

LIGNIN BIO-BASED MATERIAL IN UNSATURATED POLYESTER

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The potential utilization of lignin, as a natural-based material, in unsaturated polyester (UPE) has been investigated. Kraft (Indulin AT) and sulfite lignin (ArboSO1) samples from forestry biomass and their consistencies in UPE were evaluated by qualitative and quantitative methods. The tensile and impact properties of the cured UPE with and without lignins, as well as fracture surfaces, were also studied. The result indicated that the ash content is quite high for lignosulfonate ArboSO1. NMR spectra show significant differences almost in the entire spectral region for the two lignins. The aliphatic hydroxyl groups were found more uniform in Indulin AT than in ArboSO1. Indulin AT seems to have more pronounced condensed units than ArboSO1. The guaiacyl units in Indulin AT were found to be more uniform and of higher magnitude than in ArboSO1, similarly to free phenolic units. However, the terminal carboxylic content in ArboSO1 was found to be higher than in Indulin AT. The investigation by SEM showed that the particles of the two lignins are porous and have different sizes, mostly less than 100 µm. The addition of different concentrations of lignins increased the viscosity of UPE; however, the viscosity was still suitable for processing at the lignin loading levels. The results also indicated that the lignin types and loadings did influence the tensile properties, but not the impact property of the UPE. The modulus of UPE decreased almost linearly with the loading of ArboSO1 for both UPEs. On the other hand, the modulus of UPE leveled up for Indulin AT only at 10 and 20 wt% loading. The positive effect of adding 10 wt% of both lignin samples on the tensile strength of UPE was demonstrated. The presence of lignin affected the fracture surface of the UPE systems, regardless of the lignin type and consistency. This novel approach could reduce costs and environmental impact of manufacturing UPE products, while improving their quality.

Keywords: lignin, unsaturated polyester, biomaterial, biocomposite**INTRODUCTION**

Polymer composites have received growing attention in several industries, such as plastics, automotive, aviation, textiles, *etc.* In the past decades, inorganic fillers have been utilized exclusively in polymer composites manufacturing. A commercial example of commonly used thermosetting matrix is unsaturated polyester (UPE). UPE has various properties, among other types of thermosets, such as its relative affordability, moldability at room temperature, and resistance to thermal and weather conditions.^{1,2}

With ever-increasing global concern over climate changes, irreversible environmental damages, and rapid depletion of non-renewable resources, there is a strong worldwide interest in developing suitable technologies that can derive

chemicals and materials from renewable biomass, such as lignin in polymer composites formulation. Lignin is a class of complex organic polymers that form key structural materials in the support tissues of vascular plants and some algae.³ Lignins are particularly important in the formation of cell walls, especially in wood and bark, because they lend rigidity and resistance to rotting. Chemically, lignins are considered as cross-linked phenolic polymers.⁴ Lignin is the second most naturally abundant bio-polymeric substance after cellulose; the natural polymer makes up to 40% of forestry and up to 30% of certain ligno-cellulosic materials in agricultural residues.^{5,6} Several methods, such as kraft process, alkaline treatment, steam explosion and organosolv processes, are utilized for obtaining

lignin. Although lignin is an attractive abundant and relatively inexpensive biomass resource, due to its complex nature and undefined chemical structure, the industrial applications of lignin are rather limited. However, based on its interesting functionalities and properties, lignin offers perspectives for higher added value applications in renewable products.^{7,8}

Presently, lignin is utilized almost exclusively as fuel to power the evaporators of the chemical recovery processes and the liquor concentration system of pulp mills.^{9,10} In recent years, much attention has been devoted to the possibility of replacing petrochemical-based polymer, filler and reinforcement materials by bio-based materials. Due to the competitive properties offered by biopolymers used as matrix, filler or reinforcement, these materials have been considered as the most promising substitute for petrochemical-based polymers.¹¹⁻¹³ In addition, lignin used as matrix, filler or reinforcement may provide special functional properties, such as oxidation resistance, stabilization, biodegradability, anti-fungal and antibiotic activity and UV-absorption resistance, to polymer composites.¹⁴

Research interest has been focused on utilizing lignin as bio-polymer or bio-filler¹⁵⁻¹⁷ in the formulation and preparation of biomaterials. Restrictively, lignin has been used as filler material in thermoplastic polymers,^{18,19} thermosetting polymers^{20,21} and rubbers^{22,23} with limited positive or even negative influences on the material's mechanical properties. In general, the properties of lignin-based composites are far from satisfactory by adding lignin as particulate filler to a polymer. This is mainly because of the complex and heterogeneous structure and chemistry of lignin, which is highly dependent on the lignin sources, recovery and processing conditions. In addition, not many studies have been done on the effect of lignin on the properties of UPE. Therefore, the aim of this investigation was to evaluate the potential of lignin as a natural material in unsaturated polyester, with a view to substituting as much as possible the unsaturated polyester by the lignin, in order to increase the green portion and reduce the production cost, with minor impact on the composite performance. In addition, the selection of the right lignin for the polymers is also a challenge and is not well understood. In this study, two types of lignin from different processes, namely kraft (Indulin AT) and

sulfite (ArboSO1) lignins, were selected and characterized by qualitative and quantitative methods. The characterization and selection of lignins as raw materials would then pave the way to prepare a bio-based UPE with similar characteristics. The influences of the lignin types and their loading on the properties of two different unsaturated polyesters were also investigated. The utilization of the lignin polymer with highly branched polyphenolic macromolecules as a raw material in substituting UPE would then be a new step towards preparing bio-based UPE materials for industrial applications. The use of green, natural-based materials in manufacturing engineered products would further enhance their green credentials.

EXPERIMENTAL

Materials

Unsaturated polyester resins R937-EPE-50 and RL2710 (so-called R9 and R2, respectively) were obtained from AOC and CCP composites (Progress), respectively. Luperox DDM-9 (mixture of methyl ethyl ketone peroxide – MEKP) from Arkema Inc., was used as an initiator at 1.5 wt% of the resin. Softwood kraft lignin (Indulin AT) and sodium lignosulfonate (ArboSO1) from MeadWestwaco and Tembec (Temiscaming, Québec, Canada) were used in this study. All the chemicals and reagents utilized for the NMR study were purchased from Sigma-Aldrich Chemicals.

Preparation of lignin UPE

Lignin samples were dried at 60 °C under vacuum for at least 4 hours prior to their utilization. Thereafter, lignins were pre-mixed with UPE using a conventional mechanical stirrer. The desired amounts of Indulin AT and ArboSO1 lignins were added slowly to R937-EPE-50 and RL2710 UPE resins, as specified in Table 1. Lignin concentrations in the resin system were varied from 10 to 40 wt%. The resulting mixtures were stirred at room temperature for 10 min at 1200 rpm.

For curing the UPE and UPE-lignin resins, Luperox DDM-9 at 1.5 wt% of the resins was added to the UPE and UPE-lignin resins. The resulting mixtures were mixed by hand for 2 min and subjected to degassing under vacuum at room temperature for 5 min. The UPE derived samples with and without lignins were then casted in aluminum molds. The casted resins were cured at room temperature for 1 day and subsequently post-cured at 100 °C for 1 h. After curing, the samples were demolded and cut to dog-bone and rectangular shaped specimens, according to the corresponding ASTM standards for tensile and impact tests, respectively.

Table 1
Formulation of UPE-lignin

Sample	R2 (wt%)	R9 (wt%)	Ab (wt%)	AT (wt%)
R2	100			
R2-10Ab	90		10	
R2-20Ab	80		20	
R2-30Ab	70		30	
R2-40Ab	60		40	
R2-10AT	90			10
R2-20AT	80			20
R2-30AT	70			30
R9		100		
R9-10Ab		90	10	
R9-20Ab		80	20	
R9-30Ab		70	30	
R9-40Ab		60	40	
R9-10AT		90		10
R9-20AT		80		20
R9-30AT		70		30

Characterization

Moisture and ash contents

Lignin samples (3 x 0.5 g) were quantitatively measured in a pre-weighed crucible and placed in an oven at 105 ± 5 °C overnight. The samples were then transferred to a desiccator at room temperature over drierite to a constant weight for moisture content determination. After measuring each sample, they were placed in an incinerator at 600 °C for a period of 3.5 h. The crucibles remained there until the incinerator temperature was 150 °C. Samples were then transferred to a desiccator and allowed to reach a constant weight at room temperature, prior to ash content determination. For each lignin, three replicates of samples were used for determining the moisture and ash contents.

³¹P nuclear magnetic resonance (NMR) spectroscopy

Quantitative ³¹P NMR spectra of all prepared lignins were obtained using published procedures.²⁴⁻²⁸ Approximately 30-40 mg of sample was dissolved in 500 µL of anhydrous pyridine and deuterated chloroform (1.6:1, v/v) under constant stirring. This was followed by the addition of 100 µL of cyclohexanol (21.38 mg/mL in pyridine and deuterated chloroform 1.6:1, v/v). This was used as an internal standard and 50 µL of chromium (III) acetylacetonate solution (5.5 mg/mL in anhydrous pyridine, while for deuterated chloroform 1.6:1, v/v) was used as relaxation reagent. Finally, 100 µL of phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, TMDP) was then added and the vial was sealed and shaken to ensure thorough mixing. The mixture was transferred into a 5 mm NMR tube for subsequent NMR analysis.

All NMR experiments were carried out at 298 K on a Varian Mercury 400 MHz NMR spectrometer,

operated with a 5 mm broadband inverse probe. ³¹P NMR spectra were recorded with the spectral width of 40650.406 Hz, operated at spectrometer frequency of 161.98 MHz. A relaxation delay of 5 s was used for 512 scans. The ³¹P chemical shifts were referenced against a water signal at 132.2 ppm. All chemical shifts are reported relative to the product of TMDP with cyclohexanol, which has been observed to give a sharp signal at 145.15 ppm referenced from the water signal (132.2 ppm) for a phosphitylating reagent. The content of hydroxyl groups was obtained by integrating the following spectral regions: aliphatic hydroxyls (150.4-145.5 ppm); condensed phenolic units (DPM: 144.4-143.1; 4-O-5': 143.1-141.7 and 5-5': 141.7-140.8 ppm); syringyl phenolic units (143.1-141.7 ppm); guaiacyl phenolic hydroxyls (140.3-138.3 ppm); *p*-hydroxyphenyl phenolics (138.3-137.3 ppm and 136.8-136.5 ppm); and carboxylic acids (135.9-134.0 ppm).

Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) analysis was performed using a multi-detection system from Viscotek (Houston, TX), consisting of a Model 302 multiple detector platform, including a PDA detector, refractive index detector, a four capillary viscometer and a 2 angles laser light scattering detector (GPC max integrated pump, auto sampler and degasser). The light scattering detector was not equipped with fluorescence filters and was only used for qualitative monitoring. The software OmniSEC from Viscotek was used for data collection and calibration. Separation was performed in tetrahydrofuran (THF) by injecting 100 µL of 1.5-2 mg/mL solutions of acetylated lignin in THF into thermostatically controlled SuperRes columns (35 °C; PAS-102, PAS102.5, PAS-103 L, each 300 mm x 8 mm; PolyAnalytik at London, ON). The flow rate was of 1 mL/min. Molar masses of the

samples were determined with universal calibration with the refractive index detector and the viscosity detector. The universal calibration curve was based on polystyrene standard from Polymer Laboratories (Amherst, MA) and Sigma-Aldrich (Oakville, ON) using the molar masses determined by the manufacturer and the intrinsic viscosities measured by the apparatus.

Fourier transform infrared (FTIR) spectroscopy

FT-IR spectra were obtained for powdered solid lignin using a Bruker Tensor Series FT-IR Spectrometer in the Attenuated Total Reflectance (ATR) analysis mode. Spectra were collected from 4000 to 500 cm^{-1} for 64 scans and 4 cm^{-1} resolution, using a zinc selenide (ZnSe) crystal.

Viscosity

The viscosity of UPE with and without lignin was measured at room temperature on a Brookfield CAP 2000+L viscometer using cone and plate geometry. A small amount of UPE or UPE with lignin samples (less than 1 mL) was utilized. The temperature was stabilized to room temperature before running the test.

Morphology

A JEOL JSM-6100 scanning electronic microscope (SEM) at a voltage of 5 kV was used to observe the lignin's surface and the fracture surface of the cured UPE and UPE-lignin after impact tests. Prior to SEM analysis, a 10–20 nm thin layer of Pd/Au was deposited on the sample using a Gatan 682 Precision Etching and Coating System (PECS) in order to minimize the charge effect due to the insulating properties of the samples.

Mechanical properties

The tensile properties of the unsaturated polyester systems with and without lignins were determined at room temperature and 50% relative humidity according to ASTM D638-2002 on an Instron 5500R machine, with crosshead speeds of 5 mm/min. Five replicate of specimens for each unsaturated polyester system with and without lignins were used for the tensile test. The notched Izod impact testing was carried on a TMI tester also at room temperature and 50% relative humidity according to ASTM D256-2002. Ten replicates of specimens for each sample were evaluated for the impact property.

RESULTS AND DISCUSSION

Indulin AT and ArboSO1 were recovered from kraft and sulfite pulping processes, respectively. Kraft or sulfate pulping processes account for more than 90% of the chemical pulping process worldwide. Delignification during kraft pulping proceeds in three distinct phases (initial, bulk and final) in an aqueous solution of sodium hydroxide

and sodium sulfide.²⁹ Lignin is recovered from this process through precipitation by lowering the pH of the black liquor with either sulfuric acid or carbon dioxide.³⁰ The isolated kraft lignin is hydrophobic and contains 1–2% sulfur by weight as an aliphatic thiol group.

The sulfite process is the second largest chemical pulping process operating on the opposite end of the pH scale of the kraft process. The lignin isolated from the acid sulfite process is called lignin sulfonate or lignosulfonate. The physicochemical properties of lignosulfonates are affected by the presence of a cationic base, such as calcium, magnesium, sodium and ammonium.³¹ Lignosulfonates are typically highly cross-linked and contain about 5% sulfur by weight as sulfonate groups. Due to the low pK_a of sulfonates ($\text{pK}_a \leq 2$), lignosulfonates are water soluble lignins.

The lignins isolated from these processes contain several important functional groups, including phenolic hydroxyl, carboxylic groups, and hydroxyl groups, which make lignin a versatile precursor in many formulations, with an overall reactivity that depends entirely on their chemical compositions.³² The chemical structure of the lignin polymer consists primarily of phenyl propanoid units, mainly *p*-coumaryl alcohol (H), coniferyl alcohol (G) and/or sinapyl alcohol (S).^{33,34} These components are cross-linked together in three dimensions *via* a radical coupling process during biosynthesis. The physical and chemical properties of lignin are highly dependent on the wood species, botanic region, and the isolation processes.^{35,36}

The moisture and ash contents for both lignin samples were determined experimentally and are reported in Table 2. The ash content is quite high for lignosulfonate ArboSO1, due to the presence of cationic base during the process.

Quantitative ^{31}P NMR analysis allowed quantifying different classes of –OH groups of lignin. The technique has been successfully implemented for the absolute determination of various phenolic and non-phenolic structures in several native and technical lignins.^{37–39} The availability of a phosphitylating reagent¹⁵ that permits excellent resolution and the quantitative spectroscopic detection of several phenolic moieties with varying substitution patterns provide an excellent opportunity for systematically exploring the complex reactions occurring in lignin during several different pulping processes.

Figure 1 shows the ^{31}P NMR spectra of ArboSO1 and Indulin AT with TMDP. The reagent allows distinguishing several different phenolic condensed units in the lignins, while

being less specific for the aliphatic OH groups. The quantification of all hydroxyl groups, as reported in Table 3, was obtained from the integration of ^{31}P NMR spectra.

Table 2
Moisture and ash contents of lignins

Lignin sample	Average moisture, (%)	Average ash, (%)
Indulin AT	2.99±0.20	2.86±0.24
ArboSO1	0.74±0.11	24.15±0.35

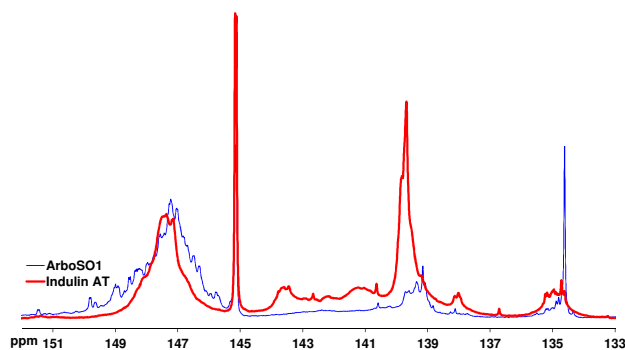


Figure 1: ^{31}P NMR spectra of Indulin AT and ArboSO1

Another important factor for elucidating the lignin profile is the characterization of its elemental composition. Since the elemental compositions of various types of lignins are exclusively different, the percent elemental composition for each lignin sample, in terms of carbon, hydrogen, nitrogen, oxygen, sulfur, and methoxy content, was analyzed. Based on these data, the empirical formula and the molecular weight of each lignin per C9 unit was calculated and reported in Table 2. Elemental analysis results and the empirical formula of the phenylpropane structural unit of lignin are given in Table 4. In addition, the molecular weights and molecular weight distribution of the lignins determined by GPC are reported in Table 4.

The comparison of the two NMR spectra shows significant differences almost in the entire spectral region. The aliphatic hydroxyl groups are more uniform in Indulin AT lignin than in ArboSO1. Indulin AT seems to have more pronounced condensed units than ArboSO1. The guaiacyl units in Indulin AT were found to be more uniform and of higher magnitude than those in ArboSO1, similarly to free phenolic units. However, the terminal carboxylic content in ArboSO1 was found to be higher than in Indulin AT. The assignments of the infrared absorption bands in lignin are rather empirical because of the amorphous nature of lignin and the complexity of its chemical components and their random linkages.⁴⁰

Table 3
Quantitative ^{31}P NMR determination of carboxylic, phenolic and primary hydroxyl groups present in lignins

Lignin sample	-OH (mmol/g)					
	COOH	Phenolic G [*]	Phenolic S [‡]	Phenolic H [§]	Condensed phenolic	Primary Total phenolic
Indulin AT	0.21	1.80	0.00	0.12	1.28	3.27
ArboSO1	0.51	0.87	0.00	0.03	0.28	5.83

*G: guaiacyl phenolic OH; ‡S: syringyl phenolic OH; §H: p-hydroxyphenyl phenolic OH

Table 4
Empirical formula of phenylpropane structural units of lignins

Lignin sample	Elemental unit (%)						C9 structural unit	Mw (g/mol)
	C	H	N	O	S	OCH ₃		
Indulin AT	60.63	5.75	0.87	29.59	1.69	12.92	C ₉ H _{8.67} O _{2.79} N _{0.121} S _{0.102} (OCH ₃) _{0.809}	191.55
ArboSO1	40.99	4.65	37.26	1.09	1.09	6.74	C ₉ H _{11.25} O _{5.95} N _{0.22} S _{0.58} (OCH ₃) _{0.612}	255.32

Table 5
General assignments for some lignin functional groups and their IR absorption bands³¹

Functional groups	IR absorption bands (cm ⁻¹)
OH stretching (H-bonded)	3600-3100
OH stretching in methylene and methyl groups	3100-2800
-C=CH ₂ and -C=CH	3092-2990
-CH ₂ and -CH	2849
Carboxylic -OH	2918
Carboxylic acid (high concentration)	2670-2397
Unconjugated -C=O stretch	1742-1710
-C=O	1771 (aromatic) and 1722 (aliphatic)
Aromatic skeletal vibrations	1601-1501 and 1425-1430
C-H deformation (asymmetric)	1460-1470
C-H deformation (symmetric)	1370-1365
Syringyl ring breathing with CO-stretching	1330-1325 and 1235-1230
Guaiacyl ring breathing with CO-stretching	1275-1270
Ether C-O	1213
Aromatic C-H in-plane deformation, guaiacyl-type	1145-1140
Aromatic C-H in-plane deformation, syringyl-type	1130
C-O deformation, secondary alcohol and aliphatic ether	1085-1090
Aromatic C-H in-plane deformation, guaiacyl type, and C-O deformation, primary alcohol	1028-1035
=CH out of plane deformation (trans)	970
Aromatic C-H out of plane (guaiacyl, syringyl, and <i>para</i> -hydroxyl phenolic)	860-750

The general assignments for some lignin functional groups and their IR absorption bands are summarized in Table 5.⁴¹

The FTIR spectra for Indulin AT and ArboSO1 lignins are shown in Figure 2 with their corresponding assignments as described below.

Indulin AT: -OH stretch, 3100-3400 cm⁻¹; C-H stretch (methylene and methyl), 2800-3000 cm⁻¹; unconjugated -C=O stretch, 1705-1740 cm⁻¹; conjugated -C=O stretch, 1675-1655 cm⁻¹; aromatic skeletal vibrations, 1420-1430, 1505-1515, 1595-1603 cm⁻¹; ether C-O, 1194 cm⁻¹; alcohol C-O, 1040 cm⁻¹ (primary) and 1128 cm⁻¹ (secondary); guaiacyl C-H in plane, 1066 cm⁻¹; guaiacyl C-H out of plane 908-831 cm⁻¹.

ArboSO1: -OH stretch, 3100-3400 cm⁻¹; C-H stretch (methylene and methyl), 2800-3000 cm⁻¹; unconjugated -C=O stretch, 1705-1740 cm⁻¹; conjugated -C=O stretch, 1675-1655 cm⁻¹;

aromatic skeletal vibrations, 1420-1430, 1505-1515, 1595-1603 cm⁻¹; ether C-O, 1194 cm⁻¹; alcohol C-O, 1040 cm⁻¹ (primary) and 1128 cm⁻¹ (secondary); guaiacyl C-H in plane, 1066 cm⁻¹; guaiacyl C-H out of plane 908-831 cm⁻¹.

The FTIR spectra of Indulin AT and ArboSO1 follow a common pattern, with a broad band at 3600-3300 cm⁻¹ corresponding to the hydroxyl groups in phenolic and carboxylic acids and several bands with variable intensity in the fingerprint region (1900 to 800 cm⁻¹). In this region, the O-H stretch (3100-3400 cm⁻¹) seems to be less broad for ArboSO1 than for Indulin AT. In addition, the C-H stretch in methyl and methylene groups (2800-3000 cm⁻¹) is less available in ArboSO1 than in Indulin AT. The next features appear at 1760 cm⁻¹ and are assigned to aromatic acetoxy groups, along with the strong band at 1616 cm⁻¹, due to unconjugated carbonyl-

carboxyl stretching with two very small shoulders at 1757 and 1706 cm^{-1} in ArboSO1. The Indulin AT spectrum showed only a small shoulder at 1657 and a strong band at 1601 cm^{-1} . The most significant features in this region were recorded for Indulin AT lignin at 1516 cm^{-1} due to the C=C and aromatic skeletal vibrations, 1462 cm^{-1} for C-H deformation combined with aromatic ring vibrations. The most noticeable bands for the ArboSO1 sample were recorded at 1224 cm^{-1} (C-C, C-O and C=O stretching) and in the region between 654-530 cm^{-1} . The bands for the Indulin AT sample were recorded at 1194 cm^{-1} (ether C-O); at 1040 cm^{-1} (alcohol C-O, primary) and 1128 cm^{-1} (alcohol C-O, secondary). The band was at 1066 cm^{-1} for guaiacyl C-H in plane and at 908-831 cm^{-1} for guaiacyl C-H out of plane.

The bands for the ArboSO1 sample were recorded at 1194 cm^{-1} (ether C-O); at 1040 cm^{-1} (alcohol C-O, primary) and 1128 cm^{-1} (alcohol C-O, secondary). The band was at 1066 cm^{-1} for guaiacyl C-H in plane and at 908-831 cm^{-1} for guaiacyl C-H out of plane. The band appearing at 617-656 cm^{-1} is assigned to the sulfonic groups (S-O stretching vibration) formed from the reaction of sodium sulfite with the secondary OH of the aliphatic side chain of lignins.

The morphology of the lignins was observed under SEM and resulting images are shown in Figure 3. The properties of lignin are related not only to the nature of the hydrophilic groups, which depends upon the pulping process, but also

to the size of the polymeric pieces, which in turn depends on the recovery technique used to process the black liquors. The grain diameters and relative proportions of the various size distributions of lignin fragments for differently isolated samples play an important role in prospective biomaterial applications. One can see that the lignin includes round particles, and fragmented and collapsed ones. The two lignin particles are porous and have different sizes, which are mostly less than 100 μm , although there are a few of them larger than 10 μm for Indulin AT. However, the particles seem a bit smaller for ArboSO1 than for Indulin AT. The results also show that more rounded particles were broken down for Indulin AT than for ArboSO1. The overall morphology seems uniform with particles having smooth surfaces. This structure can be influenced by the chemistry, isolation and drying processes of the lignins. The viscosity of UPE resins can impact the processing and subsequently affect the performance of the final products. Therefore, the viscosity of UPE and UPE-lignin is important to be evaluated. The viscosity of the mixtures of two different UPE resins with the two lignins at different lignin loadings was tested. Figure 4 shows the viscosity of UPE resins with and without lignins. In general, the presence of lignin in the two UPE resins changed the rheological behavior of the resins toward non-Newtonian.

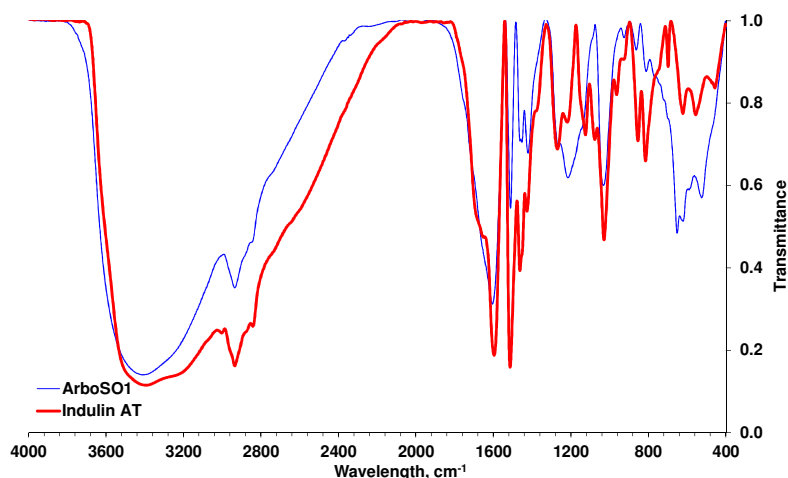


Figure 2: FTIR spectra of Indulin AT and ArboSO1 lignins

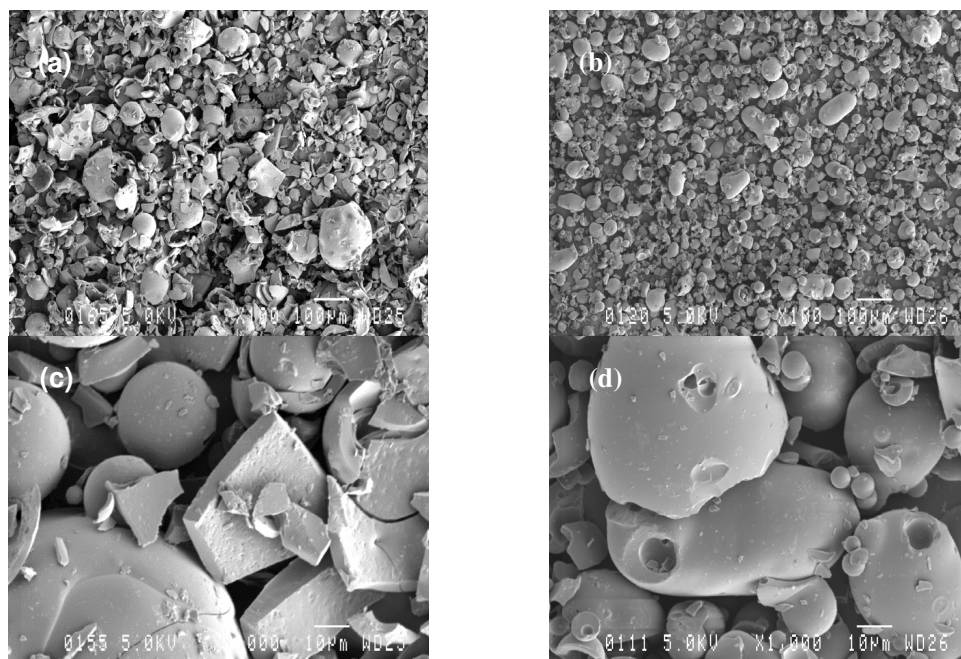


Figure 3: SEM images of Indulin AT (a, c) and ArboSO1 (b, d) under two different magnifications

This means that their viscosities do not remain constant over a given range of shear rates. In the strict sense, the rheological behavior of UPE-lignin is a combination of non-Newtonian and Newtonian behaviors. At lower shear rates, it behaves as non-Newtonian, but as the shear rate increases, it tends to exhibit a Newtonian behavior. The results show that the presence of lignins increases the viscosity of UPE resins. The results also indicate that the more lignin is added the higher is the viscosity. However, the changes in viscosities were quite complex and closely related to the quality of the lignin dispersion and solubility in the UPE, as well as to the interaction between lignin and UPE molecules. Although the viscosities increased in all the cases, they are still acceptable for processing at loading levels up to 40 wt% of Ab and 30 wt% of Indulin AT in the UPE resins.

The tensile properties of the two UPEs prepared with the two types of lignin at different concentrations are shown in Figure 5. Data indicate the modulus of UPE decreases almost linearly with the ArboSO1 loading for both UPEs. This is similar to the works reported by Yeo *et al.*,⁴² where the modulus of the UPE lignin reduced as the lignin loading increased. However, the modulus of the UPE-lignin levels up for Indulin AT only at 10 and 20 wt% loading. A

similar observation was found for both UPE resins. The results also show the positive effect of adding 10 wt% of both lignin samples on the tensile strength of the UPE. Therefore, lignins are not only considered as filler for UPE, but somehow, they reinforce the UPE resins and improve the tensile strength of the UPE resin. Yeo *et al.*⁴² also reported increasing numbers of the tensile strength and modulus of UPE-lignin after they modified the lignin with allyltrimethoxy silane. Other works were reported by Ikeda and his team where the tensile stresses of the biocomposites significantly increased with an increase in the lignin content. However, in their study, the matrix was a rubber base.²³

In our study, the selection of the lignin and its concentration can positively increase the tensile strength without any modifications. However, higher concentrations of both lignins in two different UPE resins have a negative impact on the tensile strength of UPE.

Generally, the mechanical properties of the polymers are influenced by many factors dependent on the structure of polymers, such as primary molecular weight of the polymers, the degree of cross-linking density and regularity of the network structure.⁴³ For composite materials, the properties are also affected by the type of reinforcement, the chemistry of the components,

as well as the interface between the polymers and the reinforcements. In our case, the tensile properties of UPE could have been also influenced by the presence of lignin, lignin type, concentration and the interaction between lignin

and UPE. Normally, inert fillers may exhibit very slight changes in the cure properties due to particle surface adsorption effects. However, lignin particles somehow retard the curing of UPE and thus affect their tensile performance.

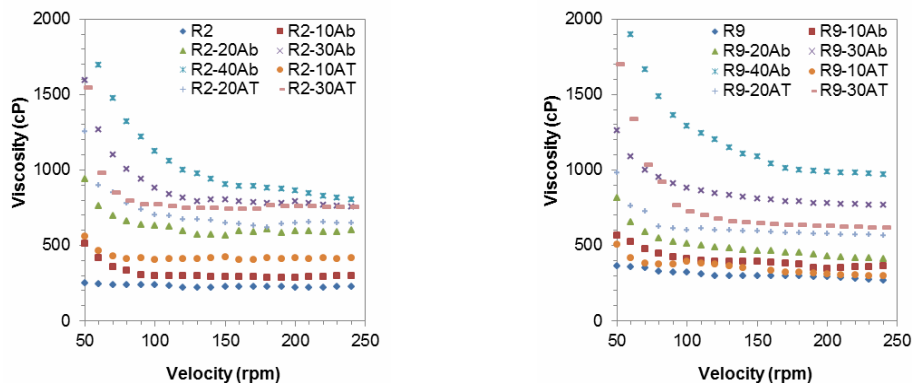


Figure 4: Viscosity of two different UPE resins with Indulin AT and ArboSO1 lignin mixtures at different lignin loadings (left) UPE RL2710 or R2 and (right) R937-EPE-50 or R9

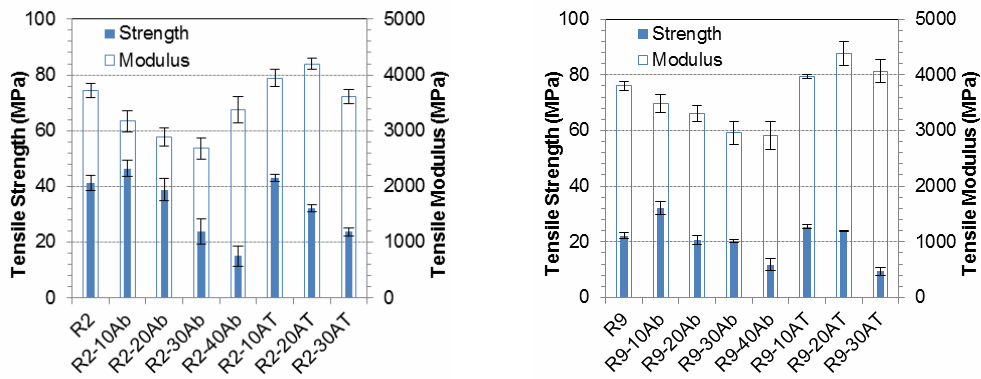


Figure 5: Tensile properties of two different UPE resins with Indulin AT and ArboSO1 (left) UPE RL2710 or R2 and (right) R937-EPE-50 or R9

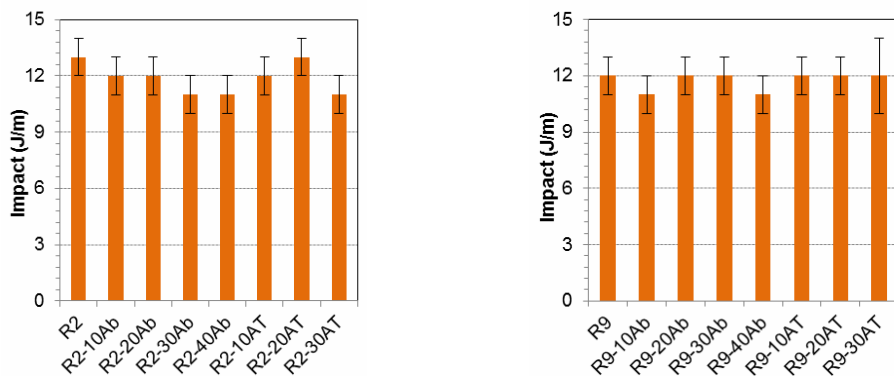


Figure 6: Impact properties of two different UPE resins with Indulin AT and ArboSO1 (left) UPE RL2710 or R2 and (right) R937-EPE-50 or R9

Impact strength is defined as the resistance of a UPE and UPE-lignin material to impact loading applied in impact testing. Figure 6 shows the

impact property of UPE with and without lignins. The results indicate the presence of lignins, their types and contents have no negative effect on the

impact energy of UPE. The impact property of UPE was greatly reduced with the presence of filler, as compared to the control UPE. Surprisingly, the impact property remains almost the same as for neat UPE for both resins up to 40 wt% of ArboSO1 and 30 wt% of Indulin AT. As reported by Yeo *et al.*, the presence of the pristine lignin in the UPE matrix reduced the impact

strength of UPE with increased lignin filler loading.⁴²

The fracture surfaces of the specimens made with different lignins were observed using SEM (Figs. 7 and 8). Neat UPE resin exhibits a relatively smooth fracture surface. There are cracks in different planes, but almost parallel to the crack-propagation direction, indicated by a white arrow (Fig. 7a and Fig. 8a).

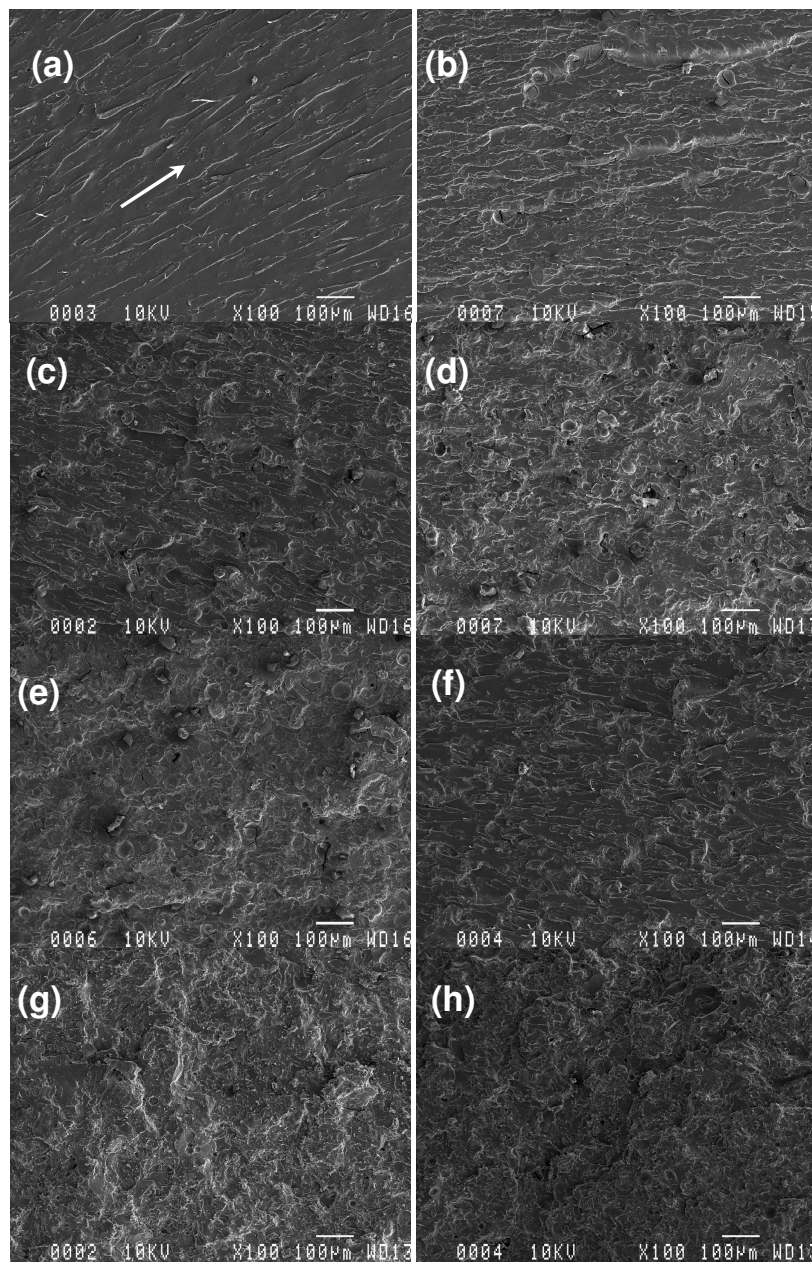


Figure 7: SEM images of UPE: (a) R2, (b) R2 with 10% Ab, (c) R2 with 20% Ab, (d) R2 with 30% Ab, (e) R2 with 40% Ab, (f) R2 with 10% AT, (g) R2 with 20% AT, and (h) R2 with 30% AT

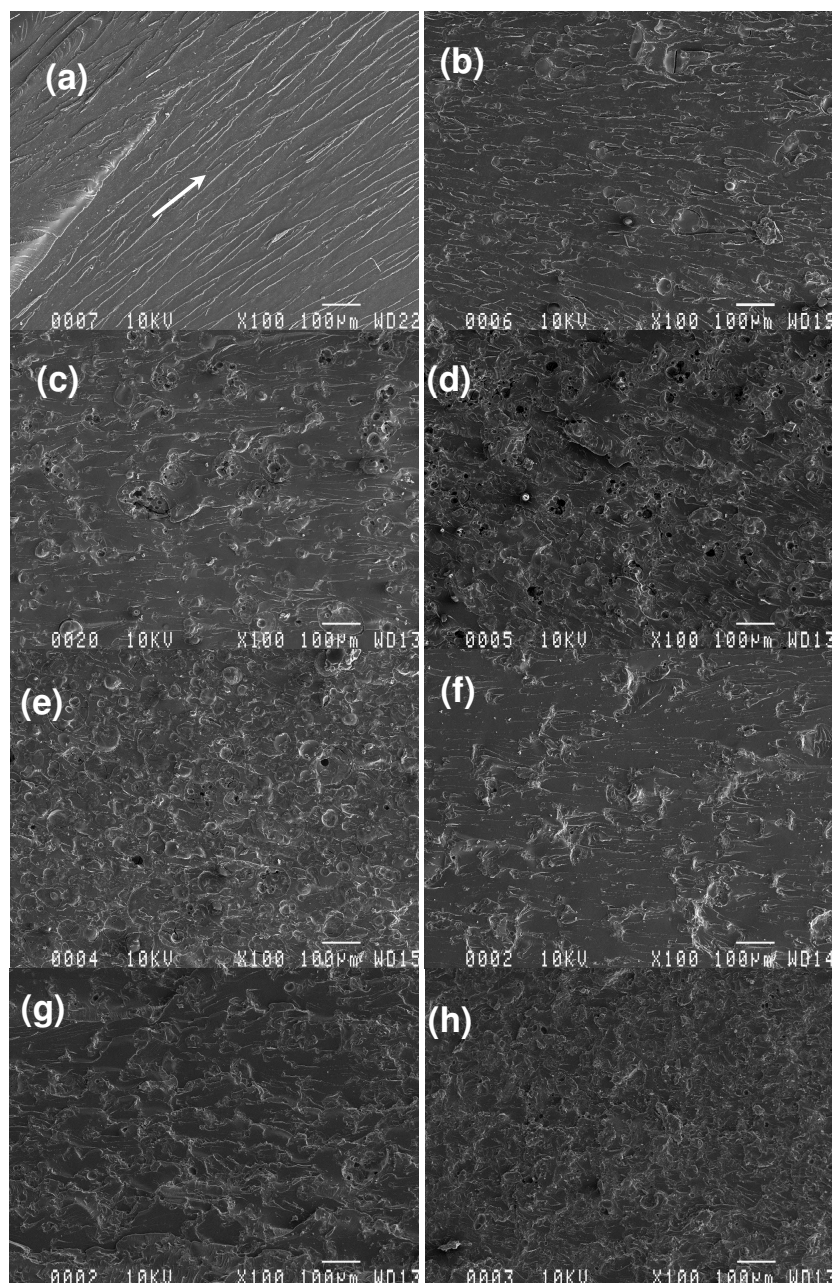


Figure 8: SEM images of UPE: (a) R9, (b) R9 with 10% Ab, (c) R9 with 20% Ab, (d) R9 with 30% Ab, (e) R9 with 40% Ab, (f) R9 with 10% AT, (g) R9 with 20% AT, and (h) R9 with 30% AT

This is a typical fractography feature of brittle fracture behavior, thus accounting for the low fracture toughness of the unfilled UPE. Compared to the case of neat UPE, the fracture surfaces of UPE with lignins show considerably different fractographic features. As a representative example, the failure surfaces of UPE containing two different lignins in various concentrations are

shown in Figures 7 and 8 (from b to h). Generally, a much rougher fracture surface is seen upon adding lignins into the UPE matrix. The increased surface roughness implies that the path of the crack tip is distorted because of the presence of lignins, making crack propagation different. More precisely, the lignin is somehow readily able to interact or interfere with the growing crack front.

The results also show that many lignin particles are observed on the fracture surface. The presence of lignin particles or aggregates may cause perturbations along the crack front, thus altering the path of the propagating crack from the straight unperturbed growth seen in the neat resin. Consequently, the cracks are deflected by the lignin particles into the regions surrounding them.

Clearly, the crack deflection observed is expected for the increase of strength and toughness obtained by incorporating lignin into the UPE matrix. Upon fracture, the lignin particles are very likely to be the stress concentration sites; therefore, good dispersion and good interaction can help reduce the negative effect of the cleavage of lignin particles.

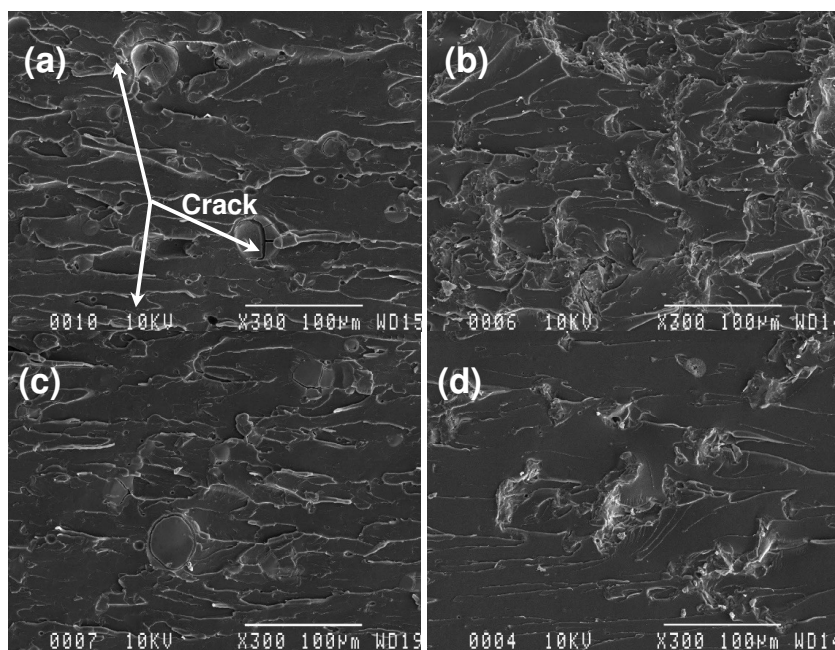


Figure 9: SEM images of UPE at high magnification: (a) R2 with 10% Ab, (b) R2 with 10% AT, (c) R9 with 10% Ab, and (d) R9 with 10% AT

In addition, Indulin AT seems to interact better with the UPE resins than ArboSO1 under similar conditions. The crack could be observed surrounding ArboSO1 particles, as indicated in Figure 9, while this is not the case for Indulin AT. This may be related to the hydrophilicity of ArboSO1, which is not compatible with UPE resins.

CONCLUSION

Kraft and sulfite lignin samples from forestry biomass were characterized by qualitative and quantitative methods. The two lignins are quite different in terms of their chemical composition, MW, morphology, *etc.* The potential uses of the lignins for the preparation of UPE-lignin materials and their performance were examined.

Although the presence of lignins and their concentrations increased the viscosity of UPE, the UPE-lignins are suitable for processing. The results indicate that the lignin type and loading

influenced the tensile properties of UPE. Indulin AT interacts better with UPE resins, as compared to ArboSO1. However, these factors seem not to influence the impact modulus of UPE. A much rougher fracture surface was obtained upon adding lignins into the UPE matrix.

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REFERENCES

- ¹ A. V. R. Prasad, K. M. M. Rao, K. M. Rao and A. V. S. S. K. S. Gupta, *Indian J. Fibre Text. Res.*, **32**, 399 (2007), <http://nopr.niscair.res.in/handle/123456789/323>.
- ² S. Waigaonkar, B. J. C. Babu and A. Rajput, *Indian J. Eng. Mater. Sci.*, **18**, 31 (2011), <https://www.niscair.res.in/sciencecommunication/researchjournals/rejour/ijems/ijems0.asp>
- ³ J. Martone Pt. Estevez, F. Lu, K. Ruel, M. Denny, C. Somerville *et al.*, *Curr. Biol.*, **19**, 169 (2009),

<https://doi.org/10.1016/j.cub.2008.12.031>. ISSN 0960-9822. PMID 19167225

⁴ S. E. Jr. Lebo, J. D. Gargulak and T. J. McNally, "Lignin, Kirk-Othmer Encyclopedia of Chemical Technology", John Wiley & Sons, Inc. 2001, <https://doi.org/10.1002/0471238961.12090714120914.a01.pub2>

⁵ G. A. Smook, in "Handbook for Pulp and Paper Technologists", second edition, Vancouver, Angus Wilde Publications, 1992, pp. 5, <http://vancouver.canadianorglist.com/company/angus-wilde-publications-inc/>

⁶ H. L. Hergert, in "Lignins: Occurrence, Formation, Structure and Reactions", edited by K. V. Sarkanen and C. H. Ludwig, New York, Interscience Publisher, John Wiley & Sons, 1971, pp. 267-297, <https://doi.org/10.1002/pol.1972.110100315>

⁷ W. Thielemans and R. P. Wool, *Biomacromolecules*, **6**, 1895 (2005), <https://www.wiley.com/en-us>

⁸ S. Gillet, M. Aguedo, L. Petitjean and A. R. C. Morais, *Green Chem.*, **19**, 4200 (2017), <https://doi.org/10.1039/C7GC01479A>

⁹ G. A. Smook, "Handbook for Pulp and Paper Technologists", Second Edition, Angus Wilde publications, Vancouver, 1992, pp. 123-152, <http://vancouver.canadianorglist.com/company/angus-wilde-publications-inc/>

¹⁰ R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema *et al.*, *Angew. Chem. Int. Ed.*, **55**, 8164 (2016), <https://doi.org/10.1002/anie.201510351>

¹¹ S. Haghdan, S. Renneckar and G. D. Smith, in "Lignin Polymer Composites", edited by O. Faruk and M. Sain, Elsevier, Amsterdam, 2016, <https://www.elsevier.com/books/lignin-in-polymer-composites/faruk/978-0-323-35565-0>

¹² S. Laurichesse and L. Avérous, *Prog. Polym. Sci.*, **39**, 1266 (2014), <https://doi.org/10.1016/j.progpolymsci.2013.11.004>

¹³ C. Jiang, H. He, X. Yao, P. Yu, L. Zhou *et al.*, *J. Appl. Polym. Sci.*, **132**, 1 (2015), <https://doi.org/10.1002/app.42044>

¹⁴ J. Datta and P. Parcheta, *Iran. Polym. J.*, **26**, 453 (2017), <https://doi.org/10.1007/s13726-017-0534-0>

¹⁵ J. H. Lora and W. G. Glasser, *J. Polym. Environ.*, **10**, 39 (2002), <https://doi.org/10.1023/A:1021070006895>

¹⁶ R. Pucciariello, V. Villani, C. Bonini, M. D'Auria and T. Vetere, *Polymer*, **45**, 4159 (2004), <https://doi.org/10.1016/j.polymer.2004.03.098>

¹⁷ D. S. Argyropoulos, *J. Biotechnol. Biomater.*, **3**, 3 (2013), <https://doi.org/10.4172/2155-952X.1000e123>

¹⁸ M. A. S. Anwer, H. E. Naguib, A. Celzard and V. Fierro, *Compos. Part B*, **82**, 92 (2015), <https://doi.org/10.1016/j.compositesb.2015.08.028>

¹⁹ H. C. Liu, C. C. Tuan, A. A. B. Davijani, P. H. Wang, H. Chang *et al.*, *Polymer*, **111**, 177 (2017), <https://doi.org/10.1016/j.polymer.2017.01.043>

²⁰ M. Liu, A. Baum, J. Odermatt, J. Berger, L. Yu *et al.*, *Compos. Part A*, **95**, 377 (2017), <https://doi.org/10.1016/j.compositesa.2017.01.026>

²¹ D. Ariawan, M. S. Salim, R. M. Taib, M. Z. A. Thirmizir and Z. A. M. Ishak, *Adv. Polym. Technol.*, **37**, 1420 (2017), <https://doi.org/10.1002/adv.21801>

²² C. D. Tran, J. Chen, J. K. Keum and A. K. Naskar, *Adv. Funct. Mater.*, **26**, 2677 (2016), <https://doi.org/10.1002/adfm.201504990>

²³ Y. Ikeda, T. Phakkeeree, P. Junkong, H. Yokhama, P. Phinyocheep *et al.*, *RSC Adv.*, **7**, 5222 (2017), <https://doi.org/10.1039/c6ra26359c>

²⁴ L. Akim, D. Argyropoulos, L. Jouanin, J.-L. Leplé, G. Pilate *et al.*, *Holzforshung*, **55**, 386 (2001), <https://doi.org/10.1515/HF.2001.064>

²⁵ A. Granata and D. Argyropoulos, *J. Agric. Food Chem.*, **43**, 1538 (1995), <https://doi.org/10.1021/jf00054a023>

²⁶ D. Argyropoulos, *J. Wood Chem. Technol.*, **14**, 65 (1994), <https://www.tandfonline.com/doi/abs/10.1080/02773819408003086>

²⁷ B. Ahvazi, E. Cloutier, O. Wojciechowicz and T.-D. Ngo, *ACS Sustain. Chem. Eng.*, **4**, 5090 (2016), <https://doi.org/10.1021/acssuschemeng.6b00873>

²⁸ B. Ahvazi, O. Wojciechowicz, P. Xu, T.-D. Ngo and J. Hawari, *BioResources*, **12**, 6629 (2017), <https://doi.org/10.15376/biores.12.3.6629-6655>

²⁹ G. A. Smook, in "Handbook for Pulp and Paper Technologists", edited by G. A. Smook, Angus Wilde Publications, Vancouver, 1982, pp. 66-75, <http://vancouver.canadianorglist.com/company/angus-wilde-publications-inc/>

³⁰ K. Koljonen, M. Österberg, M. Kleen, A. Fuhrmann and P. Stenius, *Cellulose*, **11**, 209 (2004), <https://doi.org/10.1023/B:CELL.0000025424.90845.c3>

³¹ G. A. Smook, in "Handbook for Pulp and Paper Technologists", edited by G. A. Smook, Angus Wilde Publications, Vancouver, 1982, pp. 58-65, <http://vancouver.canadianorglist.com/company/angus-wilde-publications-inc/>

³² J. Gierer, *J. Wood Sci. Technol.*, **19**, 289 (1985), <https://doi.org/10.1007/BF00350807>

³³ A. C. Neish, in "Constitution and Biosynthesis of Lignin", edited by K. Freudenberg and A. C. Neish, Springer-Verlag, Berlin, 1968, pp. 5-43, <https://www.springer.com/gp/book/9783540042747>

³⁴ A. B. Wardrop, in "Lignins: Occurrence, Formation, Structure and Reactions", edited by K. V. Sarkanen and C. H. Ludwig, Interscience Publisher, John Wiley & Sons, New York, 1971, pp. 19-41, <https://doi.org/10.1002/pol.1972.110100315>

³⁵ F. E. Brauns and D. A. Brauns, "The Chemistry of Lignin", Supplement Volume, Academic Press, New York, 1960.

³⁶ G. G. Gross, in "The Structure, Biosynthesis and Degradation of Wood. Recent Adv. Phytochem. 11", edited by F. A. Loewus and V. C. Runeckles, Plenum

Press, New York, 1977, pp. 141-184,
<https://www.springer.com/gp/book/9781461588757>

³⁷ D. S. Argyropoulos, B. Hortling, K. Poppius-Levlin, Y. Sun and M. Mazur, *Nord. Pulp Pap. Res. J.*, **10**, 68 (1995),
<https://www.ncbi.nlm.nih.gov/nlmcatalog?term=0283-2631%5BBISSN%5D>

³⁸ Y. Sun and D. S. Argyropoulos, *J. Pulp Pap. Sci.*, **21**, 185 (1995),
<http://www.paptac.ca/en/publications/jppsbackissues>

³⁹ P. M. Froass, A. J. Ragauskas and J. Jiang, *Pulp. J. Wood Chem. Technol.*, **16**, 347 (1996),
<https://doi.org/10.1080/02773819608545820>

⁴⁰ H. L. Hergert, in "Lignins. Occurrence, Formation, Structure and Reactions", edited by K. V. Sarkanen and C. H. Ludwig, Wiley Interscience, New York, 1971, pp. 267-293,
<https://doi.org/10.1002/pol.1972.110100315>

⁴¹ O. Faix, in "Methods in Lignin Chemistry", edited by S. Y. Lin and C. W. Dence, Springer-Verlag, Berlin, Germany, 1992, pp. 83-110,
<https://www.springer.com/gp/book/9783642740671>

⁴² J.-S. Yeo, J.-H. Lee and S.-H. Hwang, *Compos. Part B*, **130**, 167 (2017),
<https://doi.org/10.1016/j.compositesb.2017.07.084>

⁴³ A. G. Mikos and N. A. Peppas, *J. Mater. Sci.*, **24**, 1612 (1989), <https://doi.org/10.1007/BF01105680>