

Sustainable Green Hybrids of Polyolefins and Lignin Yield Major Improvements in Mechanical Properties When Prepared via Solid-State Shear Pulverization

Krishnan A. Iyer[†] and John M. Torkelson^{*,†,‡}[†]Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States[‡]Department of Materials Science and Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

S Supporting Information



ABSTRACT: Lignin, a byproduct of paper and pulp industries, is a sustainable, inexpensive biomaterial with potential as composite filler. Past research on polyolefin/lignin composites made by melt processing has led to modest increases in Young's modulus and drastic reductions in tensile strength and elongation at break relative to neat polymer. Here, green hybrids of low density polyethylene (LDPE) and polypropylene (PP) with 5–30 wt % lignin are made by solid-state shear pulverization (SSSP). Microscopy shows that SSSP leads to superior lignin dispersion and suppressed degradation when compared to melt-mixed composites reported in the literature. Composites made by SSSP exhibit major improvements in Young's modulus (81% and 62% increases for 30 wt % lignin in LDPE and PP, respectively, relative to neat polymer), tensile strength equal to or better than that of neat LDPE and near that of neat PP, and much better strain at break than reported in the literature for polyolefin/lignin composites. The SSSP-produced hybrids exhibit major increases in hardness, with 70/30 wt % PP/lignin hybrids reaching values near that of polycarbonate. Well-dispersed lignin improves LDPE and PP thermo-oxidative stability as shown by thermogravimetric analysis (~ 35 °C increase in 20% mass loss temperature in air with 20 wt % lignin addition) and isothermal shear flow rheology. Lastly, SSSP-processed composites exhibit slightly improved crystallizability and melt viscosities at moderate to high shear rates that differ relatively little from those of neat LDPE and PP.

KEYWORDS: Lignin, Composites, Polypropylene, Polyethylene, Extrusion, Antioxidant, Tensile properties, Rheology

INTRODUCTION

There has been scientific and commercial interest in producing green polymer composites using natural fibers, such as coir, jute, sisal, hemp, flax, etc., for decades.^{1–12} Synthetic organic fillers derived from nature (often after chemical modification) have also been the subject of considerable focus in producing polymer hybrids; such fillers include cellulose nanocrystals, microcrystalline cellulose, and starch.^{13–16} Economic and environmental factors have provoked renewed interest in producing green hybrids with organic and inorganic fillers without chemical modification; such fillers are based on waste materials or byproducts from agricultural or municipal sources such as rice husk ash, eggshell, cardboard, and wood flour.^{17–23}

In addition to the benefit of sustainability, lignocellulosic fillers in thermoplastics offer other advantages, e.g., biodegradability, increased stiffness, low abrasion to equipment, and low density.^{17,23} However, incorporation of such fillers has led to inferior material properties including major reductions in ultimate strength and elongation at break and increase in moisture absorption. Degradation and viscosity increases are challenges commonly encountered with these fillers during processing.²⁴

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Lignin is an organic, aromatic macromolecule binding the cells, fibers, and vessels that constitute wood and lignified elements of plants.^{25–28} It is a highly cross-linked material based on a phenylpropanoid monomer structure. The rigidity and degree of cross-linking depend on the source from which it is obtained (softwood/hardwood) with typical molecular weights of 1000–20 000 g/mol.²⁵ The hydrophobic nature of lignin makes the outer cell wall of plants impermeable to water.²⁶ After cellulose, it is the most abundant renewable carbon source on earth. As a major waste, nearly 50 million tons of lignin are generated each year worldwide as a byproduct of the pulp and paper industries.²⁷ The vast majority of this lignin is burned onsite to provide steam for heat and power production. The abundant, low cost supply of lignin (~USD 150–200 per metric ton²⁸) makes it an excellent candidate as reinforcing filler for thermoplastics, hydrogels, thermosets, and rubber.^{26,29–52} In addition, a small amount of lignin is used as plasticizers, antioxidants, coatings, lubricants, and surfactants.^{24,26,29–34}

Literature studies of polyolefin/lignin composites have generally reported poor results, which have been attributed to the polar character and three-dimensional structure of lignin. The polar nature makes lignin inherently incompatible with nonpolar polyolefin matrices, which is postulated to complicate dispersion during melt processing.^{35–52} In particular, Young and co-workers noted challenges associated with melt processing of lignin in hybrids with polypropylene (PP).²⁴ They found that lignin underwent rapid degradation at temperatures above 170 °C, resulting in deterioration of some composite properties. Additional challenges arose from high-pressure flow during injection molding along with the production of air bubbles from volatiles.²⁴ Incorporation of 30 wt % lignin in PP by careful melt mixing led to a 37% decrease in tensile strength.²⁴ They suggested that retention of low molecular weight compounds in lignin was necessary to retain high composite elongation and hardness.²⁴ Alexy et al.³⁷ reported similar decreases in tensile strength (40% decrease for 30 wt % lignin in PP). Rusu et al.³⁶ employed Berstorff-type laboratory rollers to produce low density polyethylene (LDPE)/lignin hybrids; relative to neat LDPE, with 30 wt % lignin hybrids, they observed a 42% decrease in tensile strength and a 96% decrease in elongation at break. Hu et al.^{47,49} incorporated 20–40 wt % lignin in high density polyethylene (HDPE) by melt mixing at 160 °C using a Haake internal batch mixer and observed 19 to 51% decreases in tensile strength.

The inability of melt processing to provide sufficiently large stresses to disperse filler effectively results in lignin agglomeration, with poor stress transfer between filler and polymer. Researchers who have used melt processing to incorporate lignin into polyolefins have suggested that a solution to this problem is to improve interfacial lignin–polymer interactions by surface treatment of lignin or compatibilizer addition.^{35–52} Such methods add cost, reduce the green nature of the composite, and are unproven as a solution to lignin agglomeration.

Solid-state processing methods impart extraordinarily large compressive and shear forces when compared to conventional melt processing.⁵³ Previously, batch solid-state processes, e.g., pan milling and ball milling, have been employed to achieve good filler dispersion by exposing blends and hybrids to high forces and stresses.^{32,54–56} The continuous, industrially scalable solid-state process method called solid-state shear pulverization (SSSP) has successfully produced well-dispersed blends and

hybrids that are very challenging or impossible to produce by conventional melt processing.^{13,14,16–18,56–66} The SSSP process is a modification of twin-screw extrusion in which materials are cooled rather than heated and are processed below their glass transition if amorphous or their melt transition if semicrystalline. This process has been used to fabricate in situ compatibilized immiscible blends and quasi-nanostructured immiscible blends.^{57–59} In addition, well-mixed thermodynamically compatible blends of polyethylene and ultrahigh molecular weight polyethylene have been produced by SSSP, overcoming the issue of extraordinary viscosity mismatch when attempts at mixing are done via melt processing.⁶⁰ SSSP can also be used to achieve excellent dispersion and exfoliation of commercial carbon-based nanofillers from bundled carbon nanotubes to graphite.^{61–63} The near-ambient temperature conditions of SSSP have facilitated maleic anhydride or ester functionalization of PP and the production of branched PP without large molecular weight reduction that typically accompanies postpolymerization modification by melt processing.^{64–66} Recently, SSSP has also been used to produce green polymer composites with fillers and nanofillers based on agricultural and municipal sources, e.g., rice husk ash, soy flour, eggshells, and cellulose nanocrystals.^{13,17–19,67}

Here, we employ SSSP for the production of sustainable hybrids of LDPE and PP with 5–30 wt % kraft lignin and perform morphological, mechanical, crystallization, thermal degradation, and rheological characterization. To demonstrate the efficacy of SSSP in achieving superior filler dispersion and material properties, comparisons are drawn to literature studies that have produced related composites by melt processing. These comparisons indicate that the green polyolefin/kraft lignin composites made by SSSP significantly outperform related composites made by melt processing and that these improvements can be achieved by SSSP with unmodified lignin and without the need for compatibilizers or additional chemistry.

■ EXPERIMENTAL SECTION

Materials. Low density polyethylene (ExxonMobil, density = 0.919 g/cm³, and MFI = 1.1 g/10 min) and polypropylene (Total Petrochemicals, density = 0.905 g/cm³, and MFI = 9 g/10 min) were used as received. Low sulfonate content kraft lignin (molecular weight = ~10 000 g/mol, 4% sulfur, as reported by the supplier) was obtained from SigmaAldrich and used as received.

Preparation of Green Polyolefin/Lignin Hybrids. Polyolefin pellets (LDPE or PP) were fed to a Berstorff ZE-25 pulverizer with a K-tron S-60 feeder at a feed rate of ~100 g/h. (Although the ZE-25 pulverizer is a pilot-plant/research-scale instrument, polyolefins have been processed at Northwestern University with a commercial scale apparatus at rates exceeding 150 kg/h.¹⁷) Lignin was added to the pulverizer using a powder feeder (Brabender Technologies Inc. DDSR 12-1 volumetric feeder) at different feed rates to obtain the desired filler content (5–30 wt %) in the final composite. The pellets and lignin were pulverized at a screw speed of 200 rpm, with the pulverizer barrels cooled by a recirculating ethylene glycol/water mix (–7 °C, Budzar industries WC-3 chiller). A screw design able to impart high specific energy to the materials (see ref 53 for a detailed description of screw design and energy inputs) was employed. Additional details of the apparatus and processing conditions are available in refs 13, 17, and 18. For comparison, a composite sample of PP with 10 wt % lignin was prepared by melt processing using an Atlas Electronic Devices MiniMax molder (cup-and-rotor mixer) at maximum rotor speed of 140 rpm with three steel balls in the cup to provide chaotic mixing. Mixing was done for 15 min at 200 °C. For characterization of hybrids, field-emission scanning electron microscopy (FE-SEM) samples were

prepared by melting and extruding the composite with a MiniMax molder. Morphologies of cryo-fractured sections of the composites were obtained via a SU8030 instrument after sputtering (Denton DeskIII) with gold/palladium. FE-SEM images of as-received lignin samples were acquired after casting from water onto clean Si wafers.

Uniaxial tensile test samples of ~ 0.7 mm thickness were prepared by compression molding using a PHI (Model 0230C-X1) press at 180 or 140 °C depending on the matrix polymer for 5 min with 5 ton ram force. Dog-bone shaped specimens were cut using a Dewes-Gumbs die and tested using an MTS Sintech 2S tensile tester according to ASTM D1708 with a 5 kN load cell using a crosshead speed of 50 mm/min.

Polymer crystallization in the composite was characterized by differential scanning calorimetry (DSC; Mettler-Toledo 822e instrument). After the samples were heated above the melt temperature, a 10 °C/min cooling rate was used to determine the nonisothermal crystallization onset temperature. The percent polymer crystallinity was obtained by dividing the specific enthalpy from the area associated with the crystallization part of the nonisothermal cooling curve by the polymer mass fraction; this value was divided by the theoretical heat of fusion for neat polyethylene or PP of 285.9 and 207.1 J/g, respectively.^{68,69} Isothermal crystallization half-times for PP/lignin composites were determined at 140 °C after cooling from the melt at 40 °C/min.

Thermo-oxidative degradation was monitored by thermogravimetric analysis (Mettler Toledo 851e) under air. Samples weighing ~ 5 mg were heated to 700 °C with a 10 °C/min heating ramp. To understand the effectiveness of lignin as a thermal stabilizer for polyolefins under isothermal shear melt flow, shear storage modulus was monitored as a function of time at 180 °C using small amplitude oscillatory shear measurements at 5 rad/s (TA Instruments ARES rheometer; 25 mm parallel plate fixture). The magnitude of complex viscosity for LDPE and LDPE/lignin composites was also measured as a function of frequency from 0.01 to 100 rad/s at 160 °C to understand the processability of SSSP-made composites.

RESULTS AND DISCUSSION

Dispersion in and Morphology of Polyolefin/Lignin Hybrids. Previous researchers have noted major difficulties with achieving good dispersion of lignin in polyolefins by melt mixing. For example, Young and co-workers²⁴ observed severe lignin filler degradation caused by long mixing times and high temperatures used with melt mixing by twin-screw extrusion. Severe filler agglomeration was also evident. With injection molding, the high viscosity and highly nonuniform nature of the polyolefin/lignin hybrids led to problems including blotched surfaces and microvoids in the injection molded output. Consistent with literature reports of poor dispersion obtained via melt mixing, 90/10 wt % PP/lignin composites produced via melt processing in this study exhibit significant filler agglomeration with agglomerates approaching ~ 1 mm in size and visible to the naked eye (see Figure S1a in the Supporting Information). In addition, the photographs make evident the presence of numerous voids and air bubbles as a consequence of filler degradation. To overcome such issues, addition of compatibilizers or surface modification of lignin has been suggested by various researchers as being necessary for improving the processability and dispersion of polyolefin/lignin composites.^{35–52}

Figure 1 shows images of compression-molded films (~ 0.5 mm thickness) of SSSP-processed LDPE/lignin and PP/lignin composites that contain 5 and 10 wt % lignin filler. In contrast to the poor dispersion achieved with conventional melt processing (see Figure S1a in the Supporting Information), polyolefin/lignin composites made by SSSP in this study show excellent dispersion of lignin with uniformly tan to brownish color; no particle agglomerates are visible to the naked eye for

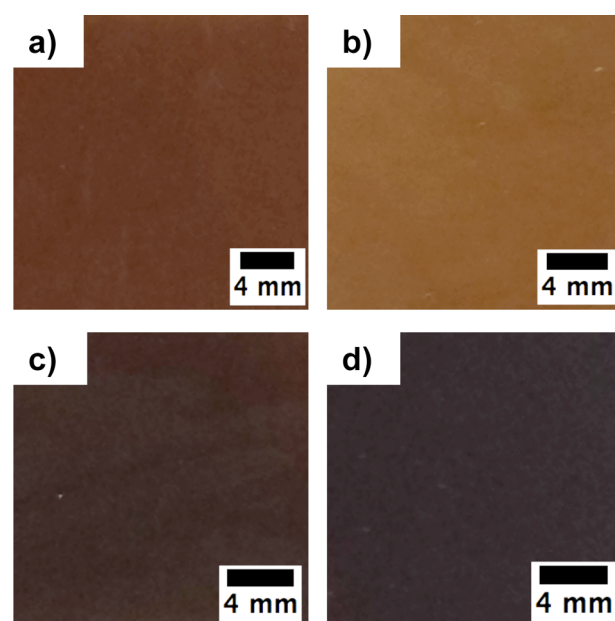


Figure 1. Photographs of LDPE and PP composites with lignin prepared by SSSP: (a) 95/5 wt % LDPE/lignin, (b) 95/5 wt % PP/lignin, (c) 90/10 wt % LDPE/lignin, and (d) 90/10 wt % PP/lignin.

lignin loadings as high as 30 wt %. The very large shear forces and stresses provided by the solid-state nature of SSSP result in break up and dispersion of lignin particles. In addition to superior dispersion, the near-ambient temperature conditions employed in SSSP prevent lignin degradation during the mixing stage. Thus, SSSP can produce polyolefin/lignin composites with very good filler dispersion in the absence of favorable polymer/filler interfacial interactions or compatibilizing agents.

Figure 2a shows an FE-SEM image of as-received lignin. Lignin agglomerates can be as large as ~ 100 – 200 μm in size because of strong interparticle affinity. The FE-SEM images of cryofractured cross sections of SSSP-processed polyolefin/lignin composites reveal that lignin particles are wetted into the polyolefin matrix (Figure 2b,c). In addition, the original, severely agglomerated lignin particles have undergone major size reduction, with some particle sizes less than or equal to 1 μm , and are well distributed in the matrix. These results demonstrate that SSSP can achieve excellent lignin dispersion without chemical modification or additives.

Mechanical Properties of Polyolefin/Lignin Composites: Tensile. Tables 1 and 2 summarize the effect of lignin on the mechanical properties of LDPE/lignin and PP/lignin composites produced by SSSP, respectively. The excellent dispersion of hard, rigid lignin in the matrix by SSSP leads to major improvements in Young's modulus of the composites. For example, relative to neat LDPE, incorporation of 10 wt % lignin leads to a 39% increase in modulus whereas 30 wt % lignin leads to an 81% increase. Similarly, relative to neat PP, the PP/lignin composites exhibit 15% and 62% increases in modulus at 5 and 30 wt % lignin contents, respectively. The yield strength of LDPE/lignin composites shows a 21% increase relative to neat polymer for 10 wt % lignin and is equal to that of neat LDPE at other lignin loadings. Relative to neat PP, the 95/5 wt % PP/lignin composite exhibits a 10% increase in yield strength while the 70/30 wt % PP/lignin composite exhibits an 18% decrease. Interestingly, the 95/5 and 90/10 wt % LDPE/lignin composites exhibit elongation at

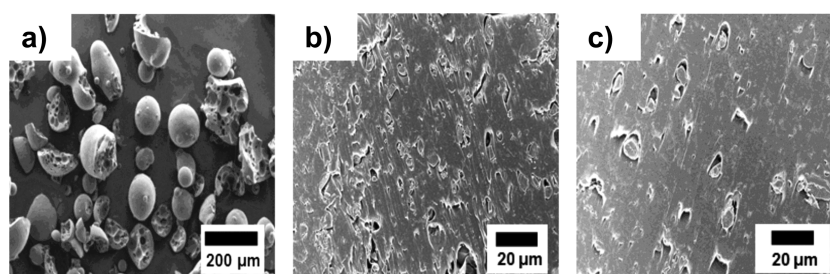


Figure 2. Field-emission scanning electron micrographs of (a) as-received lignin, (b) 80/20 wt % LDPE/lignin prepared by SSSP, and (c) 80/20 wt % PP/lignin prepared by SSSP.

Table 1. Mechanical Properties of LDPE/Lignin Composites Produced by SSSP

sample	Young's modulus E (MPa)	yield strength σ (MPa)	elongation at break ϵ (%)
neat LDPE	155 ± 5	10.0 ± 0.3	500 ± 30
95/5 wt % LDPE/lignin	195 ± 15	10.3 ± 0.5	500 ± 10
90/10 wt % LDPE/lignin	215 ± 10	12.1 ± 0.6	450 ± 30
80/20 wt % LDPE/lignin	230 ± 10	10.4 ± 1.0	370 ± 20
70/30 wt % LDPE/lignin	280 ± 20	10.0 ± 1.2	180 ± 40

Table 2. Mechanical Properties of PP/Lignin Composites Produced by SSSP

sample	Young's modulus E (MPa)	yield strength σ (MPa)	elongation at break ϵ (%)
neat PP	1000 ± 50	32.0 ± 0.2	700 ± 40
95/5 wt % PP/lignin	1150 ± 50	35.1 ± 1.0	680 ± 40
90/10 wt % PP/lignin	1450 ± 70	31.2 ± 0.6	150 ± 20
80/20 wt % PP/lignin	1550 ± 30	27.8 ± 0.7	50 ± 10
70/30 wt % PP/lignin	1620 ± 50	26.1 ± 0.2	30 ± 8

break values that are unchanged within error from that of neat LDPE (500% elongation at break), and the 70/30 wt % LDPE/lignin composite retains an elongation at break value of 180%. Similarly, the 95/5 wt % PP/lignin composite exhibits the same elongation at break within error as neat PP (700% elongation at break). Due to some degradation during melt-state compression molding of PP composite tensile samples, the 90/10 wt % PP/lignin composite has an elongation at break value of 150% and the 70/30 wt % PP/lignin composite a value of 30%. Nevertheless, all composite materials made by SSSP retain ductile behavior after melt processing into tensile specimens.

Comparison with Literature Reports of Mechanical Properties of Polyolefin/Pristine Lignin Composites. The most dramatic deterioration in mechanical properties of polyolefin/lignin composites made by melt processing occurs with tensile strength and elongation at break, which are strongly influenced by filler dispersion and degradation. For example, Rusu et al.³⁶ reported poor outcomes for both tensile strength and elongation at break values for LDPE/lignin hybrids made by melt mixing. Relative to neat LDPE with tensile strength of ~10.6 MPa and elongation at break of ~730%, tensile strength decreased by ~22 and ~40% and elongation at break by ~85 and ~96% in LDPE composites with 5 and 30 wt % lignin, respectively. Similarly poor outcomes have been reported for HDPE/lignin hybrids made by melt mixing. Relative to neat HDPE with tensile strength of 28.6 MPa and elongation at break of 1167%, Hu et al.⁴⁹ reported 19% and 99% decreases in tensile strength and elongation at break with 80/20 wt %

HDPE/lignin hybrids. In contrast, LDPE composites made by SSSP exhibit tensile strengths that increase (21% increase with 10 wt % lignin) or remain unchanged from that of neat LDPE for other filler loadings. Interestingly, the 95/5 and 90/10 wt % LDPE/lignin composites made by SSSP had an elongation at break within error unchanged from that of neat LDPE, and the 70/30 wt % LDPE/lignin composite showed only a 64% decrease in elongation at break to a value of 180%.

Poor outcomes have also been reported in the literature for tensile strength of PP/lignin composites made by melt mixing. Relative to neat PP, Alexy et al.³⁷ reported 14% and 40% decreases in tensile strength with 90/10 and 70/30 wt % PP/lignin composites, respectively. For 70/30 wt % PP/lignin composites, Toriz et al.²⁴ reported a 37% decrease relative to neat PP. In contrast, when made by SSSP, 95/5 wt % PP/lignin composites exhibit tensile strength that is 10% higher than that of neat PP, 90/10 wt % PP/lignin composites exhibit tensile strength identical within error to that of neat PP, and 70/30 wt % PP/lignin composites exhibit only an 18% decrease. In good agreement with literature studies, 90/10 wt % PP/lignin composites produced by melt mixing in this study (see details in the Supporting Information) showed 25–34% decreases in yield strength with large sample-to-sample variability depending on the choice of specimens. No comparison of the elongation at break values of the SSSP-processed PP/lignin composites can be made to literature values for hybrids made by melt mixing. In spite of the fact that tensile strengths for PP/lignin hybrids have been reported by Alexy et al.³⁷ and Toriz et al.,²⁴ neither group reported elongation at break values. However, the 90/10 wt % PP/lignin composites produced in this study by melt processing showed a 7% elongation at break compared to 150% exhibited by a 90/10 wt % PP/lignin composite produced by SSSP.

In contrast to the substantial reductions relative to neat polymer in tensile strength and elongation at break reported for polyolefin/lignin composites made by melt mixing, values of Young's modulus generally increase in such melt-mixed composites. Based on reports of other melt-mixed polymer composites, it is expected that addition of a poorly dispersed, high modulus filler to a significantly less rigid polymer matrix will lead to an increase in Young's modulus; examples include melt-mixed composites of PP with graphite,^{62,63} carbon nanotubes,⁶¹ starch,¹⁶ rice husk ash,¹⁷ soy flour,⁶⁷ and eggshell.¹⁸

Rusu et al.³⁶ prepared LDPE/lignin composites by melt compounding for 18–20 min using an LDPE sample with a reportedly low Young's modulus of 80 MPa. Relative to neat LDPE, they reported a ~110% increase in modulus to ~170 MPa with 10 wt % lignin and a ~240% increase to ~270 MPa with 30 wt % lignin. In comparison, relative to the stiffer LDPE

used in the current study with Young's modulus of 155 MPa, well-dispersed composites of LDPE/lignin produced via SSSP displayed a 39% increase in modulus to 215 MPa with 10 wt % lignin and an 81% increase to 280 MPa with 30 wt % lignin. Thus, based on raw values of Young's modulus, the SSSP-processed LDPE composites exhibit values that are better than those reported in the literature for melt-mixed composites over a range of lignin content. Compared to the present study, the reportedly higher percentage improvement in modulus by Rusu et al.³⁶ may be rationalized in part based on the marked difference in stiffness of the matrix polymers employed in the two studies. (However, we note here that the incredible percentage enhancements in Young's modulus obtained by Rusu et al.³⁶ are questionable at several levels. First, they reported that the LDPE/lignin composite modulus was essentially independent of lignin content from 5 to 20 wt %, with a value of ~ 170 MPa corresponding to an apparent $\sim 110\%$ increase in modulus. A trend with increasing lignin content would be expected, especially since they reported yet higher modulus values when lignin content exceeds 20 wt %. Second, such a large modulus enhancement at 5 wt % lignin is difficult to resolve with many reports of smaller modulus enhancements with polyolefin composites made by melt mixing or via SSSP, which employs stiffer filler than lignin, e.g., with graphite nanofiller^{62,63} or cellulose nanocrystals.¹³ Third, and possibly most important, the neat LDPE (ARPECHIM) used by Rusu et al.³⁶ was reported as having MFI = 1.48 g/10 min but a modulus of 80 MPa. Such a low modulus value is unexpected for an LDPE sample with that MFI value. For example, an LDPE sample (Braskem) reportedly has MFI = 30 g/10 min and a modulus of 80 MPa.⁷⁰ We report a 155 MPa modulus for LDPE with MFI = 1.1 g/10 min, and an LDPE sample (ARPECHIM) with MFI = 2.02 g/10 min has been reported as having a modulus of 200 MPa.⁷¹ These results suggest that Rusu et al.³⁶ may have reported a neat LDPE modulus significantly below its true value, which would provide an explanation for the extraordinarily large percentage enhancements in modulus they reported with lignin addition.)

Hu et al.⁴⁹ produced HDPE composites with 20 wt % lignin by melt mixing and reported a 15% increase in Young's modulus relative to neat HDPE, from 502 to 577 MPa. The 80/20 wt % LDPE/lignin composite produced by SSSP exhibited a 48% increase in modulus relative to neat LDPE, from 155 to 230 MPa. Comparisons with literature data for PP/lignin composites made by melt processing reveal that SSSP processing yields better enhancement of Young's modulus than melt mixing. With melt-mixed PP/lignin composites, Toriz et al.²⁴ reported the same Young's modulus within (large) error for neat PP and 90/10 wt % PP/lignin composites. For 80/20 and 70/30 wt % PP/lignin composites they reported 21 and 44% increases in Young's modulus relative to neat PP. We note here that composites of polyolefin/lignin made by melt processing exhibit large sample-to-sample variability in material properties as a direct consequence of poor dispersion. Depending on the choice of specimens (location where voids, bubbles, or agglomerates are present), a 90/10 wt % PP/lignin composite produced by melt processing in this study showed either a 20% increase or no improvement in modulus values compared to neat PP. These results contrast significantly with those obtained by SSSP, with 15%, 45%, and 55% increases in Young's modulus with 10, 20, and 30 wt % lignin content, respectively, relative to neat PP.

Relative to neat polymer, literature results for melt-mixed polyolefin/lignin composites generally indicate some enhancement in modulus but significant deterioration in tensile strength and massive reduction in elongation at break. Use of SSSP leads to lignin agglomerate breakup and superior dispersion, which in turn result in hybrids with either no reduction or small enhancement in tensile strength, as with LDPE hybrids, or small enhancement or small reduction in tensile strength, as with PP hybrids. The major deterioration of elongation at break with lignin incorporation by melt mixing is fully suppressed by SSSP at 5–10 wt % lignin in LDPE and 5 wt % lignin in PP and is significantly suppressed at higher lignin content. Filler agglomerate break up and dispersion have a much smaller effect on Young's modulus than on other tensile properties. Nevertheless, with the exception of a questionable report by Rusu et al.,³⁶ SSSP leads to composites with Young's modulus values comparable to or better than those of melt-mixed polyolefin/lignin composites. Thus, relative to literature results, excellent dispersion of pristine lignin by SSSP leads to polyolefin composites with major improvements in tensile strength and elongation at break and, with one exception, comparable or higher values of Young's modulus.

Mechanical Properties of Polyolefin/Lignin Composites: Hardness. As shown in Figure 3, major increases in

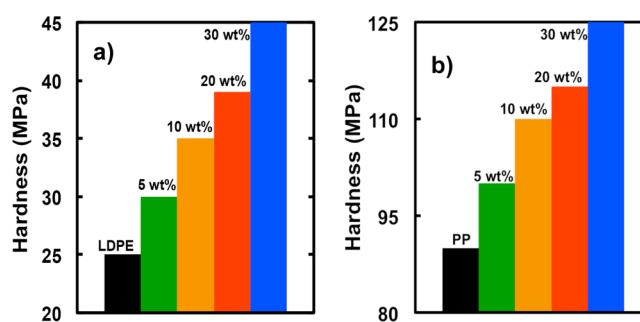


Figure 3. Vickers hardness values for polyolefin/lignin composites prepared by SSSP: (a) LDPE/lignin values as a function of lignin content, and (b) PP/lignin values as a function of lignin content. (Standard deviations for hardness values are 0.2 MPa.)

Vickers hardness are obtained upon incorporation of well-dispersed lignin in LDPE and PP. Addition of as little as 5 wt % lignin in LDPE and PP leads to significant increases in surface hardness, and 90/10 wt % LDPE/lignin and PP/lignin composites have Vickers hardness values that are 10 and 20 MPa higher than those of neat LDPE and neat PP, respectively. 30 wt % loadings of lignin increase the surface hardness by 20 and 35 MPa for LDPE and PP composites, respectively. In the case of PP/lignin composites, Figure 3b shows that effective dispersion of ~ 30 wt % lignin can lead to surface hardness that is competitive with more expensive, glassy engineering thermoplastics such as polycarbonate (Vickers hardness = 131 MPa¹⁷). In contrast to the major enhancements in hardness shown here with lignin composites produced by SSSP, Hu et al.⁴⁹ reported no improvement within error in hardness (Shore D) for HDPE/lignin composites prepared by melt mixing.

Crystallinity and Crystallization Behavior of Polyolefin/Lignin Composites. Table 3 compares crystallization behavior of polyolefin/lignin composites produced by SSSP with neat polymer. Small enhancements in nonisothermal onset crystallization temperature ($T_{c,onset}$) are observed in composites.

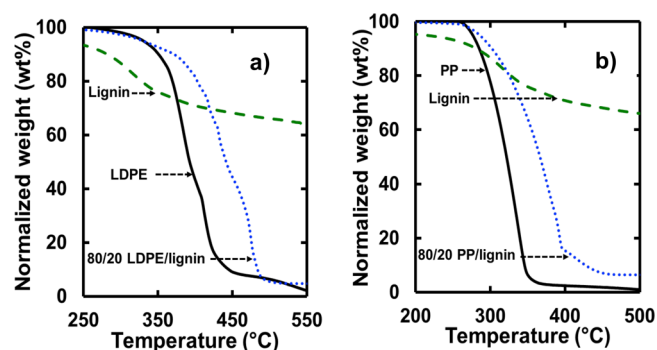
Table 3. Crystallization Behavior of LDPE/Lignin and PP/Lignin Composites Produced by SSSP

sample	onset temperature for crystallization $T_{c,onset}$ (°C)	percent polymer crystallinity X_c (%)	isothermal crystallization half time measured at 140 °C $\tau_{1/2}$ (min)
neat LDPE	97	30	
95/5 wt % LDPE/lignin	97	31	
90/10 wt % LDPE/lignin	98	30	
80/20 wt % LDPE/lignin	99	33	
70/30 wt % LDPE/lignin	97	35	
neat PP	122	48	33
95/5 wt % PP/lignin	124	52	28
90/10 wt % PP/lignin	126	52	27
80/20 wt % PP/lignin	127	52	25
70/30 wt % PP/lignin	127	50	20

For example, compared to neat polymer, 80/20 wt % LDPE/lignin composites show a 2 °C increase in $T_{c,onset}$ whereas 80/20 wt % PP/lignin composites show a 5 °C increase. Composite materials made by SSSP exhibit a significant increase in LDPE crystallinity from 30% for neat polymer to 35% for the 70/30 wt % LDPE/lignin composite. Compared to neat PP with 48% crystallinity, PP/lignin composites exhibit PP crystallinities of 50–52%. Incorporation of lignin leads to small improvement in crystallization rate as measured by isothermal crystallization half time ($\tau_{1/2}$); at 140 °C, $\tau_{1/2}$ = 20 min for a 70/30 wt % PP/lignin composite and 33 min for neat PP. Canetti et al.³⁸ studied the crystallization behavior of PP/hydrolytic lignin composites made by melt mixing and noted a 7–9 °C increase in $T_{c,onset}$ with PP crystallinity levels in the composites varying from 55 to 67% relative to neat PP crystallinity of 60%. They also indicated that under some processing conditions and lignin levels, both α - and β -crystalline forms of PP are present. (The effect of SSSP on the crystalline form of PP in PP composites is a subject for future study.)

Past research with SSSP has employed a variety of fillers with much larger effect on polyolefin crystallization behavior. In comparison with carbon-based and some bio-based fillers, well-dispersed lignin has a relatively small effect on improving the crystallization rate of polyolefins.^{13,17,18,61–63} For example, for composites made by SSSP, $T_{c,onset}$ values for PP crystallization increased by 21 °C with 2.5 wt % graphite,⁶² 8 °C with 19 wt % rice husk ash,¹⁷ 11 °C with 20 wt % eggshell,¹⁸ and 7 °C with 5 wt % cellulose nanocrystal.¹³ Similarly, relative to PP/lignin composites, much larger effects on $\tau_{1/2}$ were reported when graphite, carbon nanotubes, rice husk ash, eggshell, and cellulose nanocrystals were used as filler.^{13,17,18,61–63}

Thermo-oxidative Stability of Polyolefin/Lignin: Thermogravimetric Analysis (TGA). Figure 4 shows the thermal degradation behavior of 80/20 wt % LDPE/lignin and PP/lignin composites produced by SSSP as well as neat lignin, LDPE, and PP as measured by TGA at a heating rate of 10 °C/min in air. We define $T_{10\%}$ and $T_{20\%}$ as the temperatures corresponding to 10 and 20% mass loss. As shown in Figure 4a, $T_{10\%}$ = 346 °C and $T_{20\%}$ = 366 °C for neat LDPE. Neat lignin is less thermally stable in air than LDPE, with $T_{10\%}$ = 282 °C and $T_{20\%}$ = 327 °C. Nevertheless, relative to neat LDPE, incorporation of 20 wt % lignin in LDPE results in an 18 °C increase in $T_{10\%}$ and a 37 °C increase in $T_{20\%}$, which indicates

**Figure 4.** Thermal degradation behavior of neat polymer, lignin, and composites prepared by SSSP in air: (a) LDPE/lignin and (b) PP/lignin.

that lignin is an antioxidant for LDPE thermo-oxidative degradation. This is consistent with results from Sadeghifar et al.⁵⁰ who observed up to a 50 °C increase in oxidation induction temperature relative to neat polymer of medium density polyethylene/lignin composites measured by DSC. By modifying the phenolic structure in lignin with methyl groups, they also demonstrated the vital role of phenolic OH groups in lignin in providing antioxidant stability to polyethylene.

Figure 4b compares the degradation behavior of 80/20 wt % PP/lignin composite to that of neat PP in air. Polypropylene is more susceptible to oxidative degradation than LDPE with $T_{10\%}$ = 275 °C and $T_{20\%}$ = 296 °C. As seen from Figure 4b, an 80/20 wt % PP/lignin composite exhibits significant improvement in its thermo-oxidative stability relative to neat PP, with a 28 °C increase in $T_{10\%}$ and a 34 °C increase in $T_{20\%}$. These results indicate that lignin significantly improves the oxidative stability of PP. A similar conclusion was reached by Canetti et al.⁴¹ who observed up to 25 °C increase relative to neat polymer in the onset degradation temperature for 15 wt % lignin in PP. Pouteau et al.⁴⁰ showed that the ability of lignin to act as an antioxidant for polymers depends strongly on the presence of phenolic groups and dispersion. Consistent with large sample-to-sample variability observed in mechanical properties of 90/10 wt % PP/lignin composites produced via melt processing in the current study, these composites show either reduced thermal stability or only modest increments depending on the choice of specimen (voids, bubbles, or agglomerates). In comparison, SSSP processing brings out the potential of lignin in being a very effective antioxidant for polymers by achieving superior filler dispersion (data given in the Supporting Information).

Thermo-oxidative Stability of Polyolefin/Lignin: Rheological Analysis. Thermal degradation of polymers is a function of both temperature and time. In addition, degradation is influenced by the forces and stresses that the material experiences during melt processing. Besides being affected by mass loss at levels as small as 1%, material properties can undergo changes by molecular weight reduction and/or branching and/or cross-linking that may accompany melt processing at elevated temperature. Thus, to illustrate the effectiveness of lignin in acting as a thermal stabilizer for polyolefins under isothermal melt flow, small amplitude oscillatory shear measurements were used to monitor time-dependent microstructural evolution during melt flow. Figure 5 shows the time-dependent normalized shear storage modulus for LDPE and an 80/20 wt % LDPE/lignin composite at 180 °C. (Values of storage modulus for neat polymer and the

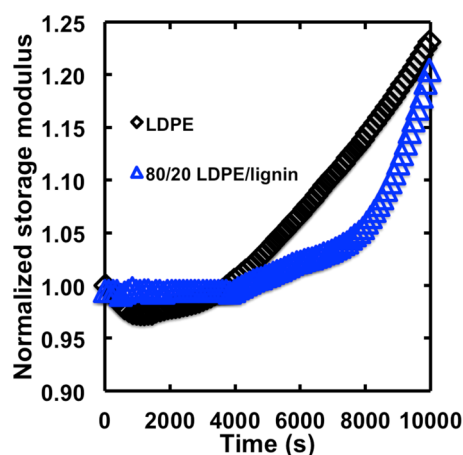


Figure 5. Time-dependent evolution of normalized shear storage modulus subject to small amplitude oscillatory shear at 180 °C for LDPE and 80/20 wt % LDPE/lignin composite prepared by SSSP. (Values of storage modulus for neat polymer and the composite are normalized by their respective values at the start of shear.)

composite are normalized by their respective values at the start of flow.) Low density polyethylene undergoes oxidative degradation by chain scission and subsequent branching.⁷² Figure 5 shows that LDPE initially exhibits a decrease in storage modulus with flow time resulting from chain scission; this is followed at ~ 2000 s by a significant increase in storage modulus with flow time resulting from chain branching. In comparison, the 80/20 wt % LDPE/lignin hybrid made by SSSP displays a constant shear storage modulus up to ~ 4000 s, i.e., there is no apparent degradation for more than an hour. Even after degradation becomes apparent in the LDPE/lignin composite, the increase in storage modulus is less than that in neat LDPE because of the ability of phenolic network structure in lignin to stabilize oxygen-based radicals in LDPE.

Shear-Rate Dependent Viscosity of Polyolefin/Lignin Hybrids. Figure 6 shows the magnitude of complex viscosity as

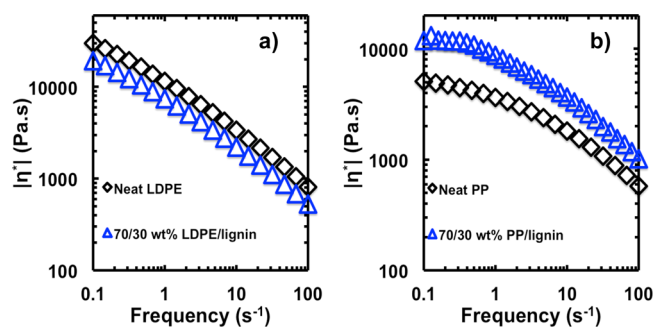


Figure 6. Magnitude of complex viscosity as a function of frequency: (a) neat LDPE and 70/30 wt % LDPE/lignin at 160 °C, (b) neat PP and 70/30 wt % PP/lignin at 200 °C.

a function of frequency for neat polymers and 70/30 wt % polyolefin/lignin composites at appropriate temperatures for melt processing. Based on the Cox–Merz rule, which indicates an equivalence between frequency in oscillatory shear measurements and shear rate in simple shear flow, Figure 6 is equivalent to a plot of shear viscosity as a function of shear rate.⁷³ Figure 6 shows that incorporating 30 wt % lignin in LDPE and PP results in relatively small changes in viscosity at shear rates of 0.1 to 100 s^{-1} . Most relevant for melt processing applications

are shear rates of $\sim 100 s^{-1}$, because shear rates near that value and higher are commonly employed in melt processing, e.g., twin-screw extrusion or injection molding. With the 70/30 wt % LDPE/lignin hybrid, viscosity at a shear rate of 100 s^{-1} is reduced by less than a factor of 2 relative to neat LDPE. A previous study of the effect of SSSP on the viscosity of neat LDPE indicated that SSSP resulted in a small reduction in LDPE viscosity, likely caused by chain scission, that increased with harshness of pulverization.⁷⁴ The 70/30 wt % PP/lignin hybrid exhibits a viscosity at a shear rate of 100 s^{-1} that is a factor of 2 higher than that of neat PP. Both the present and previous studies^{13,17,18,63} indicate that, due to excellent dispersion, SSSP can produce polyolefin composites with shear viscosity that is changed relatively little compared to neat polymer. Thus, little or no adjustment is needed in melt processing conditions for polyolefin composites made by SSSP relative to those for neat polymer.

CONCLUSIONS

Solid-state shear pulverization was used for the first time to produce polyolefin/lignin hybrids with up to 30 wt % lignin. The composites made by SSSP exhibit excellent lignin dispersion, much better than that achieved by conventional melt processing. Well-dispersed lignin results in major enhancement in Young's modulus, e.g., 81% and 62% increases for 70/30 wt % LDPE/lignin and PP/lignin hybrids, respectively, relative to neat polymer. Polyolefin/lignin composites show significant retention of tensile strength (the same as neat LDPE for 70/30 wt % LDPE/lignin or an 18% decrease in 70/30 wt % PP/lignin relative to neat PP) and remarkable elongation at break (180% for 70/30 wt % LDPE/lignin and 30% for 70/30 wt % PP/lignin). These tensile properties are significantly better than those reported in studies that produced similar hybrids by melt processing. Polyolefin/lignin hybrids made by SSSP show major improvements in surface hardness with increasing lignin content, achieving values close to that of polycarbonate, an engineering thermoplastic. These enhancements are achieved by SSSP without any surface modification of lignin or use of compatibilizers to improve compatibility between the polar lignin filler and the nonpolar polyolefin matrix.

Thermogravimetric analysis in air reveals that 20 wt % lignin incorporation results in exceptional thermo-oxidative stability (34–37 °C increase in 20% mass loss relative to neat polymer). This excellent thermo-oxidative stability is consistent with oxygen-centered radicals in polyolefins being stabilized by the phenolic network of lignin. The evolution of melt-state shear storage modulus also shows that lignin incorporation results in thermo-oxidative stabilization during isothermal melt flow. Additional rheological measurements reveal that 70/30 wt % polyolefin/lignin composites have shear viscosities that are changed by factors of 2 or less from that of neat polymer at shear rates relevant for melt processing.

ASSOCIATED CONTENT

Supporting Information

Additional characterization of PP/lignin composites made by melt processing and using the same PP and lignin samples as those used in making PP/lignin composites by SSSP. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*J. M. Torkelson. E-mail: j-torkelson@northwestern.edu.

Notes

The authors declare no competing financial interest.

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