capacity were recorded for longer incubation times.

As expected, PHF did not show any ability in this respect, while all blends exerted radical scavenging activity, which increased with the incubation time. Additionally, for shorter incubation times, higher capacity was measured for PHF-S blends, while for longer times, the activity of PHF-B10 reached that of PHF-S10. The lower degree of interaction of the suberin components with the PHF macromolecules resulted in faster diffusion through the film and thus greater antioxidant activity. Conversely, betulin, also because of the larger size, displays a lower diffusion coefficient and therefore a lower antioxidant ability for shorter incubation times.

Antibacterial Activity. Natural molecules can be used as substitutes of traditional antimicrobial agents, mainly consisting of metal ions and nanoparticles. Among bioderived compounds, essential oils are the most used, and their activity against various bacterial and fungal strains has been demonstrated in both polyolefins and biopolymer formulations.⁴⁵ Literature reports agree on the antimicrobial activity of

birch bark extracts, generally correlated with the polyphenols^{17,21} and triterpenoids⁴⁶ content. Also, suberin has been demonstrated to possess bactericidal capacity, mainly ascribed to the formation of supramolecular structures, called suberinesomes²⁰ or to the phenolic constituents,³³ even if it has been reported that aliphatic moieties also have the potential to influence the cells' vitality, due to the strong interaction of the long-chain acids and alcohols with the cell outer layer.⁴⁷

As to the antibacterial mechanism, both suberin and triterpenoids target the cell membrane, influencing its correct functioning by acting on its permeability, fluidity, and energy metabolism.^{20,46} Higher activity against Gram-positive with respect to Gram-negative strains is usually detected,^{20,21,33} and the results are explained based on the presence of an additional outer membrane on the Gram-negative bacteria, compared to the thick peptidoglycan layer of Gram-positive ones.²¹

In this work, the bactericidal effect was studied against both Gram-negative and Gram-positive strains on PHF and composite blend films. The results of the test, collected in Figure 4B, highlight in all cases an evident antimicrobial activity with respect to the control (PHF). Three specific trends can be described: (i) the percentage of killed cells is enhanced by an increased concentration of the extract, (ii) higher activity has been observed in all cases against *E. coli* with respect to *S. aureus*, and (iii) films containing betulin exerted a more effective bactericidal action as compared to the films loaded with depolymerized suberin.

The data demonstrate lower antibacterial activity, and an opposite trend between Gram-negative and Gram-positive strains with respect to the free additives.^{20,21} To this respect, it must be pointed out that, in this case, the extracts are embedded in a polymer matrix, so the activity is reasonably lower and slower. Nevertheless, the results achieved are of interest as the addition of the extracts allowed to kill, after 24 h of contact with the film surface, at least 55% of the bacterial cells, reaching values as high as 93% against *E. coli* in the case of PHF-B10. A direct comparison with other biopolymeric systems is not straightforward, as different methods to determine the antibacterial efficacy are commonly employed, with the most diffused one being the evaluation of the zone of inhibition. Additionally, the concentration of the additive and the morphology of the specimen, e.g., films or fibers, may play an important role. In a previous work, fully suberin-based films were capable of inhibiting the growth of *E. coli* and *S. aureus* by 94.3 and 99.9%, respectively, after 12 h of incubation.³³ As regards biocomposites, the literature data report that PLA electrospun fibers loaded with 3.2% of resveratrol showed a maximum value of inhibition against *Pseudomonas aeruginosa* equal to 57% with respect to the control after 24 h of incubation.⁴⁸ In another work, three essential oils (garlic, clove, and cinnamon) have been incorporated as antimicrobial agents against *S. aureus* and *Campylobacter jejuni* in polylactide films. All three components showed low efficacy against *S. aureus*, while cinnamon and clove oil demonstrated higher activity (about 7 log reduction) against *C. jejuni*.⁴⁹ In general, these studies highlight that natural molecules have a certain effect, yet lower compared to inorganic agents such as the Ag⁺ complex, quaternary ammonium ions, or traditionally employed organic compounds like triclosan or chlorhexidine.⁵⁰ Last, but not the least, it must be pointed out that so far, the antimicrobial activity of biobased molecules or

extractives embedded in furan-based polyesters has not yet been documented.

CONCLUSIONS

Four PHF-based blends containing bark extracts, namely, betulin and depolymerized suberin, have been successfully prepared by a combination of solvent casting and compression molding. The incorporation of the two additives permitted to modulate the physicomechanical characteristics of the polymer matrix depending on the nature and content of the filler and, more importantly, to introduce additional features, i.e., antimicrobial and antioxidant action, to obtain fully biomass-derived active packaging.

Specifically, due to the presence of polar functional groups, both betulin and suberin enhance the hydrophilic character of PHF, strictly linked to the content of the additive; that is, the higher the amount of additive, the higher the hydrophilicity. Furthermore, it is possible to significantly reduce the elastic modulus of the homopolymer and increase its elongation at break without any detrimental effect on the stress at break, overall resulting in a significant increase in the resilience. The additives exert a dual function: on the one side they act as plasticizers, lowering the elastic modulus; on the other, the ability to generate weak interactions with the PHF chains allows for the formation of cross-links, causing an increment of toughness. The reduction of the elastic modulus can also be partially ascribed to the slight decrease of the degree of crystallinity induced by the presence of the fillers.

In terms of gas barrier properties, a significant increment of the CO₂/O₂ permselectivity has been observed, as the additives do not influence the diffusion of oxygen, which remains in all cases comparable to or even improved with respect to PHF. Contrarily, an increase of the permeation to carbon dioxide, more evident in the case of suberin-containing blends, was measured. It might be hypothesized that the lower degree of crystallinity and the possible presence of a higher concentration of disclinations may create preferential pathways for the diffusion of CO₂ molecules, which, despite the greater size compared to oxygen, have more chaotic motion. Further analysis will be necessary to confirm this assumption.

Last, but not the least, all blends highlighted high antioxidant activity and demonstrated the ability to reduce the number of vital cells of both Gram-negative and Gram-positive bacterial strains.

This study demonstrates for the first time that biobased mixtures of low-molecular-weight extracts, easily isolated from birch bark through simple and inexpensive solvent-based strategies, can be efficiently incorporated into a Bioplastic matrix and, most importantly, into high-performance furan-based polyesters with a tangible improvement of the characteristics of the starting material.

In conclusion, the prepared blends represent a novel valorization strategy for compounds having high potential, but usually treated as waste, in agreement with circular economy paradigms that aim at achieving a zero-waste society through smarter and more efficient utilization of resources.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c04943>.

Materials employed; protocols for molecular characterization of PHF and bark extracts, and SEM, thermogravimetric, and water contact angle analysis; ¹H NMR spectrum of PHF; SEM micrographs of the film cross sections; thermogravimetric curves; gas permeability data; and antioxidant activity of bark extracts (PDF)

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Author Contributions

[∇]G.G. and D.M. contributed equally to the work as first authors. G.G. and D.M.: investigation and methodology; M.G.: conceptualization, funding acquisition, data curation, supervision, writing—original draft and review and editing, project administration; M.S.: conceptualization, data curation, supervision, writing—original draft and review and editing; V.S.: investigation and methodology on gas barrier properties; C.C.: resources, funding acquisition, writing—review and editing; N.L.: resources, funding acquisition, writing—review and editing, project administration.

Notes

The authors declare no competing financial interest.

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