

Melt-blown compostable polyester films with lignin

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ABSTRACT: Compostable films for such uses as packaging and agricultural soil covering materials were first produced on commercial scale from blends of biodegradable polyesters and a modified kraft lignin. The lignin consisted of an industrial product isolated according to the LignoBoost process. The lignin modification involved homogeneous phase reaction with propylene oxide, and the films were melt-blown from a pelletized compound consisting of up to a 30% blend of lignin derivative with commercial biodegradable polyester. The 12–93 μm thick films combined the characteristics of lignin as modulus-building and environmentally degradable polymer with those of the strength-building thermoplastic polyester. Although the modified lignin paralleled the behavior of native lignin in wood by resisting rapid and full conversion to carbon dioxide in a simulated composting environment, two thirds of the film mass biodegraded within 12 weeks of composting, with the remainder turning into (humus-like) water-soluble solids and particles <2 mm in size. The lignin derivatives suffered from the release of trace amounts of malodorous volatiles containing reduced sulfur when subjected to melt-blowing. The objectionable odor was virtually unnoticeable in injection-molded solid parts.

Application: The use of kraft lignin as a contributing thermoplastic polymer component of melt-blown film and injection-molded products from sustainable resources with environmental compatibility helps the kraft pulping process advance toward a multi-purpose biorefining technology with increased income potential.

This report describes the first commercial application of industrially generated, chemically modified kraft lignin in melt-blown, environmentally degradable (compostable) polyester film products following hydroxypropylation.

Lignin is the second most abundant natural (sustainable) polymer on earth. It is also the most abundant aromatic polymer in nature that serves land plants as matrix component in cellulose fiber-based composites; as modulus-raising copolymer with non-crystalline polysaccharides; and as natural defense against biological and atmospheric degradation [1,2]. Lignin is separated from the plant-biocomposite (mostly wood) in large quantities during papermaking. This resource, which is generated in amounts of approximately 0.5 ton per ton of pulp, is used primarily as in-house process fuel or as polymeric, water-soluble dispersant/surfactant (about 1,000,000 tons per year worldwide) [3]. Recent advances have improved the option of recovering lignin from the kraft pulping process, and this isolation method is beginning to be adopted on industrial scale [4]. Isolated kraft lignin is therefore considered a new resource for the development of sustainable and environmentally degradable polymeric materials on the scale of as much as 78 million tons per year worldwide [5]. In addition to kraft pulping, the emerging cellulosic biofuels industry is projected to potentially generate about 62 million tons of lignin by 2022 [5-8].

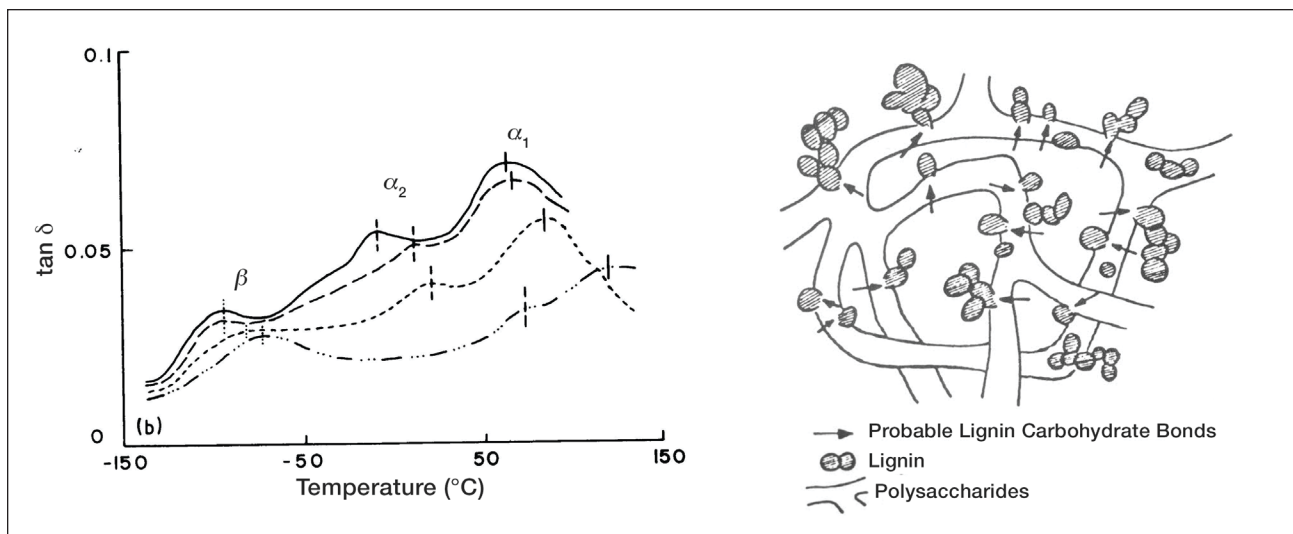
Lignin nature and sources

In its native state, lignin is insoluble (with the exception of minor fractions that are solvent-soluble, such as *Brauns* native

lignin [1]), exhibiting typical network character. It is also thermally undeformable. Its insolubility has long been considered to be the result of its crosslinked network structure [1,2]. This has, however, been demonstrated to be mostly incorrect. In moist wood or other plant biocomposites, lignin does show a surprisingly low glass-to-rubber transition temperature (T_g), which signifies a loss in modulus in response to heating [9-11]. This T_g of lignin is in the same range as linear polystyrene.

Under dynamic mechanical thermal analysis (DMTA), an analytical method typically used in polymer science to identify phase structure and compatibility of multi-phase materials in composites and blends, the mechanical response of moisturized wood to heating revealed two distinct molecular phases [9]. This indicates that the amorphous matrix of the biocomposite consists of two molecular entities, each of sufficient independent size (sub-micron) to raise its own T_g , representing non-crystalline heteropolysaccharides (also called hemicelluloses) and lignin (**Fig. 1**, left) [9]. The T_g of wood, which is generally significantly below the T_g of isolated lignin, is somewhat species-dependent [10,11].

The absence of network character necessitates an alternate explanation for the insolubility and thermal non-deformability of the non-crystalline matrix of the biocomposite. In the last 40+ years, this behavior has been attributed to block (or graft) copolymer instead of network architecture [12,13]. Figure 1 (right) shows a simplified view of its structure [13]. As a result of the copolymer structure, the two-phase amorphous matrix displays network-like properties, insolubility and thermal non-deformability, which necessitate hydrolysis of ether



1. Dynamic mechanical thermogram of solid wood (left) illustrating the glass-to-rubber transitions of the biphasic amorphous matrix component of biocomposite wood at different moisture contents. α_1 and α_2 represent the thermal transitions of lignin and non-crystalline carbohydrates, respectively. (After Kelley et al. [9]). Model of block copolymer (right) illustrating the lignin-carbohydrate complex according to Košíková et al. [12].

bonds connecting lignin with carbohydrates for such matrix removal as needed for fiber liberation by pulping.

The lignin-carbohydrate complex has long been recognized as fragile (i.e., susceptible to hydrolytic cleavage) and renewable in the presence of moisture [14-19]. This behavior is considered the basis of the understanding of wood as an “intelligent composite material” [20-23]. The molecular basis of this reversibility (i.e., of hydrolytic depolymerization and repolymerization) revolves around the ease of forming reactive intermediates, quinone methides, that may recombine with carbohydrates and restore insolubility and non-deformability. This dynamic regeneration process of copolymer architecture is responsible for the need to apply lignin-degrading chemistry for obtaining bleached (lignin-free) pulp fibers, which has been corroborated by numerous studies over many years [14-19].

The isolation of the highly crystalline polysaccharide component (cellulose) from wood in fiber form, which requires the dissolution of the matrix (i.e., the delignification or pulping process) can be accomplished using aqueous solutions with pH levels ranging from very low (acid sulfite process) to very high (kraft process), or with organic solvents having solubility parameters resembling those of lignin (organosolv process). By these treatments, lignin becomes soluble (a) in aqueous medium in salt-form, sulfonate or phenolate (lignin sulfonate or kraft lignin), or (b) as organic solvent-soluble molecules with reduced (by hydrolysis) molecular weight (organosolv lignin). In addition to hydrolysis of the lignin-carbohydrate bonds, efficient delignification requires chemical action aimed at (a) raising the degree of modification with sulfonate groups through the use of aqueous solutions of sulfur dioxide or bisulfite salts (sulfite process), (b) effective hydrolytic cleavage (assisted by the addition of semi-catalytic sulfide salts) of alkyl-aryl ether bonds within lignin, causing a

rise in phenolic hydroxyl group content (kraft process), or (c) mild hydrolytic separation of solvent-soluble lignin fragments with reduced molecular weight from the lignin-carbohydrate complex (organosolv process) [1,2]. Each process carries the risk for side reactions that typically result in an increase in the T_g of lignin [24,25].

The resulting solubilized lignins are distinct from each other while retaining their elevated molecular weight, their varied functional character, and their branched nature [11,24,25]. As sulfonated entities (i.e., lignin sulfonates), they remain water-soluble at any pH-level. As kraft lignins, they gradually lose their water solubility at pH levels below about 8-9. As organosolv lignins, they become insoluble when exposed to environments with adjusted solubility parameter (so-called non-solvents) and/or temperature. The separation of lignin from the native lignin-carbohydrate complex (i.e., the block copolymer) requires chemical action resulting in structural modifications of different types and degrees [24,25]. Unwanted side reactions involving necessary reactive intermediates, such as benzylic cations and quinone methides, may give rise to condensed structures with reduced solubility and reduced thermal deformability (i.e., raised T_g) while preserving their major varied functionality [24]. This change in structural character is more pronounced in sulfite and kraft lignins than in organosolv lignins. The latter, therefore, retain a high degree of solubility (in organic solvents) and a more moderate T_g .

Lignin sulfonates remain water-soluble polymers with high molecular weight. When isolated from associated inorganic salts and sugars by such processes as ultrafiltration, ion exchange, or spray drying, they are powerful surfactants and dispersants. These products have captured commercial markets in excess of 1 million tons per year worldwide [3].

Kraft lignins are rarely isolated in separated form and instead used mostly for fuel purposes after concentration by water evaporation. This process is designed to recover inorganic pulping chemicals (sodium hydroxide and sodium sulfide), plus steam for electric power. Much research effort has focused on the use of kraft lignins in polymeric materials, with or without chemical modification, such as water-soluble surfactants, adhesive additives (phenolic resins and other thermosets), and in components of thermoplastics, mostly after some type of chemical modification aimed at overcoming the recognized molecular intractability based on the absence of solubility and thermal deformability.

Organosolv lignins have been much sought-after polymers for materials applications [8,26]. Their potential contribution to desirable properties paralleling those of lignin in the native biocomposite has been widely demonstrated in the laboratory and on a semi-industrial scale. However, this type of lignin is constrained by cost and availability factors. There are presently no known commercial suppliers.

This introduction is to emphasize that, while all isolated lignins preserve most of the inherent polymer properties, such as modulus, multi-functionality, sustainability, and biological degradability, significant differences exist between isolated lignins that invite strategies for developing materials applications in which the native properties are used for the benefit of the final product [27-29].

Lignin modifications

For lignins to make an effective entry into commercial materials markets, specialized isolation methodologies or chemical modification approaches must become practical. Numerous studies have demonstrated that lignin can be readily converted into a soluble, reactive, and thermally deformable polymer by chemical modification. This topic has been the subject of several recent reviews [8,29-31]. Among the many modification methods explored, one of the simplest, most property-altering, and most cost-effective techniques involves a reaction with alkylene oxides, especially propylene oxide [27-50]. As a component of thermoplastic and thermosetting materials, lignin is capable of contributing its inherent properties as modulus-builder and slow-degrading organic matter that is considered pre-humus. These characteristics have attracted the attention of such industrial polymer users and producers as IBM, for printed circuit boards [26]. However, the limited availability of isolated, water-insoluble lignins from industrial operations has deterred potential users. This situation, and the quest for greater reliance on sustainable resources, is beginning to change.

The modification of lignin with propylene oxide (i.e., the formation of hydroxypropyl lignin [HPL] derivatives), which commenced in the early 1970s, transforms lignin into a thermoplastic (melt-deformable), (organic) solvent-soluble, functionally uniform aromatic polymer of (mostly) small size [32-50]. Its surprising T_g -lowering and solubility-raising effect that initially seemed to contradict the conventional understanding

of lignin as a crosslinked polymer is consistent with the recent view of lignin as a compact aggregate of molecules assembled on the basis of non-covalent π - π interactions [51,52]. Just as esterification separates cellulose molecules sufficiently to create solubility by disturbing crystallinity (i.e., by creating distance between polysaccharide chains), hydroxypropylation of lignin seems to separate stacked aromatic structures sufficiently to render the modified product soluble in organic solvents and compatible with other macro-molecules [46-50]. Simple modification reactions capable of resolving non-covalent aromatic interactions, such as oxyalkylation, methylation [43], or esterification [30,31] are thus appropriate strategies for converting isolated lignins into important components of thermoplastic materials.

MATERIALS AND METHODS

Lignin and polyester sources

Isolated kraft lignin was obtained from the Domtar Paper Company in Plymouth, NC, USA, (www.domtar.com/en/pulp/lignin/10387.asp), which uses primarily southern pine as wood feedstock. The lignin composition was listed as 63%–66% carbon, 5.7%–6.2% hydrogen, 2%–2.5% sulfur, and <1.0% ash. The lignin was used as received for modification.

The BASF-supplied biodegradable polyester product, ecoflex F Blend C1200, is described as a statistical, aliphatic-aromatic copolyester based on the monomers 1,4-butanediol, adipic acid, and terephthalic acid (PBAT) in the polymer chain (www.basf.com) [53].

Modification and structure analysis

The oxyalkylation reaction was carried out as previously described [37] with modification to accommodate needs associated with the scale-up to the tonnage scale [44]. The resulting HPL product was filtered and washed, and used in dry powder form. It was analyzed by hydrogen-nuclear magnetic resonance (H-NMR) spectroscopy in dimethyl sulfoxide (DMSO) solution, as described previously [54].

Compounding and melt blowing

Melt processing was performed using pelletized blends composed of 0%–40% HPL in PBAT in a compounder with screw designed for filler dispersion, which allowed for superior mixing. The material was all fed at room temperature (zone 0). The temperature of the zones then varied from 110°C (zone 1) to 140°C for zones 3–10. Actual melt temperature was reached between 185°C–190°C at a screw speed of 200 rpm. A noticeable release of objectionable odor typical of kraft pulping was recognized. Film blowing was performed on a small pilot film blowing line using an 80 mm die, a die gap of 0.8 mm, and a blow-up ratio of 3.5:1. Films were made in 12 μ m, 25 μ m, and 30–93 μ m thicknesses. All films contained varying portions of gel (non-melt) particles that apparently resulted from incompletely fluidized HPL. These impurities created instability of the 12 μ m film at higher HPL content, which tended to collapse.

LIGNIN PRODUCTS

Mechanical property testing

Film testing was performed at least 1 week after melt-blowing for the 12 μm films, according to ISO 527-3:1996 “Determination of tensile properties – Part 3: Test conditions for films and sheets,” at 23°C and 50% humidity using preconditioned strips with an effective measured length of 50 mm and a width of 10 mm. The results reported represent the median of five samples. The visual detection of some gel particles in the blown films indicated that the HPL sample used for the prototype films was incompletely homogenized, resulting in an apparent reduction in tensile strength.

Biobased/degradation/composting evaluation

The determination of biobased as opposed to fossil carbon composition by carbon dating was performed by Xceleron (Germantown, MD, USA). The results of percent-biobased have an uncertainty of $\pm 3\%$, according to ASTM D6866 “Standard test method for determining the biobased content of solid, liquid, and gaseous samples using radiocarbon analysis.” The quantitative bio-disintegration of 43 μm film samples was evaluated by Organic Waste Systems (OWS; Gent, Belgium), in a pilot-scale aerobic composting test, according to ISO 16929 (2013) “Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test.” In brief, a sample of blended polymer composed of about 25% modified lignin, 15% calcium carbonate, and 60% PBAT was processed on a laboratory blown film line to produce a 43 μm film. This film was cut into 10 cm $\times$ 10 cm pieces and added in 1% concentration to bins of pure biowaste. Conditions remained at optimum levels of $>60^\circ\text{C}$ and $<75^\circ\text{C}$ for 1 week before the temperature dropped to $>40^\circ\text{C}$ for the consecutive 5 weeks. Tests were performed in duplicate and lasted for 12 weeks. Disintegration results were determined by sieving, in accordance with ASTM D 6400-12 “Standard specification for compostable plastics” and ISO 17088 (2012) “Specifications for compostable plastics.”

Film degradation by exposure to ultraviolet (UV) light radiation was conducted by BASF using an accelerated test protocol for 10 days.

Headspace analysis for volatiles

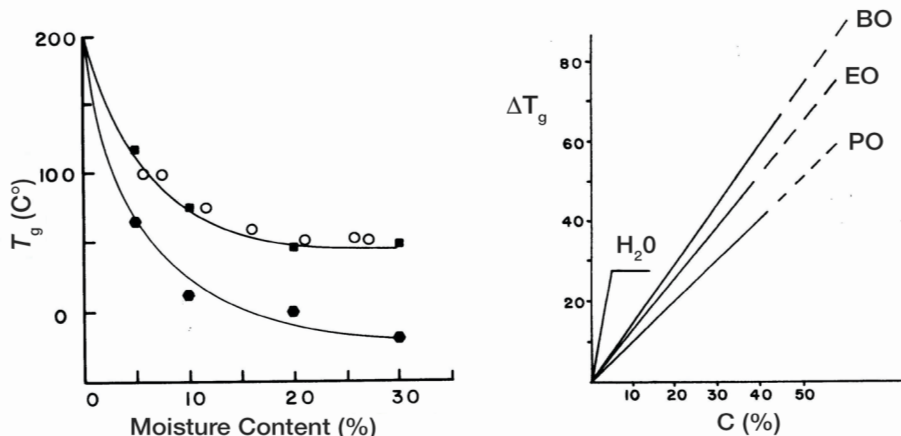
Headspace analysis was performed by the University of Dayton Research Institute (UDRI; Dayton, OH, USA) using the system for thermal diagnostic studies (STDS). This analysis is based on a temperature-programmable test section connected to an inline gas chromatography-mass spectrometer (GC-MS). An added sorbent trap was swept with about 10 mL/min of dry helium heated to 250°C at 20°C/min and held at 250°C for 10 min. Desorption of the trap produced a gas stream that was guided through the GC-MS. The resulting total ion chromatogram was analyzed using the National Institute of Standards and Technology (NIST) mass spectral library.

RESULTS AND DISCUSSION

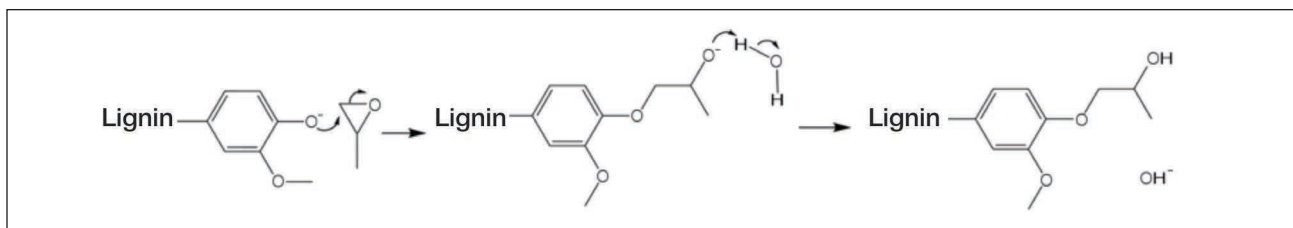
Lignin modification

In dry state, all isolated lignins have high glass transition temperatures, often at or near the thermal degradation temperature of the polymer. However, thanks to their multi-functionality, lignins respond to plasticization (**Fig. 2**). Water (**Fig. 2, left**), which serves as such an effective plasticizer for non-crystalline polysaccharides (hemicelluloses), also has a great effect on lignin's T_g , but its effect is limited to only the first 5–10 (wt.%) moisture (plasticizer) content. The alternate option to T_g -reduction is chemical modification, which amounts to internal plasticization (**Fig. 2, right**).

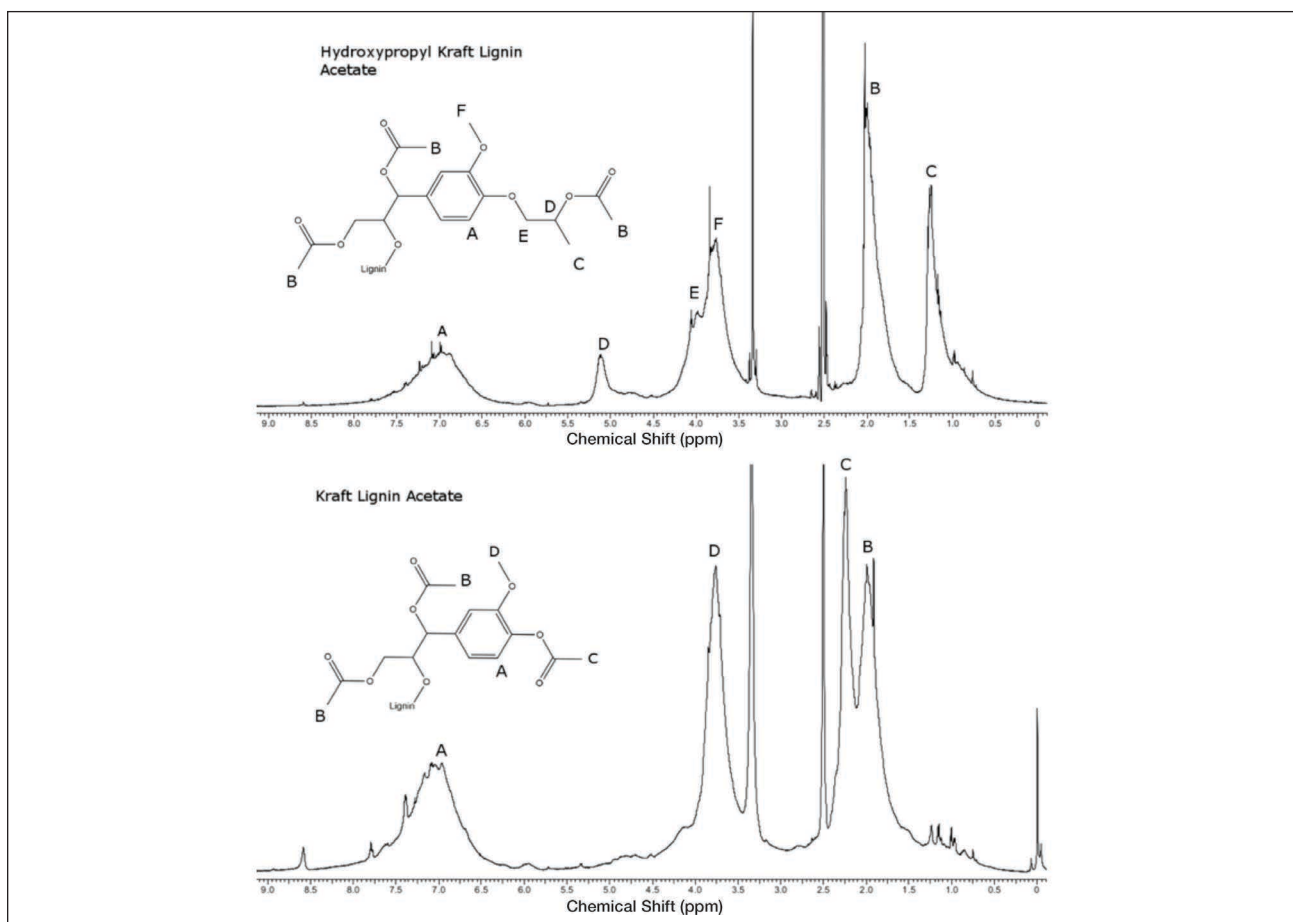
One of the most effective methods of altering the properties of lignin in terms of solubility and thermal properties involves reaction with alkylene oxides (**Fig. 3**) [32–37]. This reaction, which was first used in the early 1970s to synthesize lignin-based polyols for polyurethane foams [32–34], has evolved over several decades into a convenient technique for incorporating water-insoluble (non-sulfonated) lignins into



2. The plasticization effect of water (left) and hydroxyalkyl ether substituent content (C) (right) on the glass transition temperature of lignin (after Lora and Glasser [8]). ΔT_g represents T_g -change in relation to control (i.e., unmodified lignin) according to the equation by Fujita-Nishimoto [8].



3. Schematic reaction of phenolic model substance representing lignin with alkylene oxide.

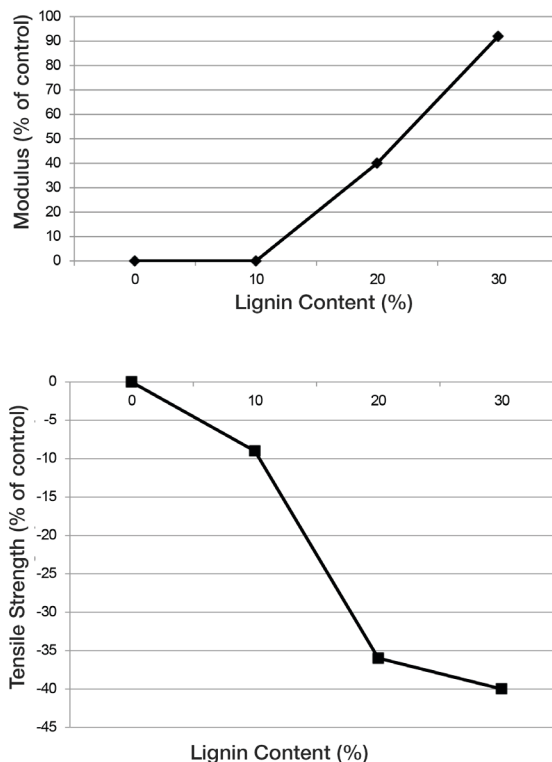


4. Hydrogen-nuclear magnetic resonance (H-NMR) spectra of acetylated kraft lignin before (A) and after (B) reaction with propylene oxide, showing the disappearance of the *aro*-OAc peak at 2.2 ppm and the formation of a larger *ali*-OAc peak and the CH₃-peak of propylene oxide (PO) at 1.2 ppm as a consequence of propoxylation.

polymeric materials with significant phase compatibility vis-à-vis a range of manufactured thermoplastic and thermosetting polymers [8].

Several factors, including reactivity, boiling point, and ease of handling, have contributed to a preference for propylene oxide (PO) as the modifying agent, although other epoxides were tested as well [31-33,54]. This chemistry has been the subject of considerable optimization throughout the research and development effort and the scale-up process [44]. Currently, the hydroxypropyl kraft lignin is manufactured economically in a batch process that produces multiple tons per batch. The resulting lignin derivatives proved to have glass transition temperatures that are 1.0°C–2.5°C/ % weight gain

lower than the starting material. They were virtually mono-functional and soluble in and compatible with a range of solvents and polymers of common use, and their polydispersity was reduced over the starting material [37,54]. The complete removal of all phenolic functionality results in a derivative with a degree of substitution with PO of about 0.2 to 0.7 per phenylpropane lignin-repeat unit, depending on initial phenolic hydroxide content and reaction conditions. H-NMR spectroscopy reveals a transformation of the phenolic hydroxyl groups (approximately 45% of total hydroxide groups in kraft lignin [24,25]) into aliphatic hydroxide and methyl groups (Fig. 4). Variability in degree of modification may result from a range of reaction parameters, especially pH, temperature,



5. Mechanical properties of 12-14 μm films in relation to lignin content.

time, and concentration, as well as product character, especially syringyl (S) and guaiacyl (G) ratio and functionality of the lignin source. This modification and analysis has developed into a state-of-art that is practiced in many laboratories and institutions world-wide. The resulting effects on solubility and thermoplasticity are well-documented.

Compounding and melt-processing

HPL in powder form was compounded in a 40 mm twin-screw extruder with the aliphatic-aromatic biodegradable polyester (PBAT) into pellets containing of 10%, 20%, and 30% HPL. The pellets were subsequently melt-blown into films of 12-14 μm (and greater) thickness. All melt-processing operations functioned without difficulties, except that the bubble became too unstable at the highest HPL concentration of 30% to allow for stable blowing operations. This was unique to the 12-14 μm films. At greater film thickness (60-90 μm), greater lignin contents were tolerated. Pellets with HPL contents as high as 50% were successfully melt-processed by injection molding without difficulties. Visually, the films provided no signs of separated phases; all (thin) films appeared transparent and with undiminished elongation at break-values. None of the films exhibited the embrittlement typical of blends with unmodified lignins.

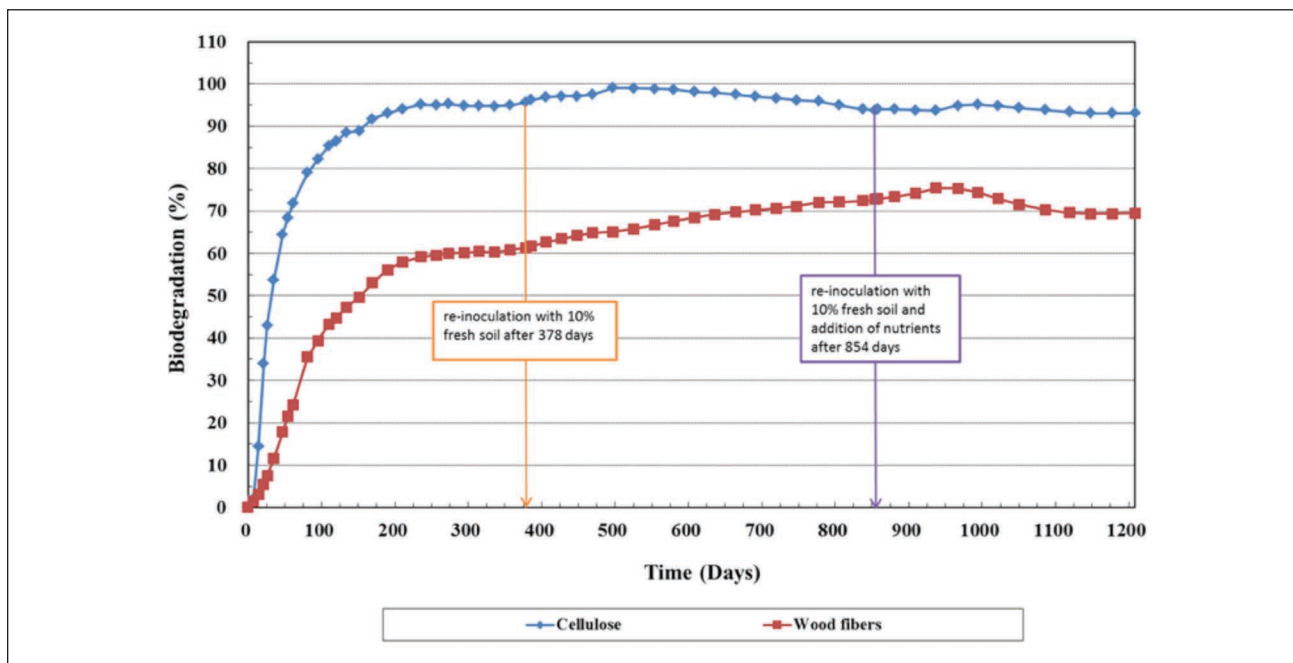
Mechanical properties

The resulting films had the expected properties of increased modulus (and slightly enhanced elongation at break) and re-

duced tensile strength (**Fig. 5**) with HPL content. The degree to which modulus responded to HPL content proved to be somewhat dependent on degree of substitution of the lignin with propylene oxide. Desired properties were subject to film thickness and HPL content. Overall, the 12-14 μm films with HPL contents of up to 20% exhibited adequate performances during processing (compounding and melt-blowing) and mechanical testing. All required performance standards were met, especially if the lignin content remained below approximately 25%-30%.

Biodegradation

The analysis of biodegradation was performed in a simulated industrial composting test according to ISO 16929 (2013). The resulting data showed that under composting conditions, lignin and modified lignin (HPL) are essentially the same with regard to carbon dioxide (CO₂) production. The two degradation experiments were performed under very similar conditions. The results are consistent with wood biodegradation tests (provided by OWS, the contract laboratory), which revealed that wood with a 30% lignin content degraded quickly and reached a CO₂ production level of 70%-75% under conditions under which standard cellulose converts to CO₂ levels of 90%-100% (**Fig. 6**). These results indicate that, even given 1200 days of composting, the lignin content of the wood does not decompose into significant amounts of CO₂. Lignin in compost is degraded, but not primarily into CO₂. This is consistent with experiments with radio-labeled lignin [55] that



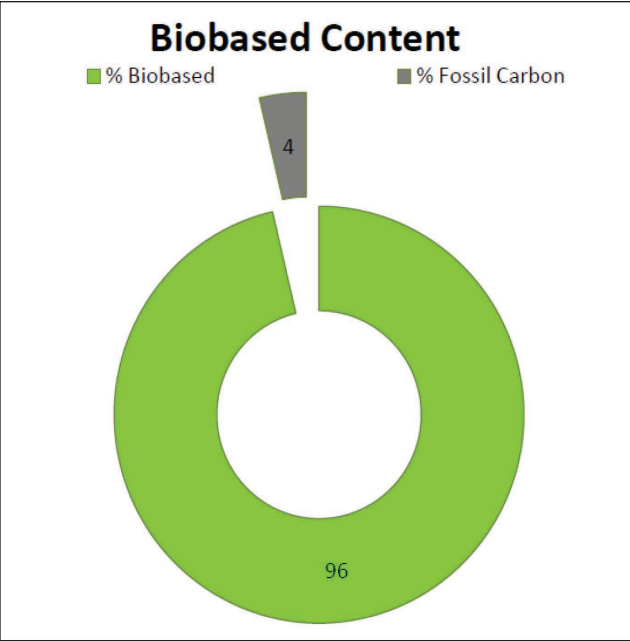
6. Biodegradation results of cellulose and lignin under simulated composting conditions.



7. Illustration of the results of simulated composting tests with 93 µm-thick films. H3070E refers to sample designation by the contractor (Organic Waste Systems).

have shown that much of lignin is converted into carbon-14 labeled water-soluble fragments instead of CO₂. Tuomela et al. [56,57] observed that lignin inhibits the degradation of carbohydrates and generates water-soluble degradation products that are mineralized or bound to humic substances and incorporated into humin or other insolubles.

In separate experiments, HPL in inoculated slurry designed to simulate a composting environment also produced a significant portion of dissolved aqueous lignin solids. After 33 days in an aqueous slurry at 60°C (at an initial pH of 7.5), along with cellulose and a commercial soil inoculant, 15.8% of the HPL sample had degraded into soluble lignin fragments, indicating that the modified lignin behaves comparably to unmodified lignin in a compost environment. The disintegration of the 10 cm × 10 cm film pieces into smaller particles proceeded well. After 10 weeks of composting the average size of the remaining pieces was approximately 1 cm × 2 cm. After 12 weeks the whole content of the bins, in which the simulated soil test was carried out, was used for sieving, sorting, further isolation and analyses, and a disintegration percentage was calculated. Disintegration is defined as a size reduction to <2 mm. Only some rather small pieces of film could be retrieved in the different fractions (**Fig. 7**). The major parts of these pieces were dark brown and fragile. By far the major part of the test material had disappeared. An average disintegration percentage of 94.0% was determined. This is well above the 90% pass level required by the ASTM D6400-12, EN 13432 (2000) "Requirements for packaging recoverable through composting and biodegradation-test scheme and evaluation criteria for the final acceptance of packaging," and ISO 17088 (2012) standards for compostable plastics. Figure 7 gives a visual comparison of the <10 mm



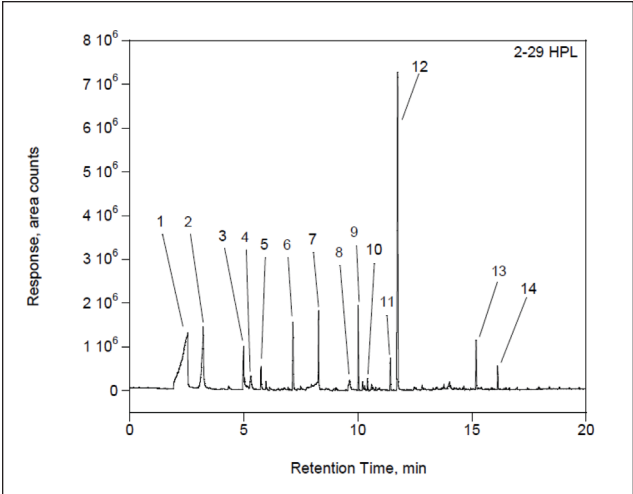
8. Determination of biobased and fossil carbon in hydroxypropyl lignin. Test conducted in accordance with test standard ASTM D6866-12 that has an uncertainty of +/- 3%.



9. Hydroxypropyl lignin-containing polyester film (12–14 μm) following photo-irradiation in test chamber illustrating the photo-bleaching effect in the exposed film area. The fringe area remained shaded by clamping.

fraction of film subjected to test compost after 12 weeks. As a consequence of these results, the 30% HPL/polyester blend films have already been successfully certified in the United States as compostable materials according to ASTM D 6400-12.

The designation of compostable material hinges on both (or either) conversion to CO₂ (within time limits) and natural polymer source. Neither lignin nor HPL (nor wood, for that matter) fully meet those criteria. However, experiments involving radiocarbon analysis produced results distinguishing bio-based from fossil-based carbon in materials. The results shown in **Fig. 8**, which were obtained according to test standard ASTM D6866-12, reveal a bio-based carbon content



10. Headspace analysis results of lignin film by system for thermal diagnostic studies and gas chromatography-mass spectrometry. Partial peak identification is given in Table I. (Peak no. 12 represents a contaminant from the vacuum oven used for gas collection and was not a product of hydroxypropyl lignin off-gassing.)

Peak No.	Assignment	Relative Area, %
2	Dimethyl sulfide	11.4
5	Propylene sulfide	1.7
6	Dimethyl disulfide	4.4
8	Dimethyl trisulfide	2.0
12	Tributylamine	23.1

I. Sulfur-containing volatiles identified in headspace films.

of >95% for the HPL produced by cycleWood Solutions, Inc., and used in the tests described in this report. The missing designation as natural polymer prevents the film blends from being so far recognized as compostable in Europe (according to EN 13432).

Photo-degradation

The initial evaluation of exposure of a prototype film (with 20% HPL content) to UV radiation was carried out in a test chamber simulating intense irradiation for 10 days. The film sample initially (within the first 7 days) responded well by displaying similar elongation at break compared with the pure polyester control sample, but the films showed distinct signs of photo-degradation by becoming totally colorless and transparent (**Fig. 9**) and severely brittle. It was obvious that the lignin component protected the polyester from being degraded until it lost its protective capacity by being degraded itself. This behavior parallels lignin’s function in the process of wood weathering [58,59], in which it serves as a guardian of the highly degradable (non-crystalline carbohydrate) portions of the biocomposite until the lignin itself has been converted

CONCLUSIONS

The use of commercially available kraft lignin in melt-processed thermoplastics was demonstrated successfully on industrial scale following a well-known chemical modification procedure with propylene oxide (**Fig. 11**).

In melt-blown film products, lignin contributed to moderate increases in modulus while providing compostability and a definite (but exhaustible) protection against photo-degradation.

Like native lignin, the modified lignin failed to degrade substantially to CO₂ in favor of the formation of water-soluble degradation products and solids usually found in humus.

Processing and material characteristics represent the first promising demonstration of the production (on commercial scale, in multiple tons) of compostable thermoplastics with (modified) lignin.

The source of lignin as byproduct of kraft pulping, the only source currently available in tonnage quantities, represents the limitation to wider commercial success because of the release of trace amounts of objectionable volatiles with reduced sulfur functionality when melt-blown. This release of volatiles is less noticeable during injection molding, and it is virtually unnoticeable in injection-molded solid parts, even at lignin contents as high as 50%.

The technology developed and tested on industrial scale is ready for adoption by biorefineries that convert plant biomass into glucose and other cellulosic products using a sulfur-free fractionation process [60]. **TJ**

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11. Illustration of several prototype and (semi-) commercial products made from lignin-containing melt-blown and injection molded polymer blends.

to volatile (vanillin) and water-soluble degradation products, and its protective capacity has been exhausted.

Analysis of volatiles

Native lignin is an odorless polymer that protects the wood composite in many ways. Among them is a thermally induced charring at high temperature that involves some volatilization [60]. When lignin is removed from pulp fibers during kraft pulping, it is modified with reduced sulfur that results in a low level (<2.5% sulfur) of mercaptan (thiol) formation [2] at the benzylic carbon position. Exposure of kraft lignin and its derivatives to temperatures typically used in some melt-processing operations might therefore result in the release of malodorous volatiles. This was apparent with the melt-blown film samples, but much less so with more solid products generated by injection-molding at HPL contents as high as 50%. An analysis of the headspace of film samples stored in a closed container for an extended period for sulfur-containing volatiles produced the results summarized in **Fig. 10** and **Table I**. The analysis identified the usual compounds known to be associated with kraft pulping, plus a minor ingredient, propylene sulfide (#5 in Table I), that might originate from the release of propoxylated thiol groups.

LIGNIN PRODUCTS

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ABOUT THE AUTHORS

Lignin is Earth's most underutilized sustainable organic resource. It is separated from plant biomaterials in delignification processes leading, among others, to pulp and paper and cellulosic ethanol products. Its isolation as aromatic (brown) polymer of high purity has become technically and economically feasible worldwide. When repurposed on the molecular level in such plastic commodity products as packaging films, it retains its native properties of high modulus (stiffness builder), bio-degradability, and photo-degradability. This has been demonstrated in a series of commercial products described in this paper.

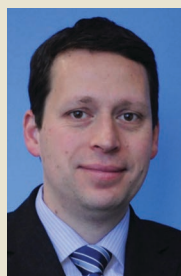
The first author (Wolfgang Glasser) has worked for 40+ years on the use of lignin in structural materials, mostly thermosetting and thermoplastic polymers of all types. One focus of this work was the understanding of (a) lignin's glass-to-rubber transition at target temperature levels by chemical modification, and (b) its flow, solubility, and compatibility properties in association with other macromolecules, natural and synthetic.

The major obstacle to lignin use in structural materials has been its notorious intractability. This required (a) the development of an in-depth understanding of the structure-property-performance relationship that makes melt-blowing and blend compatibility possible, and (b) finding a modification method that is sufficiently simple and affordable to be used on tonnage scale.

One of the interesting challenges of this study



Glasser



Loos



Cox



Cao

was the process of transferring research explored (and demonstrated) on laboratory bench-scale to industrial scale within a short time.

Pulp and paper mills that are often limited by chemical recovery capacity can profitably extend this capacity by the recovery of isolated lignin (or its modified derivatives), which are useful in sustainable and biodegradable components of polymeric materials.

The next step in this research is to incorporate the process of isolation/modification into existing mill operations on-site, and to extend product use to other polymeric materials, thermosets (such as phenolics, epoxies and polyurethanes), and thermoplastics (other than biodegradable polyesters, such as polyolefins and PVC).

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