Composites Part C: Open Access 2 (2020) 100044

Contents lists available at ScienceDirect

Composites Part C: Open Access

journal homepage: www.elsevier.com/locate/jcomc

Use of lignin as additive in polyethylene for food protection: Insect repelling effect of an ethyl acetate phenolic extract

Jérôme Vachon[a,*], Derar Assad-Alkhateb[a], Stéphanie Baumberger[b], Jacco van Haveren[c], Richard J.A. Gosselink[c], María Monedero[d], José M. Bermudez[d]

[a] SABIC Europe B.V., Urmonderbaan 22, 6160 AH Geleen, the Netherlands
[b] Institut Jean-Pierre Bourgin, INRAE, AgroParisTech, Université Paris-Saclay, 78000 Versailles, France
[c] Wageningen Food & Biobased Research, Bornse Weilanden 9, 6708 WG Wageningen, the Netherlands
[d] ITENE, C/Albert Einstein 1, 46980 Paterna Valencia, Spain

ARTICLE INFO

Keywords:
Lignin
Insect repellent
Food packaging
HDPE
Antioxidant
Antimicrobial

ABSTRACT

Lignocellulose biorefinery processes, including the separation of plant cell-wall components, generate lignin-rich streams referred to as "lignin fractions". Three lignin fractions with different phenol group content were dry blended with high density polyethylene (HDPE) and further extruded. The materials obtained were subsequently tested for their mechanical properties which were little affected even with 5wt% of lignin. The lignin fraction with the highest phenol group content, an ethyl acetate extract (EAL) from a technical soda lignin, showed the best performance when blended with HDPE. Besides antioxidant and antimicrobial properties (especially on *S. Aureus*) competing with other natural extract, the fraction conferred to the material insect repellent properties towards two types of insects, an invader (*Sitophylus oryzae*) and a penetrator (*Plodia interpunctella*). These combined properties make films made out of this material ideal candidates for protecting food that suffers attack from such insects.

1. Introduction

Dry packed food and consumer goods (e.g. wheat, rice, cacao, walnuts, pasta, flour, tobacco, etc…) is a common target for insects which are able to perforate packages and cause irreversible damages [1]. This results in food weight loss up to 40% on grains, rice can be turned to dust and loss in nutritional content (mineral, vitamins) can occur. Moreover, secondary pests and fungi can transmit diseases. Additionally, insects in packed food can lead to lasting or irreversible negative impression on a specific brand. Insects eat and contaminate food, primarily on stored cereal seed: food loss ranges from 5% to 50% in some countries such as Australia, USA and tropical countries (and to some extent some temperate countries due to international trade in food products) [2]. Such infestation can occur not only at the processing plant and ware-houses, but also in transit, at the store or in consumers' home [3]. One strategy to prevent infestation, and thus limit quality hazards, is to design food packaging resistant to insect attacks. Such packaging have to address two main insect targets: "penetrators" which bore holes through packaging (paper, plastic, foil, cellophane) and "inviders" which enter through existing holes and air vents.

Not all materials have the same resistance to such insects. A study ranked several packaging materials according to their insect resistance. While polycarbonate, PET and polyester nylon plastics proved to be insect proof, cellulose acetate, polyamide, PVC and thick PE (250 microns to 10 mils) showed some insect resistance properties. The authors of this study claimed that acrylonitrile, PLA and thinner PE (125 microns) were susceptible to insect penetration while EVA, kraft paper, PVDC and thin PE films (<100 microns) showed no resistance [4]. To overcome this issue, synthetic pesticides were the only effective measure for controlling infestation. However, pesticides can be toxic to humans and the environment and were therefore excluded from packaged foods. There is thus a need to use natural non-toxic environmentally friendly compounds, keeping in mind that repellents are not considered as insecticides. Repellents can be added within (i) a coating, (ii) an adhesive, lacquer or paint, (iii) a margin (welding or gluing part) or (iv) a polymer matrix [5]. N,N-Diethyl-meta-toluamide (DEET), Neem [6], essential oil and its derivatives (e.g citronella, limonella, cinnamon oils) [7] are the most common solutions proposed [8]. Regarding the specific use of such repellent into packaging materials intended for food protection, one can mention recent examples such as (i) the use of insect repellent such as permethrin,

---

Abbreviations: HDPE, high density polyethylene; LDPE, low density polyethylene; OIT, Oxidation Induction Time; NMR, Nuclear Magnetic Resonance; GPC, gel permeation chromatography; TGA, thermogravimetric analysis; DSC, differential scanning calorimetry; CFU, Colony Forming Unit.

[*] Corresponding author.
E-mail address: jerome.vachon@sabic.com (J. Vachon).

https://doi.org/10.1016/j.jcomc.2020.100044
Received 1 July 2020; Received in revised form 26 August 2020; Accepted 11 September 2020

cypermethrin, deltamethrin and pyrethroids in polystyrene [9], (ii) the use of star anise oil in PP and LDPE against *Plodia interpunctella* [10], (iii) the use of eugenol in banana plastic cover to repel various pests [11], (iv) the use of propionic acid incorporated in biodegradable coatings applied onto carton intended for packaging cereal good [12], (v) the use of citronella applied as part of a coating on the carton board [8a] and (vi) the use of essential oils in plastic films to protect and preserve horticulture products and foods [13]. There is thus only a few available insect repelling solutions and technologies described in literature with specific drawbacks such as volatility, low thermal stability, high additive price, toxicity and high processing costs, which limit their industrial use. The present study intended to address such challenges with the development of an insect repellent polyethylene based material. Several techniques are described in literature regarding the assessment of materials with respect to their repellent efficiencies towards different types of "invaders" and "penetrators" [3,14]. In this work, two insect species were selected, namely *Sitophylus oryzae*, as invader, and *Plodia interpunctella*, as penetrator as there are known to target a very wide range of stored products [4a]. *S. oryzae* is one of the main pests of rice in the field as well as in warehouses, being able to attack any cereal, whereas *Plodia interpunctella* is a worldwide widespread moth attacking food, and in particular nuts, chocolate and cereals. This last species has the ability to penetrate many of the types and combinations of paper, films, and foils used in packaging.

In the last decades, research has been ongoing to find application and use of ligno-cellulose side stream materials [15]. The dry matter from woody plants consists primarily of cellulose, hemicellulose and 20 to 35 wt% of lignin which is one of the most abundant organic polymers and the main natural source of aromatic compounds on Earth. Lignin overall structure is based on phenyl-propanoid monomers of the *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) types that are linked together through C-C, C-O and cyclic structures [16]. Industrial biorefinery processes, like cellulosic pulp or bioethanol production, generates isolated lignin fractions with average molecular weight (MW) ranging between 1000 – 20,000 Da and different contamination rates by carbohydrates and other possible components. Those fractions called "technical lignins" are recognized as high-value functional bio-based materials with a wide range of potential applications, yet there are only few examples of proper industrial use [17]. Using lignin fractions as additive in food packaging might offer an opportunity to exploit the multifunctionality of some industrial by-products while providing bio-based technical solutions to improve food quality. Among the lignin fractions available, grass soda lignins have the advantage of being already commercial and to count among the most efficient antioxidant ones [18], whereas lignin-rich residues from bioethanol production process require to be valorized to improve the competitiveness of cellulosic ethanol production [19]. A strategy to valorize technical lignins is to apply solvent extraction, a technic which is transposable to industrial scale and that provides lignin fractions with improved homogeneity and higher phenolic content [20].

The first attempt to incorporate lignin as filler in thermoplastics dates back to the 70s where good compatibility between lignin and HDPE was observed [21]. Blends with lignin up to 70 wt% were also achieved where increased modulus and elongation at break of the material with both HDPE and LDPE were observed [22]. From this pioneering work, several polyolefins blends with different types of lignins were more thoroughly studied which led to contradictions regarding the actual compability of such materials as the incorporation of some lignins like lignosulfonates results in altered mechanical properties [23]. These apparent contradictions resulting from the structural variability of technical lignins emphasize the need to consider thoroughly lignin functional groups to understand and optimize the properties of the materials. Besides their influence on mechanical properties, lignins have shown to confer to polyolefin thermoplastics specific properties that fall into three main categories: (i) stability against oxidation initiated by UV, (ii) stability against thermal oxidation and (iii) partial biodegradability [24]. Additionally, lignin extracts displayed antimicrobial and antifungal properties [24], yet, such properties have been demonstrated only within a few polymer matrix such as PBS [25], PVOH [26], polyurethane [27] and PLA [28]. Moreover, insect repellency of lignins has not been investigated so far.

The objective of the present paper was to demonstrate that technical lignins could be used as insect repellent additive of interest for food packaging made of HDPE. For this purpose, blends of HDPE with isolated lignin fractions (from 2 to 5 wt%) were produced by extrusion. Higher loadings of lignin could results in processability issues with the need to add additional compatibilizers. The resulting films were assessed for their mechanical and thermal properties, as well as for their antioxidant and antimicrobial properties. In addition, for the first time regarding lignin-based materials, insect repellence of these HDPE-lignin films was investigated, using the pristine-HDPE as a reference and the two types of insects *Sitophylus oryzae* and *Plodia interpunctella*. Three lignin fractions were selected for this study which differed in their structure, and in particular their content in phenol groups known to primary influence antioxidant and antimicrobial properties. One of these fractions was a lignocellulosic residue recovered from a bioethanol production process and the two other ones were a commercial soda lignin and its ethyl acetate extract. For the sake of simplicity, these samples were all designated by the term "lignin", though containing other compounds in variable proportion. The results allowed identification of one of these samples as an excellent candidate for protecting food that suffers attack from such insects.

2. Materials and method

2.1. Materials and lignin compositional analysis

SABIC® VESTOLEN HDPE (unstabilized powder grade, MFI 0.2 dg/min at 190 °C, see Table S1 for molecular weight details) was used as an unstabilized powder. A commercial soda lignin sample (PB1000), isolated from mixed wheat straw/sarkanda bagasse, was purchased from Green Value Entreprises LLC (USA). An ethyl acetate soluble fraction (EAL) of this sample was obtained according to a published solvent fractionation process [20]. This process uses a stationary phase in a packed column where a lignin packed bed is made. The fractionation occurs by flushing the column with a succession of solvents of increased polarity, ethyl acetate being the first and least polar one. The lignin fraction is recovered after evaporation of the solvent under reduced pressure. An acidic lignin (AL) was obtained from wheat straw as side stream of a cellulosic ethanol production process after hydrolysis, fermentation and distillation. This sample was a mix of lignin, carbohydrates and proteins (Table 1) which was characterized according to published methods [29]. For molar mass determination, the lignins were analysed by alkaline SEC using two serial connected TSKgel GMPWxl columns at 30 °C with a 1 mL/min flow, 0.5 M NaOH eluent, and using sodium polystyrene sulphonates as standards (method D) [26].

2.2. Polyethylene lignin blends preparation

HDPE and lignin powders were dry blended and let dry at 70 °C in a vacuum oven overnight. The blend was fed to a mini-extruder line (Thermo Scientific Process 11 twin-screw, corotating extruder with a 11 mm diameter barrel a L/D ratio of 40) from the hopper with a temperature gradient ranging from 35 °C (feed zone) to 190 °C (die plate). The screw speed was set at 250 rpm. The extruded strands were cooled in a water bath and further granulated. Materials were made with either 2 wt% or 5 wt% of each tested lignin.

2.3. Material characterization

Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q20 equipped with a RCS 90 cooling sys-

Table 1
Characteristics of lignins.

		AL	PB1000	EAL
TOTAL OH	[mmol/kg]	5.7	5.8	6.2
CARBOXYLIC OH	[mmol/kg]	0.2	0.9	1.1
ALIPHATIC OH	[mmol/kg]	4.5	1.5	0.9
AROMATIC OH	[mmol/kg]	1.0	3.4	4.2
NON-CONDENSED GUAIACYL + P-HYDROXYL	[mmol/kg]	0.5	1.3	1.7
LIGNIN[a]	[wt%]	53.3	88.0	82.3
TOTAL POLYSACCHARIDES	[wt%]	32.41	1.99	0.02
URONIC ACIDS	[wt%]	1.23	0.84	0.32
PROTEINS	[wt%]	6.51	2.83	0.10
ASH (900 °C)	[wt%]	3.98	1.94	0.04
Mn	(g/mol)	723[b]	800	610
Mw	(g/mol)	7196[b]	2242	1271
PD	Mw/Mn	10[b]	2.8	2.1

[a] Acid-insoluble lignin (AIL) corrected for ashes content plus acid soluble lignin (ASL) after the two-step acid hydrolysis.

[b] Value relative to the alkali-soluble lignin fraction (about 60% of the lignin was solubilized).

tem. About 3–5 mg of polymeric sample was weighed inside an aluminum pan and subjected to DSC measurements under nitrogen atmosphere. Unless otherwise noted, polymers were screened twice from -100 °C to 200 °C at a constant heating/cooling rate of 20 °C/min. The T_m, and the melting enthalpy (H_m) were determined from the second heating curve.

Thermogravimetric Analyses (TGA) were performed by using TA instrument. All measurements were performed under nitrogen from 30 to 300 °C for the lignin and from 30 to 500 °C for the HDPE and HDPE – EAL blend, with a heating rate of 10 °C/min.

SEM imaging were performed on Phenom ProX scanning electron microscope to study the cross-section morphologies of HDPE and the corresponding blends with 5 wt% lignin. Compression molded plaques (180 °C, 90 bars) with 50 × 50 × 3.03 mm dimensions were first prepared. A cross section on the plaque was made at cryogenic conditions using liquid nitrogen. Samples were mounted on a metal stub using a sticky carbon disc and coated with a gold powder to enable SEM recording.

Oxidation Induction Time (OIT) was measured by DSC on molten polymer according to standard ASTM D3895-1998. About 3–5 mg of polymeric sample was weighed inside an aluminum pan and subjected to DSC measurements under nitrogen atmosphere (50 mL/min). The polymer was heated until 200 °C at 10 °C/min heating rate and left at this temperature for 5 min. Nitrogen was switched to oxygen and the time before an exothermal peak is detected was recorded.

2.4. *Mechanical properties*

Tensile bars were made by injection molding (using Xplore microinjection moulder IM 12 with a shot volume of 12 ml) under pressure (∼10 bars) in a hot mold (70 °C). Mechanical properties (tensile strength, Young's modulus, maximum elongation at break) were measured by using ISO 527 and Zwick-Roell machine. Tests were performed on five specimens (thickness = 60–110 μm, width = 15 mm, length = 50–53 mm) on MD direction at room temperature (test speed = 50 mm/min). The same tensile bars were used to measure Izod Pendulum Impact Resistance. Tests were performed on three specimens at – 30°C, both on notched and un-notched samples according to ASTM D256.

2.5. *Antimicrobial tests*

Antimicrobial efficacy measurements were performed following ISO22196 “Measurement of antibacterial activity on plastics and other non-porous surfaces” and was performed at Intertek Fragnes La Loyere using the following conditions. The pellets of the samples were compression molded into 50 × 50 × 3.03 mm plates (according to ISO 17855-2 conditions) at a temperature of 180 °C and 90 bars pressure. The samples were decontaminated with ethanol 70° during 15 min. The plaques were covered with PET (size 4 × 4 × 0.1 cm). The test temperature and culture temperature were set to 32.5 °C ± 2.5 °C. The temperature of incubation was set to 32.5 ± 2.5 °C. The bacterial strains used were *Escherichia coli* (DSM 1576 – ATCC 8739, number of viable bacteria in the inoculum = 1.3×10^8 CFU/mL) and *Staphylococcus aureus* (DSM 346 – ATCC 6538P, number of viable bacteria in the inoculum = 1.5×10^8 CFU/mL) and analyses were performed in triplicate (negative control included). Antimicrobial activities are given in logarithmic reduction R. R is calculated according to the bacterial concentration in the negative control and the concentration after 24 h of contact with the treated products (see supplementary information for further information on the mode of calculation of Log R and Tables S2–S7 for the full result details).

2.6. *Insect repellence tests*

Concerning insect repellence tests, there are currently no particular standards established. Therefore, laboratories working on the topic have developed their own methods for both repellence test and penetration test [3,14]. The tests that were used in this study have been developed based on such prior art, acquired knowledge, as well as through continuous improvements to guarantee the robustness of the results. Accordingly, a significance criteria on the results obtained have been incorporated in order to provide enough confidence to the reported results from the tests performed.

2.6.1. *Repellence test against* Sitophilus oryzae

The insect repellence test of the materials agasint invadors was carried out as follows. The polymer blends were processed by cast extrusion using a twin-screw extruder (DSE 20-40D, Brabender, Germany), equipped with a flat sheet die, obtaining sheet samples of 8–8.5 cm wide. A temperature profile from the first barrel zone to the die was set at 210-215-215-220-230-230 °C working at a screw speed of 90 rpm. Bags of approximately 20 × 8 cm were made for which two different sections can be distinguished. One half of the bag was made with the film obtained with the samples to be studied and the other half of the bag was made of the HDPE reference film. Both halves were thermosealed. Then, 10 individuals of the weevils were incorporated into the bags and allowed to move freely for 3 days. During these 3 days, the number of insects that were positioned in each of the 2 zones of the bag was recorded. The bags were kept horizontal on a table at room temperature and with light-dark cycles (8 h on and 16 h off). The data collected

Table 2
Weight loss from TGA experiments of AL, PB1000 and EAL lignin fractions.

	Temp @ 1% wt loss	Temp @ 5% wt loss	Weight loss % @190 °C	Total weight loss % @300 °C
AL	84.0	207.9	3.6[a]	21.0
PB1000	115.6	202.1	4.1[a]	16.2
EAL	120.4	169.4	7.2[a]	21.7

[a] ∼ 2% is related to water weight loss.

were analyzed by multifactor analysis of variance (ANOVA) to determine significant differences among the different film samples and time. Means were compared by the multiple range test based on Fisher's least significant difference (LSD) to determine statistical differences at 95% of confidence level (p value < 0.05). Statistical analyses were carried out using Statgraphics Plus for Windows 2.1.

2.6.2. *Penetration test of* Plodia interpunctella

The insect repellence test of the materials against penetrators was carried out as follows. 8 bags of approximately 8 × 8 cm were formed with the different materials which were filled with 15 g of a food product used to feed the insects. The bags were totally sealed. The bags were placed inside a plastic box in vertical position to let insects attack the bags by both sides. Then, 80 adults of *P. interpunctella* were placed inside the plastic box. After 1 week, other 60 adults were additionally placed inside the plastic box. The purpose was to have adults laying eggs for 2 weeks to ensure a continuous infestation of eggs and thus a continuous presence of larvae in the boxes, which are those that penetrate the food packages. Then the boxes were kept with the adults for 4 weeks inside a climatic chamber at 28 °C and 70% RH, with a photoperiod of 18:6 hours (light:darkness). After this time, the plastic boxes were opened, and the plastic bags were collected to be analyzed. Then, the presence and enumeration of individuals (larvae, chrysalises or adults) inside the bags was determined. The data collected were analyzed by multifactor analysis of variance (ANOVA) to determine significant differences among the different film samples. Means were compared by the multiple range test based on Fisher's least significant difference (LSD) to determine statistical differences at 95% of confidence level (p value < 0.05). Statistical analyses were carried out using Statgraphics Plus for Windows 2.1.

3. Results and discussion

3.1. *Thermal analysis of lignins and blends with HDPE*

Thermal stability of each lignin sample was evaluated by TGA under nitrogen. Results are shown in Fig. S1 and Table 2. The first weight loss step is typically related to the presence of moisture, which is common in lignin materials. At 190 °C, a noticeable weight loss was observed for each sample. This data led to impose a maximum extruder temperature at 190 °C to minimize lignin degradation or evaporation of low MW species during extrusion.

To confirm that limited degradation of the lignin occurred during processing, the TGA of the HDPE ref was compared to the one of the HDPE – EAL lignin blend (5 wt% loading), both recorded under nitrogen atmosphere to avoid any thermo-oxidative degradation. As can be seem in Fig. 1 (and Fig. S2), a typical TGA of an HDPE material was observed, with an onset of degradation at 464 °C related to the pyrolysis of the hydrocarbon backbone [30]. The onset of degradation of the HDPE lignin blend occurred at a slightly lower temperature (457 °C) which is related to initial weight loss of the lignin part. At the extruder temperature of 190 °C, almost no weight loss is observed for HDPE ref (∼0.1%) while a small loss of ∼1 wt% of the lignin blend occurred, showing the rather good stability of the material during processing. Upon increase of temperature to 300 °C, a little weight loss of 0.6% is noticed for HDPE ref which typically corresponds to low MW oligomers escaping the molten material. In the HDPE lignin blend, it amounts to 1.8 wt%. The difference between the two, i.e 1.2 wt%% can be nicely correlated to the content of lignin which, in a pure state, lost ∼22% of its mass (Table 2). The lignin being at 5 wt% content in the LDPE, the theoretical weight loss is thus 1.1 wt%% which matches the 1.2 wt% observed.

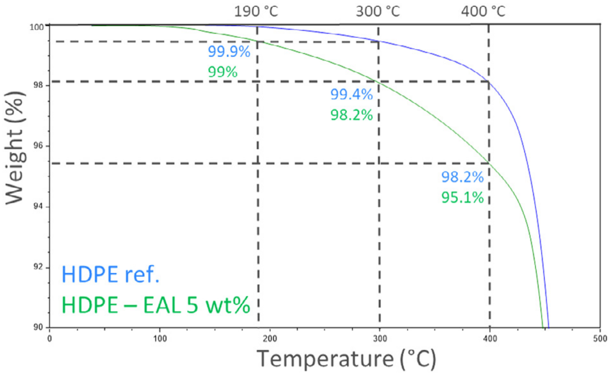

Fig. 1. TGA of HDPE ref. (blue) and HDPE – EAL 5 wt% (green) with remaining sample weight indicated at 190 °C, 300 °C and 400 °C

DSC measurements were performed to evaluate the impact of lignin, which by itself is a non-crystalline materials due to its highly branched structure [31], onto the initial crystallinity of HDPE (Xc = 67%) as shown in Table 3 and Fig. S3. Results indicate that 5 wt% of lignins PB1000 and AL had little effect, as could be expected from the addition of an amorphous lignin, on the initial PE crystallinity while Tc was slightly lowered. EAL fraction showed a small decrease of both Xc and Tc, yet to a low level that should not affect the overall material mechanical properties resulting from the semi-crystallinity of the HDPE matrix. This tends to indicate a partial miscibility of EAL fraction with the PE matrix, which could be explained by its lower molar mass average and lower content in polar compounds such as carbohydrates.

3.2. *Mechanical properties*

As mentioned above, mechanical properties of PE could be altered by the presence of lignin due to the limited compatibility between the two materials. This phenomenon was reviewed by Kun and Pukanszky, and in spite or rather contradictory results from the literature, a general trend for polyolefin/lignin blends was claimed with a typical modulus increase of the material together with a strength and deformability decrease [33]. The same authors recently showed that due to the weak dispersion forces developed in polyolefins, the mechanical properties of the blends with lignins were poor [34]. In order to check the influence of the lignin into the mechanical properties of our HDPE blend materials, tensile bars were made by injection molding and were subjected to controlled tension until failure. Ultimate tensile strength, maximum elongation as well as the E modulus of the material were determined for the three lignin blends and compared to the HDPE reference (Fig. S4 and Table 4). Results show that overall strain at break was retained for all HDPE-lignin blends. However, a noticeable decrease (∼15%) of stress at break was noticed for all samples, again probably due to the limited compatibility between the lignins and PE. Consequently, the strength of the materials is reduced due to the potential thin interface between

Table 3
Thermal properties of each HDPE-lignin blend from DSC measurements

Sample	Cooling Tc (°C)[a]	2nd heating ΔHc (J/g)[a]	Tm (°C)[a]	ΔHm (J/g)[a]	% cryst.[b]	PE % cryst.[c]
HDPE ref	118.6	191	130.0	191	67	67
HDPE-PB1000 5 wt%	117.0	183	130.1	185	65	68
HDPE-AL 5 wt%	116.4	178	130.2	179	63	66
HDPE-EAL 5 wt%	116.2	165	129.6	168	59	62

[a] Determined via DSC.
[b] The degree if crystallization was calculated by the following formula, where ΔH (100%) = enthalpy of 100% crystalline PE (286.2 J/g): $\frac{\Delta H}{\Delta H(\ 100\%)} * 100\%$ = degree of crystallinity, according to ref. [32].
[c] Calculated from total crystallinity with respect to the actual amount of PE in the material.

Table 4
Strain at break and Force from tensile tests

	Strain at break (%)	Force (MPa)	$E_{modulus}$ (MPa)
HDPE ref	20,8 ± 1,4	98,7 ± 3,3	107 ± 46
HDPE-PB1000 5wt%	19,8 ± 1.1	82,3 ± 2.2	156 ± 48
HDPE-EAL 5wt%	19,4 ± 1.5	84,2 ± 7.9	174 ± 58
HDPE-AL 5wt%	19,4 ± 1.1	87,1 ± 8.3	120 ± 13

PE and the lignins. This can already be seen on a macroscopic level on the broken tensile bars after testing where a different color in the inner bar is noticed which shows the inhomogeneity of the blends (Fig. S4). SEM images of a cross-sections of plaques made from each sample were recorded (Fig. S5). Results seem to indicate that the structure is the smallest for HDPE-EAL 5 wt% when compared to the 2 other samples, confirming the better compatibility of such lignin, yet, differences are visually minimal.

The Izod tests were aimed at studying if the toughness of the HDPE-lignin blends were impacted by the presence of lignin. Since HDPE materials typically possess good impact properties, tests were performed at –30 °C (on three specimens), both on notched and un-notched samples (Fig. 2). Using such a low temperature allowed to discriminate any negative effect the lignin could bring to the material which might not have happened by using room temperature conditions. Results indicate that concerning the notched tests, no major difference between the samples could be seen and that variations mostly fell under the standard deviations. A potential chain orientation from injection molding might have played a role in such deviations. A more noticeable difference is seen on the unnotched tests where a significant decrease in Izod for the sample containing AL lignin was observed while EAL lignin gave a similar performance as the HDPE reference. Such results can be explained by the fact that AL lignin contains a high amount of polar compounds (mostly polysaccharides) that give a lower compatibility of such lignin with the apolar HDPE matrix.

3.3. Antioxidant properties

Auto-oxidation of polyolefins is an exothermal process, the oxidation reaction being characterized by an induction period which can be easily detected by DSC. The Oxidation Induction Time (OIT) is measured by DSC on molten polymer and is a known method to assess thermal stability of polyolefins. The length of induction period increases with antioxidant concentration and antioxidants such as hindered amines, organophosphites and phenols usually provide such stabilization when used at several hundred-ppm concentrations. Due to the presence of phenolic structures in lignins, antioxidant properties of these materials have been studied intrinsically [35] but also in polyolefin matrices [36]. In this work, we looked at the influence of the amount of lignin in HDPE (with 0, 2 and 5 wt% loading of each lignin), as well as the influence of the phenolic content of the lignin using OIT technique (Table 5 and Fig. 3).

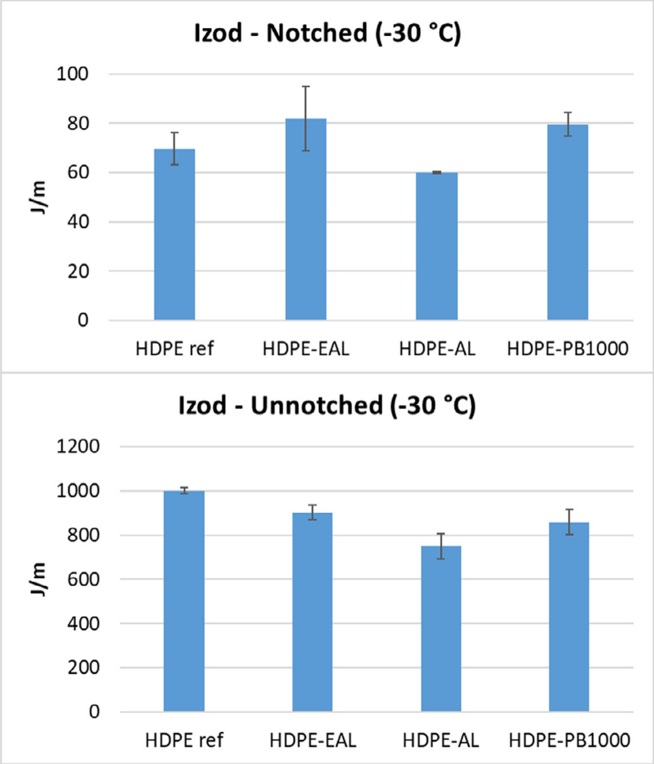

Fig. 2. Izod test on both notched (top) and unnotched (bottom) samples

Table 5
OIT results.

Sample	OIT at 5 wt% lignin	OIT at 2 wt% lignin
HDPE ref	1.1 min (0 wt%)	
HDPE-AL	31.0 min	16.2 min
HDPE-PB1000	57.3 min	50.8 min
HDPE-EAL	80.2 min	63.5 min

In agreement with the fact that the HDPE used was unstabilized, an immediate thermal oxidation occurred within a few seconds. Interestingly, the addition of lignins gave a significant induction time increase. As expected from the highest phenol content of the EAL sample, the best result was obtained for this fraction, with an OIT of ~ 80 min at 5 wt% lignin content. This performance was similar to those obtained with commercial synthetic primary antioxidants (such as the one derived from 3,5-di-(tert-butyl)-4 hydroxyphenyl propionate) albeit present at a few hundred ppm concentration [37]. Thus, these results suggest that HDPE-EAL blends may not need further stabilizing agents.

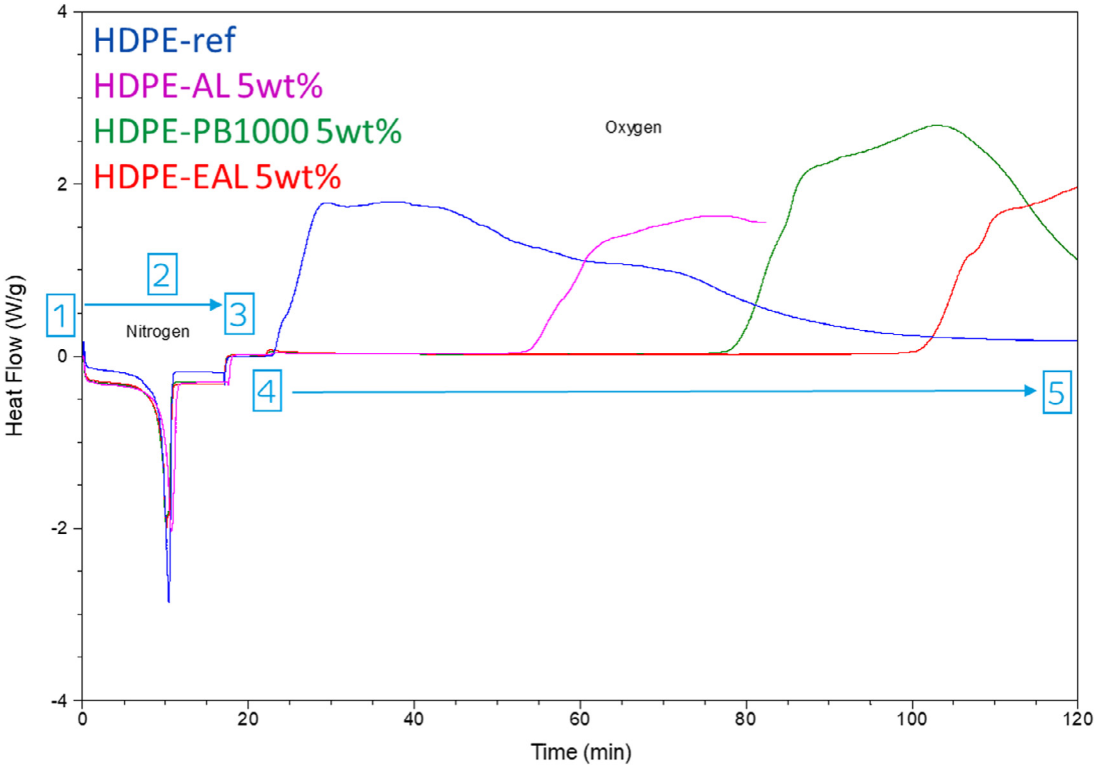

Fig. 3. OIT measurement of the 5 wt% HDPE-lignin blends (exothermic peak is up) with step 1: Nitrogen flow 50 ml/min; step 2: heating from 25 to 200 °C at rate 10 °C/min; step 3: isothermal for 5 min; step 4: switch gas to oxygen; step 5: End of measurement.

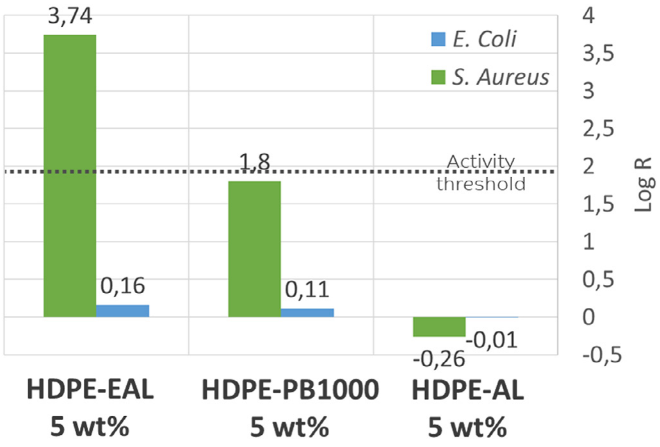

Fig. 4. Antimicrobial activities of HDPE-lignin blends at 5 wt%.

3.4. Antimicrobial properties

The intrinsic antimicrobial and antifungal properties of lignins have been already demonstrated and shown to be superior to those of cellulose and other structural polysaccharides [24]. Therefore, the antimicrobial properties of the three different HDPE-lignin blends with 5 wt% lignin content were assessed according to the ISO22196 method (Fig. 4). It is commonly accepted that, according to this method, the threshold of antimicrobial activity of a material is reached when at least 99% bacterial reduction is obtained (> log 2). While HDPE-AL material gave no antimicrobial response, HDPE-PB1000 had a noticeable effect on gram-positive bacteria with a log R ~1.8 (98.4% bacterial growth reduction), thus close to the activity threshold (commonly accepted to be with a log R > 2, i.e 99% bacterial growth reduction after 24 h). This effect was further improved with lignin EAL which showed antimicrobial properties above this threshold of activity, yet again only on the gram-positive bacteria with a log R ~ 3.74 (99.98 bacterial growth reduction after 24 h). A plausible explanation for such discrepancy is coming from the structural difference of the membrane structure between the two types of bacteria, where no outer lipid membrane is present in gram-positive cell wall. As such, gram-positive bacteria were reported to be more sensitive towards antibacterial substances than gram-negative bacteria [38]. Similarly to the antioxidant property, the higher phenolic group content of EAL could primarily explain its higher antimicrobial activity in the material, yet there could be several other factors that could be considered. Besides this factor, the morphology of the blend and in particular the concentration of phenolic compounds at the surface of the material can be mentioned. Indeed, the low molar mass of EAL compounds might favor their migration at the surface of the material and subsequently induce higher antimicrobial activity. Migration of low molecular weight and polar species is a phenomenon that typically occurs for polyethylenes as they possess a very low Tg (~-120 °C). At room temperature, chain mobility of polyethylenes is high enough to allow migration to the surface of polar compounds that have limited affinity with the apolar PE matrix.

3.5. Insect repellent properties

Thin HDPE films obtained by extrusion (for both HDPE reference and with 2 wt% of each lignin sample) were specifically prepared for the insect repellence tests. While attempting to perform ~50 μm thick HDPE-AL and HDPE-PB1000 films, difficulties were encountered as they both showed some dark spots along the film leading to inhomogeneous materials (see pictures in Fig. S6). For HDPE-PB1000, these imperfections resulted in the appearance of a few holes in the films. In order to reduce the occurrence of these holes, the thickness of the HDPE-PB1000 film was increased to 70 μm (Table S8). In contrast, HDPE-EAL showed a more homogeneous aspect with the presence of some sporadic dark

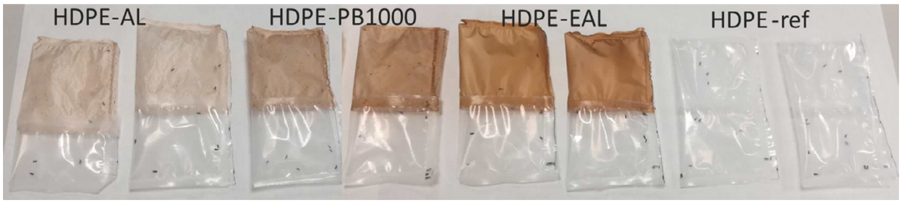

Fig. 5. Thermosealed bags for the insect repellence test on *Sitophilus oryzae*.

Fig. 6. Plastic box with the bags containing food for testing insect repellence (left box: HDPE-EAL; right box: HDPE-ref.).

Table 6
Insect repellence results on *Sitophilus oryzae* measured as the number of insects in the treated zone.

Sample code	N-insects	Effect
HDPE ref	4.2[a]	No repellence (4-6)
HDPE-AL 2 wt%	6.7	Attractant (>6)
HDPE-PB1000 2 wt%	4.55[a,b]	No repellence (4-6)
HDPE-EAL 2 wt%	3.2	Repellence (<4)

[a] Values for HDPE ref and HDPE-PB1000 2 wt% are statistically similar at a 95% confidence level.

[b] Average of 2 values performed on two different samples.

spots along the film, which confirmed the indication that EAL was more compatible with the PE matrix. None of them resulted in the presence of holes in the film.

Insect repellence tests were performed on thermosealed bags with the *Sitophilus oryzae* insects inside, as shown in Fig. 5. Results from ANOVA (Table 6) show that the counting of insects was significantly affected by the type of sample (p value < 0.05) but not by the sampling time (p value $= 0.61$), thus showing that the materials exerted its effect quite constant along the testing time (Table S9). As expected, the HDPE reference material had no insect repellence effect (score between 4 and 6). HDPE-AL proved to be attractant for weevils with a value of 6.7 while HDPE-PB1000 had no effect, being statistically similar as the HDPE reference. Finally, sample HDPE-EAL displayed noticeable repellence activity with a score of 3.2. This means that insects tried not to be onto the treated zone of the bag, preferring the other side of the testing bag with no additive. Thus, the three lignin samples exhibited contrasted and even antagonist effects towards insects, which can be explained by their differences in composition. The attractant effect conferred by the AL lignin could be explained by the high amount of polysaccharides (cellulose and hemicelluloses) making this material close to natural lignocelluloses commonly found in *Sitophilus oryzae* natural diet. On the contrary, the enrichment of EAL in phenolic compounds is most likely responsible for its insect repellent effect. Here again, the phenol group content appeared as a relevant parameter to predict lignin protecting effect.

The penetration test with the moth was performed on bags containing food that were placed inside a plastic box in vertical position to let insects attack the bags by both sides as illustrated in Fig.6, Figs. S9 and S10. In Table 7 is shown the mean value for the counting of insects inside the 8 bags of each sample.

As can be observed, the HDPE ref, HDPE-AL and HDPE-PB1000 were all contaminated with larvae while HDPE-EAL showed no infestation. Bags made of HDPE ref also showed the higher number of insects inside while HDPE-AL and HDPE-PB1000 were statistically similar (p value $= 0.0543$). Moreover, HDPE ref was the only sample that showed the presence of adults. This could be consequence of a faster ability for penetration of the larvae for this sample in comparison to the other samples. In this way, insects had more time to develop their cycle. Regarding the number of bags that were infested, 6 bags out of 8 for HDPE ref, 4 bags out of 8 for HDPE-AL and 8 bags out of 8 for HDPE-PB1000 were found to have insects inside (see Fig. S11 pictures of the HDPE ref bag infested by *P. interpunctella*). In contrast, HDPE-EAL films showed no penetration at all, EAL appearing here again as the most performant sample. Unexpectedly, in this specific test, HDPE-AL outperformed HDPE ref and HDPE-PB1000, in spite of its lower phenolic content and lower purity.

Table 7
Insect repellence results on *Plodia interpunctella*.

Material	Number of small larvae	Number of larger larvae	Number of Pupals	Number of adults	Total
HDPE-ref	4.5 ± 1.2	2.4 ± 1.1	3.6 ± 1.6	1.6 ± 1.3	12.1 ± 4.5
HDPE-AL 2 wt%	0.6 ± 0.4	1.0 ± 0.7	1.5 ± 0.8	0	3.1 ± 1.6
HDPE-PB1000 2 wt%	3.9 ± 0.6	2.5 ± 0.6	0.8 ± 0.4	0	7.1 ± 1.0
HDPE-EAL 2 wt%	0	0	0	0	0

4. Conclusion

In this work, we have successfully blended HDPE with three lignin fractions which displayed different phenolic contents. At 5 wt% lignin incorporation rate, HDPE mechanical and thermal properties were only little affected. The lignin sample enriched in phenolic compounds (ethyl acetate soluble fraction EAL) was found miscible with the HDPE matrix and led to the best performances in terms of antioxidant property (as assessed through OIT) and antimicrobial property, yet only significantly on gram positive *Staphylococcus aureus*. In addition, when used at only 2 wt% content in HDPE, the same sample showed again the best performance in terms of protection against insects, with both good repellence against *Sitophilus oryzae* and a full resistance to penetration against *Plodia interpunctella*. These results demonstrate for the first time the protective effect of lignin against insect within a polymer matrix and offers new bio-based solution for protecting food that suffers attack from such insects. In the cascading valorization process of lignin currently developed [39], this application could provide a valuable outlet for the first stage ethyl acetate soluble fraction.

Associated content

Supporting information. Experimental data, TGA, DSC and pictures of materials tested.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Data availability

The raw/processed data required to reproduce these findings cannot be shared due to confidentiality.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This project has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation program under grant agreement No. 720303.

We thank Nuria Agustí, Cristina Castañé and Jordi Riudavets from IRTA (Institute of Agrifood Research and Technology) for its collaboration in the penetration test of *Plodia interpunctella*.

We are grateful to Frederic Legée (INRAE Versailles) for performing the Klason lignin determination and to Florian Pion (INRAE Versailles) for ensuring lignin supply and for fruitful discussions. We also thank Jacinta van der Putten, Jacqueline Donkers and Guus Frissen (all from Wageningen Food & Biobased Research) for performing the analytical characterization of the lignin samples and the fractionation of PB1000. Maria Soliman and Miguel Cordova Chavez from SABIC are acknowledged for their help in improving the manuscript quality.

The IJPB research unit benefits from the support of the LabEx Saclay Plant Sciences-SPS (ANR-10-LABX-552 0040-SPS).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jcomc.2020.100044.

References

[1] (a) S. Navarro, D. Zehavi, S. Angel, S. Finkelman, Natural nontoxic insect repellent packaging materials, Intelligent and Active Packaging for Fruits and Vegetables, Wilson C.L (Ed.). Boca Raton, FL: CRC Press, 2007, pp. 201–236; (b) S. Navarro, S. Finkelman, Protecting food packaging materials by natural nontoxic insect repellents, 2014 Acta Hortic., 1015 137–144, doi:10.17660/actahortic.2014.1015.15.

[2] D. Kumar, P. Kalita, Reducing postharvest losses during storage of grain crops to strengthen food security in developing countries, Foods 6 (2017) 8–30, doi:10.3390/foods6010008.

[3] I-H. Kim, J. Han, J.H. Na, P-S. Chang, M.S. Chung, K.H. Park, S.C. Min, Insect-resistant food packaging film development using cinnamon oil and microencapsulation technologies, J. Food Sci. 78 (2013) 229–237, doi:10.1111/1750-3841.12006.

[4] (a) M.A. Mullen, J.M. Vardeman, J. Bagwell, Insect-Resistant Packaging; Chapter 12 from Stored Product Protection, Kansas State University, 2012; (b) M.W. Hassan, Gulraize, U. Ali, F. Ur Rehman, H. Najeeb, M. Sohail, B. Irsa, Z. Muzaffar, M.S. Chaudhry, Evaluation of standard loose plastic packaging for the management of Rhyzopertha dominica (F.) (Coleoptera: Bostrichidae) and Tribolium castaneum (Herbst) (Coleoptera: Tenebriondiae), 2016 J. Insect Sci., 16 1–9, doi:10.1093/jisesa/iew075; (c) A. van Ryckeghem, Insect resistant packaging: the last line of defense, 2011 Fumigants Pheromones, 99 2, doi:10.1093/jisesa/iew075.

[5] P. Appendini, J.H. Hotchkiss, Review of antimicrobial food packaging, Innov. Food Sci. Emerg. Technol. 3 (2002) 113–126, doi:10.1016/s1466-8564(02)00012-7.

[6] X. Hou, P. Fields, W. Taylor, The effect of repellents on penetration into packaging by stored-product insects, J. Stored Prod. Res. 40 (2004) 47–54, doi:10.1016/S0022-474X(02)00063-2.

[7] S. Bedini, S. Guarino, M.C. Echeverria, G. Flamini, R. Ascrizzi, A. Loni, B. Conti, Allium sativum, Rosmarinus officinalis, and Salvia officinalis essential oils: a spiced shield against blowflies, Insects 11 (2020) 143–161, doi:10.3390/insects11030143.

[8] K.K.Y. Wong, F.A. Signal, S.H. Campion, R.L. Motion, Citronella as an insect repellent in food packaging, J. Agr. Food Chem. 53 (2005) 4633–4636, doi:10.1021/jf050096m; (b) F. Licciardello, G. Muratore, P. Suma, A. Russo, C. Nerín, Effectiveness of a novel insect-repellent food packaging incorporating essential oils against the red flour beetle (Tribolium Castaneum), Innov. Food Sci. Emerg. Technol. 19 (2013) 173–180, doi:10.1016/j.ifset.2013.05.002; (c) T. Maji, I. Baruah, S. Dube, M. Hussain, Microencapsulation of Zanthoxylum Limonella Oil (ZLO) in glutaraldehyde crosslinked gelatin for mosquito repellent application, Biores. Tech. 98 (2007) 840–844, doi:10.1016/j.biortech.2006.03.005.

[9] L. Yang, Q. Li, H. Sun, L. He, Q. Yu, Y. Wang, Transparent Polystyrene Material Capable of Repelling Insects and Preparation Method Thereof, Patent CN110437554 A (2019).

[10] M.A. Park, Y. Chang, I. Choi, J. Bai, N. Ja-hyun, J. Han, Development of a comprehensive biological hazard-proof packaging film with insect-repellent, antibacterial, and antifungal activities, J. Food Sci. 83 (2018) 3035–3043, doi:10.1111/1750-3841.14397.

[11] V. Lopez, J. Alvaro, O. Vargas, Plastic Case Composed of Active Botanical Ingredients for Pest Control in Harvested Bananas, Patent WO 2018130235 A1 (2018).

[12] G.S. Germinara, A. Conte, L. Lecce, A. Di Palma, M.A. Nobile, Propionic acid in bio-based packaging to prevent Sitophilus granarius (L.) (Coleoptera, Dryophthoridae) infestation in cereal products, Inn. Food Sci. Emerg. Technol. 11 (2010) 498–502, doi:10.1016/j.ifset.2010.03.001.

[13] R.A. Garcia, Essential Oils in Plastic Film, Patent US 2004/0034149 A1.

[14] S. Navarro, S. Finkelman, D. Zehavi, R. Dias, S. Angel, F. Mansur, M. Rindner, Pest-Impervious Packaging Material and Pest-Control Composition. U.S. Patent 20050208157-A1 and European Patent Application 04101309.5.

[15] (a) J.H. Lora, W.G. Glasser, Recent industrial applications of lignin: a sustainable alternative to nonrenewable materials, J. Polym. Env. 10 (2002) 39–48, doi:10.1023/A:1021070006895; (b) A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, C.E. Wyman, Lignin valorization: improving lignin processing in the biorefinery, Science 344 (2014) 1246843 -1246843, doi:10.1126/science.1246843; (c) N. Mandlekar, A. Cayla, F. Rault, S. Giraud, F. Salaün, G. Malucelli, J.-P. Guan, An overview on the use of lignin and its derivatives in fire retardant polymer systems, lignin, trends and application, IntechOpen (2018) Chapter 9, doi:10.5772/intechopen.72963.

[16] K. Gabov, R.J.A. Gosselink, A.I. Smeds, P. Fardim, Characterization of lignin extracted from birch wood by a modified hydrotropic process, J. Agric. Food. Chem. 62 (2014) 10759–10767, doi:10.1021/jf5037728.

[17] M.N. Collins, M. Nechifor, F. Tanasă, M. Zănoagă, A. Mcloughlin, M.A. Stróżyk, M. Culebras, C-A. Teacă, Valorization of lignin in polymer and composite systems for advanced engineering applications – a review, Int. J. Bio. Macromol. 131 (2019) 828–849, doi:10.1016/j.ijbiomac.2019.03.069.

[18] (a) M.P. Vinardell, V. Ugartondo, M. Mitjans, Potential applications of antioxidant lignins from different sources, Ind. Crops Prod. 27 (2008) 220–223, doi:10.1016/j.indcrop.2007.07.011; (b) J. Ponomarenko, M. Lauberts, T. Dizhbite, L. Lauberte, V. Jurkjane, G. Telysheva, Antioxidant activity of various lignins and lignin-related phenylpropanoid units with high and low molecular weight, Holzforschung 69 (2015) 795–805, doi:10.1515/hf-2014-0280.

[19] M. Padella, A. O' Connell, M. Prussi, What is still limiting the deployment of cellulosic ethanol analysis of the current status of the sector, Appl. Sci. 9 (2019) 4523–4536, doi:10.3390/app9214523.

[20] R.J.A. Gosselink, J.C. van der Putten, D.S. van Es, Fractionation of Technical Lignin, Patent WO2015/ (2015) 178771.

[21] R.D. Deanin, S.B. Driscoll, R.J. Cook, M.P. Dubreuil, W.N. Hellmuth, W.A. Shaker, Lignin as a filler in commodity thermoplastics, Soc. Plast. Eng. Tech. Pap. 24 (1978) 711.

[22] J. Kubat, H.E. Stromvall, Properties of injection molded lignin-filled polyethylene and polystyrene, Plast. Rubber Process. Appl. 3 (1983) 111–118.

[23] B. Bozsódi, V. Romhányi, P. Pataki, D. Kun, K. Renner, B. Pukanszky, Modification of interactions in polypropylene/lignosulfonate blends, Mater. Des. 103 (2016) 32–39 and references therein, doi:10.1016/j.matdes.2016.04.061.

[24] W.O.S. Doherty, P. Mousavioun, C.M. Fellows, Value-adding to cellulosic ethanol: lignin polymers, Indus. Crops Prod. 33 (2011) 259–276 and references therein, doi:10.1016/j.indcrop.2010.10.022.

[25] J. Domínguez-Robles, E. Larrañeta, M.L. Fong, N.K. Martin, N.J. Irwin, P. Mutjé, Q. Tarrés, M. Delgado-Aguilar, Lignin/poly(butylene succinate) composites with antioxidant and antibacterial properties for potential biomedical applications, Int. J. Biol. Macromol. 145 (2020) 92–99, doi:10.1016/j.ijbiomac.2019.12.146.

[26] K.F. El-Nemr, H.R. Mohamed, M.A. Ali, R.M. Fathy, A.S. Dhmees, Polyvinyl alcohol/gelatin irradiated blends filled by lignin as green filler for antimicrobial packaging materials, Int. J. Env. Anal. Chem. (2019), doi:10.1080/03067319.2019.1657108.

[27] S.E. Klein, A. Alzagameem, J. Rumpf, I. Korte, J. Kreyenschmidt, M. Schulze, Antimicrobial activity of lignin-derived polyurethane coatings prepared from unmodified and demethylated lignins, Coatings 9 (2019) 494–510, doi:10.3390/coatings9080494.

[28] W. Yang, E. Fortunati, F. Dominici, G. Giovanale, A. Mazzaglia, G.M. Balestra, J.M. Kenny, D. Puglia, Effect of cellulose and lignin on disintegration, antimicrobial andantioxidant properties of PLA active films, Int. J. Biol. Macromol. 89 (2016) 360–368, doi:10.1016/j.ijbiomac.2016.04.068.

[29] S. Constant, H.L.J. Wienk, A.E. Frissen, P. de Peinder, R. Boelens, D.S. van Es, R.J.H. Grisel, B.M. Weckhuysen, W.J.J. Huijgen, R.J.A. Gosselink, P.C.A. Bruijnincx, New insights into the structure and composition of technical lignins: a comparative characterisation study, Green Chem 18 (2016) 2651–2665, doi:10.1039/c5gc03043a.

[30] İ. Kayacan, Ö.M. Doğan, Pyrolysis of low and high density polyethylene. Part I: non-isothermal pyrolysis kinetics, Energy Sources Part A: Recov. Util. Environ. Effects 30 (2008) 385–391, doi:10.1080/15567030701457079.

[31] M.E. Jazi, G. Narayanan, F. Aghabozorgi, B. Farajidizaji, A. Aghaei, M.A. Kamyabi, C.M. Navarathna, T.E. Mlsna, Structure, chemistry and physicochemistry of lignin for material functionalization, SN Appl. Sci. 1 (2019) 1094–1112, doi:10.1007/s42452-019-1126-8.

[32] C.M. Cormier, B. Wunderlich, Heat of fusion of polyethylene, J. Polym. Sci. 5 (1967) 987–988.

[33] D. Kun, B. Pukanszky, Polymer/lignin blends: Interactions, properties, applications, Eur. Polym. J. 93 (2017) 618–641 and reference therein, doi:10.1016/j.eurpolymj.2017.04.035.

[34] V. Romhanyi, D. Kun, B. Pukanszky, Correlations among miscibility, structure and properties in thermoplastic polymer/lignin blends, ACS Sus. Chem. Eng. 6 (2018) 14323–14331, doi:10.1021/acssuschemeng.8b02989.

[35] Z. Mahmood, M. Yameen, M. Jahangeer, M. Riaz, A. Ghaffar, I. Javid, Lignin as natural antioxidant capacity, Lignin (2018) 181–205, doi:10.5772/intechopen.73284.

[36] (a) K. Levon, J. Huhtala, B. Malm, J.J. Lindberg, Improvement of the thermal stabilization of polyethylene with lignosulphonate, Polymer 28 (1987) 745–750, doi:10.1016/0032-3861(87)90223-0; (b) A. Gregorová, Z. Cibulková, B. Košíková, P. Šimon, Stabilization effect of lignin in polypropylene and recycled polypropylene, Polym. Degrad. Stabil. 89 (2005) 553–558, doi:10.1016/j.polymdegradstab.2005.02.007; (c) D. Ye, S. Li, X. Lu, X. Zhang, O.J. Rojas, Antioxidant and thermal stabilization of polypropylene by addition of butylated lignin at low loadings, ACS Sustain. Chem. Eng. 4 (2016) 5248–5257, doi:10.1021/acssuschemeng.6b01241; (d) H. Sadeghifar, D.S. Argyropoulos, Correlations of the antioxidant properties of softwood kraft lignin fractions with the thermal stability of its blends with polyethylene, ACS Sustain. Chem. Eng. 3 (2015) 349–356, doi:10.1021/sc500756n.

[37] J.R. Pauquet, R.V. Todesco, W.O. Drake, Limitations and applications of oxidative induction time (OIT) to quality control of polyolefins, in: International Wire & Cable Symposium Proceedings, 1993, pp. 77–86.

[38] H. Cetin-Karaca, M.C. Newman, Antimicrobial efficacy of natural phenolic compounds against gram positive foodborne pathogens, J. Food Res. 4 (2015) 14–27, doi:10.5539/jfr.v4n6p14.

[39] A. Majira, B. Godon, L. Foulon, J.C. van der Putten, L. Cézard, M. Thierry, F. Pion, A. Bado-Nilles, P. Pandard, T. Jayabalan, V. Aguié-Béghin, P.H. Ducrot, C. Lapierre, G. Marlair, R.J.A. Gosselink, S. Baumberger, B. Cottyn, Enhancing the antioxidant activity of technical lignins by combining solvent fractionation and ionic liquid treatment, ChemSusChem 12 (2019) 4799–4809, doi:10.1002/cssc.201901916.