Lignin Use in Nonwovens: A Review

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While lignin has been gaining wide research interest for a variety of applications across many industries, relatively little work has been published on its applications in nonwovens. Consequently, this article offers an overview of the underlying principles and both the present and future applications of lignin within the nonwoven industry. Due to the distinct structure of lignin, processing, fiber production, composites with polymers, dye dispersant, and fire-retardant applications are all unique opportunities for lignin application in nonwovens discussed in this review. Conventional nonwoven processing techniques, such as electrospinning, have been reported to successfully produce lignin-based nonwovens, specifically lignin/polymer composite nonwovens. This account points to pivotal polymer matrix/lignin composite compatibility issues that define various processing technologies. However, lignin use is not limited to incorporation within nonwoven fibers mats and is currently used in dye dispersion with the potential of phase out petroleum-based dye dispersants. Finally, the high phenolic content of lignin endows it with fire-retardant and antimicrobial properties, among others, that present additional opportunities for lignin in the nonwoven industry. Throughout this review, an effort is made to outline the advantages and challenges of using lignin as a green and sustainable ingredient for the production of nonwoven materials.

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INTRODUCTION

Nonwovens: Definition and Description

Defining and segmenting nonwoven fabrics has been the topic of much discussion since the 1930s when pilot-scale production of these materials is reported to have begun. Although some consider nonwovens a part of the textile industry, others consider it a separate entity. Overall, however, it is certain that nonwovens' technology is closely linked to the textile, pulp and paper, and fiber/polymer extrusion industries (Batra and Pourdeyhimi 2012).

The first, simplistic definition of a nonwoven was presented by the American Society for Testing and Materials (ASTM) in 1962. They defined nonwovens as "textile fabrics made of carded web or fiber web held together by adhesives" (Batra and Pourdeyhimi 2012). Today, ASTM's definition is more evolved, yet still quite broad. Contained within their Standard Terminology Relating to Textiles (D123-19), a nonwoven fabric is defined as "a textile structure produced by bonding or interlocking of fibers, or both, accomplished by mechanical, chemical, thermal, or solvent means and combinations thereof" (ASTM 2019). Elsewhere, in the literature, Burkinshaw, states that a nonwoven is "an assembly of individual fibers or filaments that are bonded by means of friction and/or cohesion and/or adhesion" (Burkinshaw *et al.* 2012).

Perhaps a more detailed description is offered by the Association of the Nonwoven Fabrics Industry (INDA), who describe nonwovens as "sheet or web structures bonded together by entangling fiber or filaments (and by perforating films) mechanically, thermally, or chemically. They are flat, porous sheets that are made directly from separate fibers or from molten plastic or plastic film. They are not made by weaving or knitting and do not require converting the fibers to yarn" (About Nonwovens).

Raw Materials

While the range of potential raw materials used in nonwoven production is generally quite extensive and can include natural, man-made, and even inorganic fibers and wood pulp, ultimately, raw material selection in nonwovens largely depends on the selected web formation type, bonding technique, and product end-use.

Natural fibers are composed of cellulosic, vegetable-based, animal, and protein fibers. Man-made fibers include regenerated/modified cellulosic fibers, polyamide, polyester, polyolefin, acrylic/modacrylic, and elastomeric fibers. Inorganic fibers are considered specialty fibers and include glass, metallic, carbon, and ceramic fibers. Finally, wood pulp is amongst the main raw materials used.

If categorized by web formation, carded staple fibers are the most used type of fibers, with polypropylene (PP) and polyethylene terephthalate (PET) being the most common. In addition, carded staple fibers can include recycled fibers, as well as bicomponent fibers used as a binder for thermal bonding. The air-laid process can use a very wide range of raw materials; from man-made fibers (PP, PET, bicomponent), recycled fibers, natural fibers (linen, flax, wool), to powders and particles and wood pulp. In wet-laid web formation, natural fibers, wood pulp, all man-made fibers, and inorganic fibers are prevalent. The spunlaid web formation technology, which includes spunbond and meltblown nonwovens, is specific in that it can only utilize thermoplastic polymers. This class of fibers are constituted of PE, PET, polyamide, and PP, with the latter being the most common polymer used in meltblown nonwovens (Karthick and Rathinamoorthy 2016).

In terms of bonding techniques, thermal bonding includes calendering and through-the-air, which is limited to thermoplastic polymers. Alternatively, chemical and hydroentangling bonding can both use a wide variety of man-made and natural fibers. Needling is web formation-dependent with regards to the raw material used; accordingly, they can only use staple air-laid and carded fibers in addition to filament spunbond fibers (Karthick and Rathinamoorthy 2016).

Industrial lignins can be obtained from paper pulp waste, fiber textile, wood hydrolysis, and lignocellulose energy operations (Chen 2015). The demand for lignin has steadily risen due to increased environmental protection coupled with the depletion of petrochemical sources. Overall, the main categories of industrial lignins include kraft, alkali, lignosulfonate, organic solvent, enzymatic hydrolysis, and steam exploded. Lastly, enzymatic hydrolysis residues of lignocellulose biomass offer more active groups due to the mild action of enzymatic hydrolysis, and thus offer more promise (Chen 2015). The abundance and unique properties of lignins present great potential for use in the nonwovens industry, a topic that has yet to be thoroughly reviewed.

The Market for Nonwovens

The nonwovens market can be compared most closely to other textile industries such as weaving, knitting, and even the paper industry. The most comparable connection between these industries is the line speeds and plant costs to produce their end products. The nonwoven industry is very comparable in speed and price point to the other industries: nonwovens can produce between 10 and 100 meters per minute compared to 1 to 2 meters/minute for weaving, 2 to 5 meters/minute for knitting, and 100 to 1000 meters/minute for the paper industry. Typical capital costs for a nonwoven plant are 10 to 100 million USD, 10 to 100 million USD for weaving, 1 to 50 million USD for knitting, and 50 to 100 million USD for the paper industry (Batra and Pourdeyhimi 2012). The nonwoven industry has the advantage of adapting techniques and knowledge from other industries. This approach helps to keep costs low, as there is little need for manufacturing innovation.

INDA represents the entire nonwoven fabric chain (INDA). As the central body for the nonwoven fabric industry, they serve as a conglomeration of companies within the industry to connect with each other and solve issues. INDA is also tasked with producing market reports, which may be accessed through resources found on their website.

According to Inkwood Research, the global nonwovens market is expected to have a compound annual growth rate of 7.43% between 2019 to 2028 and a volume compound annual growth rate of 7.54% during that same time. This would lead to a revenue of $36.5 billion by 2028. The expected growth is from rising demands in prominent markets that are difficult to replace with woven products. Markets such as incontinence care products, hygiene, and medical applications are expected to grow as the population continues to expand. The quickly rising demand for baby diapers is expected to be the main driver across all sectors. Other market sectors such as carpet, furniture, agriculture, and industrial applications are expected to grow as GDP grows globally. The furniture sector is predicted to have the highest compound annual growth rate across all sectors in both revenue and volume. Global growth for the nonwoven industry will be hampered by raw material price instability, regulations, investment cost, and substitutions. The market is projected to remain the highest in Asia, followed by Europe and North America. The production techniques are expected to remain similar between 2019 and 2028, with spunbonded as the most utilized, followed by staples, meltblown, and composites following (Inkwood Research).

The nonwoven filter market is also expected to experience tremendous growth. Nonwovens are ideal for filtration, as they can be engineered for excellent porosity, such that they able to capture particles passing through. The growth can be expected from every sector as an increasing population, combined with an increased concern for health, leads to a higher demand for water filtration, air filtration, pollution filtration, and industrial filtration. Increased regulation is also a driver of the industry as environmental concerns propagate across federal and local governments. Finally, improvements in technologies and capabilities have led to more efficient, less expensive filtration capabilities (North American Nonwovens Filter Market) 2018.

The Market for Lignin

Each year, 50 to 70 million tons of lignin are produced (Suhas *et al.* 2007; Mandlekar *et al.* 2018); however, 5% of annually produced lignin is used for commercial applications (Bai *et al.* 2019), and only 1 to 2 % of the lignin is used for value-added products (Aro and Fatehi 2017; Zhang *et al.* 2020d). A significant portion of the non-utilized lignin is burned to produce energy as a method of disposal and utilization (Mandlekar *et al.* 2018; Bai *et al.* 2019; Zhang *et al.* 2020d).

There are many kinds of lignin processes; however, the kraft and sulfite pulping processes have been used abundantly worldwide for effective lignin separation from cellulose and hemicellulose. Kraft lignin, which accounts for 85% of the world's lignin production, is separated with sodium hydroxide and sodium sulfide (Argyropoulos 2013; Schreiber *et al.* 2014). Lignosulfonates are derived from the sulfite process, which treats lignin with sulfurous acid, sulfite salt, as well as magnesium, calcium, sodium, or ammonium sulfites and bisulfites (Sadeghifar and Argyropoulos 2015; Zhang *et al.* 2020d). As of the writing of this paper, lignosulfonates account for 90% of the total market of commercial lignin, and the worldwide production of lignosulfonates is approximately 1.8 million tons (Dallmeyer *et al.* 2013; Sadeghifar and Argyropoulos 2015; Aro *et al.* 2017).

The global lignin market has been steadily increasing. According to Global Market Insights, the lignin market size exceeded $730 million in 2019 and is estimated to experience a 5.7% compound annual growth rate between 2020 to 2026. The compound annual growth rate from 2020 to 2026 is expected to increase in the lignosulphonate segment by 5.9%, in the polymer application segment by 5.4%, and phenol downstream potential by 3.6%. These increases are due to the realization of usability in several industries (Global Market Insights 2021).

The top eight global lignin-based product manufacturers are: Borregaard LignoTech, Changzhou Shanfeng Chemical Industry Co., Ltd., Domsjo Fabriker AB, Domtar Corporation, Nippon Paper Industries Co., Ltd., MeadWestvaco Corporation, Tembec, Inc., and UPM-Kymmene Corporation (Global Market Insights 2021). The profitability of lignin in the nonwoven industry currently heavily relies on the price of petroleum (LigniMatch 2010). Technologies are under continuing development to bring down the cost of lignin incorporation, but political and environmental factors fluctuate and influence the financials. As previously stated, there are currently no reviews of lignin use pertaining to the nonwoven industry. Thus, this review will help increase lignin incorporation into industrial processes and assist in determining new directions of lignin nonwoven research.

Nonwoven Industry Applications

Production of nonwoven materials is characterized by high production rates and low costs. Nonwoven techniques are able to produce larger batches in contrast to woven processes such as yarn spinning, knitting, and weaving. Annual nonwoven production and deliveries for the Greater Europe region (Western, Central, and Eastern Europe, Turkey and Commonwealth, and the Independent States) has reached >1.6 million tonnes. Applications include single-use liquid absorbent hygiene products, representing over one-third of total production as well as durable products such as geosynthetics, filters, home furnishings, synthetic leather, automotive headliners, and floor coverings. There are various manufacturing routes for nonwovens, which essentially depend on whether the precursor web comprises a continuous filament (spunbond), or staple fiber and, in the latter case, whether it is formed either by dry (dry-laid) or wet (wet-laid) techniques; the ensuing mats can be bonded mechanically, thermally, or chemically to produce the nonwoven fabric (Burkinshaw *et al.* 2012). The unique properties of different lignins, a topic discussed throughout this review, endow lignins with the potential to applied across a wide range of applications.

Lignin Presence in Nonwovens

Lignin has been researched as a functional material for nonwovens and textile finishing processes for over 20 years. However, the presence of lignin in nonwoven finishings has not been fully organized and reviewed yet. This effort attempts to bridge this gap in the literature.

There are several types of lignin that have the ability to be incorporated in composites, including sulfur free lignin (Aslanzadeh 2017), but kraft lignin has shown the most potential. Kraft lignin is a readily available source of lignin that may be fractionated into materials with different functional group contents, thereby offering significant benefits for many applications (Argyropoulos 2014).

While new technologies are being explored based on enzymatic fractionation (de Avila Delucis *et al.* 2017; Li *et al.* 2017), an early differentiation of these highly heterogeneous materials (Sadeghifar and Argyropoulos 2016) is based on fractionation using acetone, creating acetone-soluble and acetone-insoluble kraft lignin fractions (Cui *et al.* 2014). Acetone-soluble kraft lignins are more branched and less polymeric and have smaller molecular weights than acetone-insoluble kraft lignin. Acetone-insoluble kraft lignins have a less branched structure and fewer wood native lignin bonding patterns than acetone-soluble kraft lignin fractions (Crestini *et al.* 2017).

Since the early acetone fractionation was proposed by Cui *et al.* (2014), other solvent fractionation systems have followed. The present review will mainly discuss the use of acetone as the partitioning solvent, since the associated science has been rather comprehensive, offering logical extensions for the use of other solvents. When processed, these fractions are shown to behave differently in polymeric blends, possessing differing spinnability and stability, and demonstrating unique antioxidant properties (Sadeghifar and Argyropoulos 2015). These factors, among others, will be discussed further in this review with a focus on the differences between high and low molecular weight lignin fractions as well as polymer composites.

Nonwoven process techniques are able to incorporate lignin seamlessly to create viable products for various applications. Current techniques such as electrospinning, spunbonding, melt bonding, and more, offer the ability for lignin composites of promise for future work.

Lignin composites currently include polyethylene oxide (PEO) (Dallmeyer *et al.* 2010; Schreiber 2012; Schreiber *et al.* 2014; Poursorkhabi *et al.* 2015; Bahi *et al.* 2017; Cho *et al.* 2020), polyacrylonitrile (PAN) (Zhao *et al.* 2015; Ding *et al.* 2016; Ogale *et al.* 2016; Go *et al.* 2018; Al Aiti *et al.* 2020; Nie *et al.* 2020; Yang *et al.* 2020; Zhang *et al.* 2020b), and polyvinyl alcohol (PVOH) (Kubo and Kadla 2003; Lai *et al.* 2014a; Nair *et al.* 2014; Ma *et al.* 2016; Ogale *et al.* 2016; Beck *et al.* 2017; Lu *et al.* 2017, 2018; Uddin *et al.* 2017; Aadil *et al.* 2018; Ko *et al.* 2018; Lee *et al.* 2018; Lee *et al.* 2019; Roman *et al.* 2019; Zhang *et al.* 2019; Camiré *et al.* 2020; Cui *et al.* 2021; Hou *et al.* 2021), which are able to be used in air filtration (Chang *et al.* 2017; Cui *et al.* 2021), water purification (Lai *et al.* 2014a; Bahi *et al.* 2017; Beck *et al.* 2017; Kwak *et al.* 2018; Zhang *et al.* 2019; Camiré *et al.* 2021; Chen *et al.* 2021; Hou *et al.* 2021), gas filtration (Amid *et al.* 2016; Chang and Chang 2016; Cui *et al.* 2021), carbonized nonwovens (Dallmeyer *et al.* 2010; Lai *et al.* 2014a; Poursorkhabi *et al.* 2015; Ago *et al.* 2016; Ding *et al.* 2016; Ma *et al.* 2016; Beck *et al.* 2017; Park *et al.* 2017; Culebras *et al.* 2019; Perera Jayawickramage and Ferraris 2019; Roman *et al.* 2019; Zhang *et al.* 2019; Al Aiti *et al.* 2020; Cho *et al.* 2020; Li *et al.* 2020; Zhang *et al.* 2020b), flame retardants (Cayla *et al.* 2016), and more. Overall, lignin has shown the ability to be incorporated into the previously enumerated applications in significant proportions, thus offering different properties with notable sustainable connotations and more.

As anticipated, amphiphilic lignosulfonates have been used rather effectively in dyestuff dispersants for over 60 years, since they possess both a hydrophobic aromatic structure and hydrophilic sulfonate groups on the side chain (Xu and Ferdosian 2017). However, additional technical lignins may be a potential resource for dye dispersants and other innovations representing viable topics for further research and potential market opportunities (Textile Chemicals). This is evident especially for polypropylene nonwovens, where coloration is currently only possible at scale through mass pigmentation with a limited number of colors (Aspland 2005). The dark color of lignin presents some challenges for dye dispersion applications, but several studies have reported the use of lignin in dye dispersion applications (Xu and Ferdosian 2017). Lignin-based dispersants have the potential to satisfy some of the market demand for biobased nonwoven processing alternatives while providing cost savings and innovations in nonwoven coloration technologies, with some limitations due to the dark color of lignin.

Kraft Lignin as a Feedstock

As discussed previously in this review, a readily available, inexpensive form of lignin is kraft lignin, which is derived from the pulp and paper process as waste after chemical (kraft) pulping is completed on woodchips. Kraft lignins are distinguished from other forms of lignin since they are rich in phenolic OH groups and high carbon content; these can provide antioxidant and fire-retardant properties respectively (Mandlekar *et al.* 2018; Lee *et al.* 2019).

Higher molecular weight lignin fractions have been seen to possess greater antioxidant activity with greater phenolic functional groups present in the fractions (Sadeghifar *et al.* 2017). Higher molecular weight lignin fractions also make fibers with better spinnability and better performance when fractionated with an enzymatic process with a laccase base and a 1-hydroxybenzotriazole (HBT) mediator. The lignin fractions arising from enzyme solubilization rather than acetone solubilization have different molecular weights and fewer OH groups. The kraft lignin water-insoluble portions increased molecular weight by 2.6 times, while the water-soluble kraft lignin portions decreased molecular weight by 60%. The study also demonstrated better spinnability of the laccase-HBT lignin fractions due to more linear lignin fractions with reduced interlinking, while water-soluble kraft lignin portions fractionated by the laccase-HBT complex resulted in more defects and therefore decreased mechanical performance (Li *et al.* 2017).

Kraft lignin with low molecular weight exhibits strong antioxidant properties, which is likely due to more exposed phenolic OH groups. When all phenolic OH groups are methylated, the fractions of kraft lignin demonstrate zero antioxidant activity, explaining the source of this behavior (Dallmeyer *et al*. 2014). To utilize this low molecular weight kraft lignin with stability, it is required to selectively methylate the remaining phenolic OH groups and their fractions to stabilize the kraft lignin and PE blend suitable for fiber usage. Lower molecular weight kraft lignin is optimized for blending with PE at low molecular weights, since the lignin is more easily distributed throughout the PE matrix. When mixed with PE, the kraft lignin increases the oxidation temperature by 50°C at 5% (w/w) of kraft lignin (Dallmeyer *et al*. 2014). This increase in both glass transition temperature (PE blend) and oxidation temperature (fiber spinning) can be explained by π stacking, giving the structure an increased rigidity, especially for the acetone-insoluble lignin fractions. Given the high temperatures involved in melt electrospinning to create nonwovens, kraft lignin fractions' antioxidant behavior again demonstrates an attractive and exciting raw material for manufacturing nonwovens (Dallmeyer *et al.* 2013, 2014; Sadeghifar and Argyropoulos 2015).

Lignin is primarily utilized as a composite material in the electrospinning method with other materials such as polyvinyl alcohol (PVOH), poly(acrylonitrile) (PAN), and poly(ethylene oxide) (PEO). Among them, PAN is a highly used material since it has high oxidative stability at high temperatures. Use of the lignin/PAN composite material at 50% lignin (w/w) led to increases in porosity of the fabric when compared to the commercial grade (74% lignin/PAN vs 42% commercial grade) (Dallmeyer *et al.* 2014; Alekhina *et al.* 2015). This is largely due to the large fiber diameter afforded by the lignin/PAN composite completed by electrospinning.

Kraft lignin is also an exciting field for nonwovens since it may demonstrate high fractionated yield through organic solvent extraction *via* the use of ethanol (Zhang *et al.* 2020a), 1-propanol (Zhang *et al.* 2020a), 1-butanol (Zhang *et al.* 2020 a), and acetone (Sadeghifar and Argyropoulos 2015, 2016; Crestini *et al.* 2017; Sadeghifar *et al.* 2017). The resulting fractionated kraft lignin is high in phenolic OH groups while maintaining a low molecular weight and maximizing antioxidant activity. Kraft lignin fiber material may also be successfully obtained by precipitation at high pH; such samples demonstrate exemplary purity, high molecular weight, and low sulfur content (Dallmeyer 2013). While these fibers may not have the same desirable properties as low molecular weight lignin (tensile strength, dispersity in blending composites), high molecular weight kraft lignin gives more thermal stability and resistance to cross-linking (Karaaslan *et al.* 2021). Furthermore, there is a possibility that lignin fractionation may be achieved *via* laccase-HBT enzymatic treatment (Li *et al.* 2017). Because this approach yields robust insoluble fractions with greater spinnability, this lignin treatment process is worthy of greater review for lignin value-added products. Overall, kraft lignin provides a cheap option for nonwoven fiber composites.

INCORPORATION OF LIGNIN IN NONWOVEN PROCESSING TECHNIQUES

Nonwovens are versatile materials, and their characteristics can be manipulated by manufacturing processes in addition to raw material qualities. There are numerous variables that impact performance from the initial web formation to finishing processes. The versatility of lignin influences different effects, depending on the selected manufacturing process. The detailed nonwoven process is elaborated in the following sections.

Web Formation

Nonwoven manufacturing processes can be divided into three steps: web formation, bonding, and finishing/converting. Depending on the web forming and bonding technologies, the basic properties of nonwoven fabrics such as fiber diameter, fiber orientation, web density, *etc*., can be highly unique. The web formation of nonwoven fabrics can be classified as follows: dry-laid, wet-laid, and polymer-based systems (Albrecht *et al.* 2004; Hutton 2016). It is commonly believed that the origins of the dry-laid technique are based in textiles, the origins of the wet-laid technique are based in papermaking, and the origins of the polymer-based technique are in the plastics and extrusion processes (Karthik and Rathinamoorthy 2016).

In the case of fiber-based raw materials, the nonwoven web is formed by dry-lay or wet-lay processes. The dry-lay web formation includes carding and air-lay processes, and the fiber raw materials are usually supplied as bale forms; thus, many other processes should be done before carding or air-lay process, such as bale opening and blending (Leifeld *et al.* 2004). In the carding process, roller cards disentangle the fiber tuffs and form the nonwoven web with staple fibers. Alternatively, the air-lay process takes cellulose fluff pulp or staple synthetic fibers conveyed by air to form nonwoven fabrics on a moving belt or continuous filter screen (forming wire) (Hutton 2016). During the wet lay process and in a manner analogous to the papermaking process (Pill and Afflerbach 2004; Hutton 2016), the fibers are dispersed in an aqueous slurry (stock), and the web is formed on a wire after the diluted stock is fed from the headbox and filtered on the wire. In addition to wood pulp and natural fibers, man-made fibers such as polyester, nylon, and rayon fibers can also be processed in this manner.

Polymer-type raw materials form nonwoven webs by spun-lay processes, including spunbonding and meltblown technologies (Hutton 2016). Spunbond and meltblown are the significant melt-spun processes. In both processes, the polymer is fed in the form of powder granules or pellets and melted by heat before extrusion. In the spunbond process, the extruded fibers are laid on the moving screen and form a web, but melted polymer resin directly forms the nonwoven webs in the melt-blown process; the polymer filaments are drawn by heated and high-velocity air to the collector, as shown in Fig. 1 (Hutten 2016). In the spunbond process, fibers are extruded, cooled, and laid down on the collector, in contrast to the meltbond process, where polymer filaments are cooled and collected on a moving collector screen.

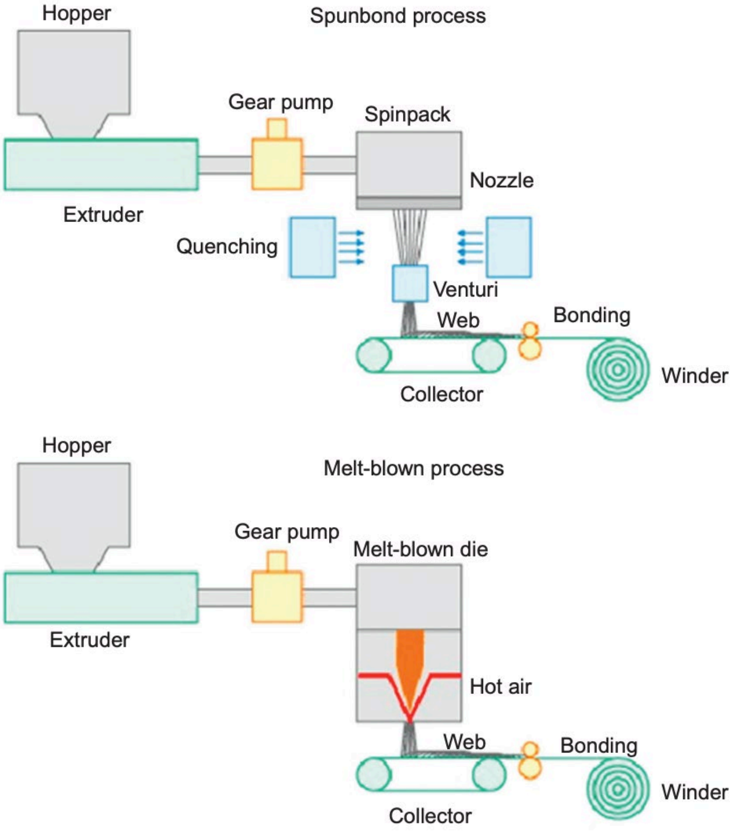


Fig. 1. Comparison of melt-spun processes (Reprinted with permission from Hutten 2016).

Similar to melt blowing, solution blowing is a commonly explored technique used for industrial-scale manufacturing. The primary difference between the two is the polymer size; solution blowing tends to create nanofibers, while melt blowing creates microfibers (Kakoria and Sinha-Ray 2018). For solution blowing, a heated polymer solution is fed through a small capillary and catalyzed by a high-velocity hot gas flow. The fiber is then collected on a surface to form a nonwoven web. This process works significantly better than melt blowing for the production of biopolymer nonwovens, since solution blowing is performed at lower temperatures, decreasing the risk of denaturing the biopolymer. The biopolymer blend can be extruded instead of melted and may then be collected on a surface to form a nonwoven web (Kakoria and Sinha-Ray 2018).

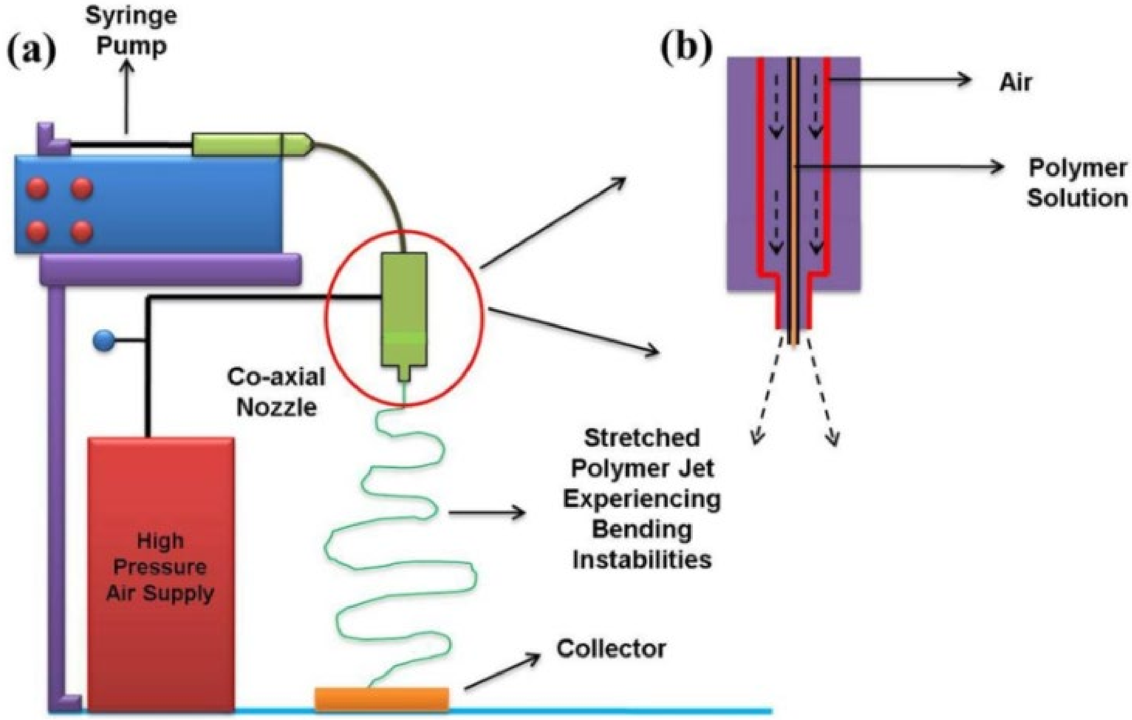


Fig. 2. Schematic representation of solution blowing with a zoomed-in view of the coaxial nozzle (Reprinted with permission from Kakoria and Sinha-Ray 2018).

Another viable fiber-spinning process with polymers is electrospinning (Asmatulu and Khan 2019). Electrospinning is a nonwoven manufacturing technique that is one of the most promising potential techniques due to its current success and versatility. Electrospinning offers the capability to create a unique structure with chemical/physical properties, stability, high surface-area-to-volume ratio, and orientation control. The basic components of an electrospinning setup include a high voltage power supply that is typically DC, a spinneret, and a collector (Kakoria and Sinha-Ray 2018). The process involves electric forces to charge and eject a polymer held together by viscoelastic forces that will solidify to form a fiber or filament (Poursorkhabi *et al.* 2015). Electrospinning relies on electrohydrodynamic phenomena to maintain homogeneity in the polymer size and morphology (Kakoria and Sinha-Ray 2018). The size of these fibers can range from as small as tens of nanometers to several micrometers (Kakoria and Sinha-Ray 2018; Nanoscience Instruments). The fibers may be oriented, randomized, or laid out in geometric shapes (Poursorkhabi *et al.* 2015). This versatility offers manufacturers the ability to manipulate and thereby adapt to various needs. Table 1 lists ranges of parameters that have been employed in electrospinning.

Table 1. Electrospinning Parameters for Lignin-based Nonwovens (selected rows from Table 2 in Kakoria and Sinha-Ray 2018)

Polymer	Solvent	Applied Voltage (kV)	Collecting Distance (cm)	Flowrate (mL/h)	Diameter (nm)	Reference
Lignin/PAN	N,N-DMF	15	10	1.2	300	Seo *et al.* 2011
	DMF	20	20	1	200-500	Jonoobi *et al.* 2010
	DMF	26	25	1	~200	Beck *et al.* 2017
	DMF	16	-	1.6	100-400	Park *et al.* 2017
Lignin/PEO	Ethanol/DMF/Water	5.5-13.5	22.5	0.1	~400	Schreiber 2012
	DMF	6.5-7.0	10	1	~1000	Wang *et al.* 2013
	DMF/Methanol/ Methylene Chloride	5.5-13.5	22.5	0.1	85-875	Das *et al.* 2018
	DMF	15	20	-	400-3261	Dallmeyer *et al.* 2010
	Water	20	22	0.2	300-12,000	Poursorkhabi *et al.* 2015
	DMF	14	20	1.5	26-809	Aslanzadeh *et al.* 2017
	DMF	20	10	0.5	300-1100	Shi *et al.* 2018
	Ethanol	9-14	14-20	1.8	234-1363	Luo *et al.* 2010
Lignin/PVA	Water	26	25	1.2	~300	Lai *et al.* 2014a
	2-propanol	26	25	1.2	~120	Lai *et al.* 2014b
	Water	22	15	1	70-290	Fang and Reneke 1997

There are two main categories into which electrospinning processes may be placed: needleless electrospinning and needle-based electrospinning. Needleless electrospinning allows for large-scale production, but at the expense of morphology and quality control. Needle-based electrospinning allows for a much larger variety of materials, greater production flexibility, and increased control of the process (Nanoscience Instruments). Electrospinning has also been demonstrated as a viable process for creating high-porosity nonwoven membranes, making them high-valued lithium-ion battery separator membranes. The increased porosity compared to other nonwoven fabrication methods increases battery potential by increasing electrolyte uptake. The usage of polymers can aid the performance of lithium-ion due to their good performance in conjunction with electro-spinning. The most common polymer, PAN, has shown properties such as flame resistance, ease of processing, electrochemical stability, and high oxidative stability (Zhao *et al.* 2015).

Electrospinning has a promising future in the nonwoven industry. The nonwoven industry is investigating methods to produce uniformly oriented fibers that do not have bending instability. Bending instability is the instability of the jet due to high charge density, which causes plastic deformation, allowing the fibers to be randomly aligned. There have been recent developments to combat bending instability by applying a low electrostatic field near the tip of the needle, lowering mass flow rate in the syringe pump, and placing an electrode plate close to the electrospinning emitter (INDA). Force spinning is another recent development that addresses material selection and efficiency. By replacing the electrostatic force with centrifugal force, the material selection can be expanded to include both conductive and non-conductive polymers (Asmatulu and Khan 2019).

Typically, lignin does not have enough viscoelastic strength to be suitable for electrospinning, so it is typically mixed with a binder such as PEO, PVOH, or PAN. These binders are typically prepared in an aqueous solution that will allow for a 50/50 mix of binder and lignin. Phenolic hydroxyl groups in lignin combine with the etheric oxygen of

PEO in alkaline solutions to create a complex formation that leads to a minimal amount of binder being required. The chains of PEO become entangled, trapping lignin, while the bridging of the PEO chains creates an association-induced complex (Poursorkhabi *et al.* 2015). Such production processes that involve the inclusion of biopolymers are not as straightforward as with synthetic or thermoplastic polymers. At high temperatures, biopolymers can denature, leading to non-thermal techniques such as electrospinning being preferred. The solvent selection for all processes is highly dependent on factors such as molecular weight, polymer purity, charge location and amount, air temperature, and airflow. These are critical factors that determine the end product quality (Kakoria and Sinha-Ray 2018). As far as electrospinning with lignin is concerned, hardwood organosolv (Alcell) lignin has been shown to be a much better starting material for electrospinning compared to kraft lignin (Kakoria and Sinha-Ray 2018).

Bonding

After the web formation, most nonwoven webs must bond to consolidate their webs. The bonding process can be classified into two groups: chemical process and physical process (Nonwoven Bonding Techniques 2016; Introduction to Nonwovens; Kittelmann *et al.* 2004). Chemical bonding uses binders to consolidate the nonwoven web and is usually triggered by heat treatment. Physical bonding processing includes mechanical and thermal processes. Needling and hydroentangling are the typical mechanical bonding processes. The needling process forms the nonwoven web using penetration of barbed needles. By such action the fiber can be reoriented in the vertical direction, entangled, and interlocked, and the nonwoven web can be consolidated. Hydroentangling, also called spunlacing or hydraulic needling, is the mechanical process that entangles the fiber webs by means of fine and high-speed water jets. The properties of nonwovens fabricated using hydroentanglement depend on fiber specifications, fiber webbing, surface chemistry, water jet specifications, and processing speed (Xiang *et al.* 2006). Multiknit stitch bonding is an additional mechanical bonding process for nonwoven fabrics (Nonwoven Bonding Techniques 2016). In multi-knit stitch bonding, both sides of the fabric are formed into a densely knitted alignment to produce a double-sided, three-dimensional nonwoven fabric. The incoming K-unit receives the intermeshing pile fibers on its surface and is able to be joined to other K-units. Other materials and compounds can also be combined in this process to produce a composite with desired properties. Thermal bonding uses heat treatments, such as thermal calendering, hot air treatment, or point bonding with embossed rollers to bond together nonwoven materials. For thermoplastics, thermal bonding is the most commonly used technique; it is used significantly in baby diapers (New Cloth Market 2021).

Finishing

The final step of nonwoven processing involves finishing treatments to complete the desired properties from the nonwovens. In many cases, nonwoven finishing shares methodology and equipment with woven or knitted textile fabrics; however, some techniques are unique to nonwovens (Stukenbrock 2004a,b; Indi *et al.* 2019). The finishing process can be distinguished by mechanical and chemical processes. Shrinking, compacting, creping, and calendering are examples of mechanical finishings to improve the dimensional stability or impart the soft or smooth surface. Chemical finishing includes washing to remove unwanted materials from the nonwoven, dyeing, printing, softening, coating, and other finishing to give the nonwoven functions such as water-repellent/absorbent, antistatic, and flame-resistant properties.

COMPOSITES

Modern nonwoven composites use lignin as an ingredient in a polymer blend with other polymers. Such addition may provide a more sustainable alternative to current carbon sources while maintaining target performance. Composites are a major material topic that shows promise for lignin applications in the nonwoven industry. The potential commercial applications are predominantly water treatment, battery membranes, carbon fibers, and carbonized mats. The three most common lignin composite polymers found across the literature are PEO, PAN, and PVOH. The field of lignin composites is rapidly evolving, and significant research is being performed to increase compatibility and improve the characteristics of such nonwoven composites. Additionally, research is ongoing to incorporate a wide range of lignin types into nonwoven composites, and each study presented in this section includes the type(s) of lignin used. Lignin-based carbon fibers are produced using techniques used by the nonwoven industry and are an important facet of lignin applications. For example, lignin/PEO composites have shown promise for carbon fiber production (Yu *et al.* 2015). Furthermore, similar materials, carbonized lignin-based nonwovens are discussed in this review. While both result in highly porous materials with high carbon content, the primary distinction between the two is the production process. Carbonized nonwovens are first produced as a nonwoven material, stabilized, and finally carbonized.

Generally, lignin composites show improved processability and fiber properties compared to lignin alone. A significant issue that arises during the electrospinning process is the formation of beaded fibers rather than smooth fibers. Beaded fibers are undesirable because the beads act as defects in the fiber structure, impacting the properties of the nonwoven. Figure 3 provides SEM images showing the difference between highly beaded fibers (a), slightly beaded fibers (b), and smooth fibers (c) (Dallmeyer *et al.* 2010).

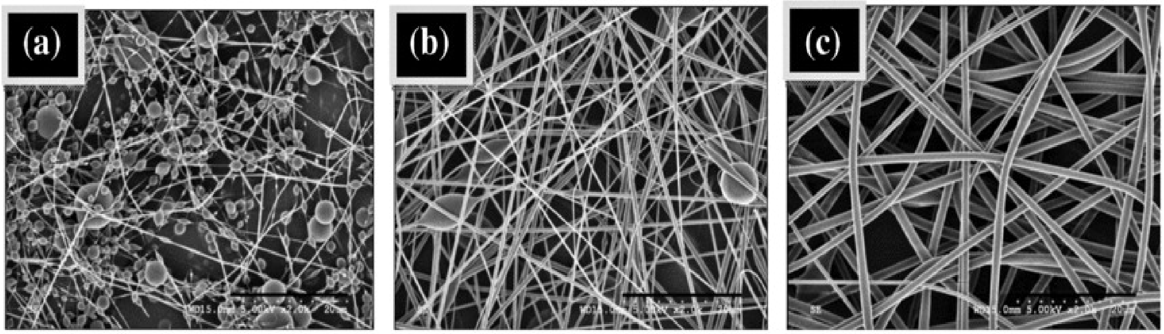


Fig. 3. Comparison of highly beaded (a), slightly beaded fibers (b), and smooth (c) fiber morphologies (adapted with permission from Dallmeyer *et al.* 2010).

Companies building from these advances and furthering the lignin composite knowledge are Prisma Renewable Composites and EUCALIVA. Prisma Renewable Composites is focused on turning lignin into high-value composites. Currently, they are focusing on “anion-exchange membranes, carbon fiber composites, and biopolymers/plastics” (Prisma Renewable Composites). EUCALIVA is a consortium composed of companies, universities, and research institutes that specializes in the isolation and use of eucalyptus kraft lignin from black liquor. They focus on the production of nonwovens from kraft lignin blends, with a focus on stretchable electronic films and activated carbon produced from nonwoven lignin mats (Eucaliva).

Compatibility Challenges

A significant issue restricting the usage of lignin as a composite is lignin/polymer compatibility. If the lignin and polymer are not compatible, then phase separation can occur in the solution prior to the fiber formation process. As a result, several issues could arise, including the inability to form fibers, the production of fibers that are composed of only one material, and degraded properties of the produced fibers. Thus, it is important to evaluate the compatibility between the composite materials prior to attempting fiber formation.

The driving factor for lignin/polymer compatibility is the abundance of hydroxyl groups on the lignin molecule. As a result, lignin is generally compatible with polar polymers and incompatible with nonpolar polymers (Yang *et al.* 2019). However, the lignin source, which was discussed previously in this review, plays a major role in compatibility. The potential for different, non-hydroxyl, side groups that arise during different pulping processes in addition to different lignin structures from different plants impacts the lignin-polymer interactions and thus the compatibility of the lignin/polymer composite. Lignin has been shown to be compatible with specific polymers, including but not limited to PEO (Dallmeyer *et al.* 2010; Schreiber *et al.* 2014; Poursorkhabi *et al.* 2015; Bahi *et al.* 2017; Cho *et al.* 2020), PAN (Zhao *et al.* 2015; Ding *et al.* 2016; Ogale *et al.* 2016; Park *et al.* 2017; Go *et al.* 2018; Al Aiti *et al.* 2020; Nie *et al.* 2020; Yang *et al.* 2020; Zhang *et al.* 2020b), PVOH (Fernandes *et al.* 2006; Ago *et al.* 2016; Ma *et al.* 2016; Aadil *et al.* 2018; Kwak *et al.* 2018; Lee *et al.* 2018, 2019; Xiong *et al.* 2018; Perera Jayawickramage and Ferraris 2019; Roman *et al.* 2019; Zang *et al.* 2019; Camiré *et al.* 2020; Ko *et al.* 2020; Chen *et al.* 2021; Posoknistakul *et al.* 2020; Zhang *et al.* 2020c; Hou *et al.* 20210, polymethyl methacrylate (PMMA) (Kai *et al.* 2015), polycaprolactone (PCL) (Kai *et al.* 2015), polylactic acid (PLA) (Cayla *et al.* 2016; Culebras *et al.* 2019), and thermoplastic polyurethane (TPU) (Culebras *et al.* 2019). Most of the polymers listed are polar, which follows the trend identified by Yang *et al*. (2019).

One common method for determining polymer compatibility is by measuring the glass transition temperature, T_g, of the lignin/polymer composite. This method is not specific to lignin composites but can be applied to determine lignin/polymer compatibility. In this method, a single T_g value indicates that the lignin is compatible with the polymer, while two or more T_g values indicate that lignin and the polymer are not compatible. For example, Ding *et al.* (2020) observed a single T_g band for a lignin/PAN composite, indicating that the lignin and PAN were compatible.

Another polymer compatibility method that has been applied to lignin is the Han plot. The Han plot method focuses on rheological compatibility, looking at the first normal stress difference, as well as elastic and viscous moduli (Han *et al.* 1985). The Han plot method was also applied to lignin/PAN mixtures demonstrating their compatibility (Ding *et al.* 2016).

Pouteau *et al.* (2004) used image analysis of films from various polymer blends to find "good polymer candidates" and "good lignin candidates" from the perspective of compatibility. It was reported that, generally, nonpolar and highly polar polymers were only compatible with lignin that had low molecular weight. In contrast, slightly polar polymers, such as polyvinyl chloride (PVC) and polystyrene (PS), demonstrated good compatibility with lignin.

Kun and Pukánszky (2017) performed a comprehensive review on the compatibility of lignin with several classes of polymers and the effects of various modifications. For nonpolar polyolefins, complete incompatibility is anticipated; however, several sources claim to have achieved successful compatibility of lignin with polyolefins. Specifically, steam-explosion lignin and lignosulfonates were found to be compatible with various types of PE (Kun and Pukánszky 2017). In addition, organosolv lignin was found to be compatible with both PP and low-density PE. However, Kun and Pukánszky questioned the validity of these claims and still conclude that lignins and polyolefins are generally incompatible.

The second class of polymers explored by Kun and Pukánszky (2017) was aromatic polymers. Due to the presence of the aromatic ring, it is expected that lignin-aromatic polymer blends will have better compatibility than lignin-polyolefin blends. Although this should generally be the trend, it was noted that due to the large variation in lignin fractions and aromatic polymer type, it is difficult to establish a rule for lignin-aromatic polymer compatibility. Lignin was reported to have both compatibility and incompatibility with various aromatic polymers, depending on the source of lignin and any additional modifications that were performed. For example, lignin treated with maleic anhydride was found to have some compatibility with PS. while unmodified lignin was largely incompatible. In general, lignin-PS and lignin-PET blends were reported to display varying degrees of compatibility (Kun and Pukánszky 2017).

The final class of polymers examined by Kun and Pukánszky were polymers that exhibit hydrogen bonding. The strong interactions due to hydrogen bonding are expected to improve the compatibility of lignin and these polymers (Kun and Pukánszky 2017). The hydroxyl, carboxyl, and methoxy groups that are part of the lignin structure can form hydrogen bonds with a polymer, leading to compatibility (Li *et al.* 2021). As with the polyolefins and aromatic polymers, there isn’t a clear rule for compatibility, with various sources claiming that a certain lignin-polymer blend is compatible with other sources reporting incompatibility for the same blend (Kun and Pukánszky 2017).

Several factors can explain the reported differences in lignin-polymer compatibility. Primarily, the importance of technical lignin fraction cannot be understated, as a wide range of lignin structures are observed depending on how the lignin was produced. In addition, different methods have been used to determine compatibility, which may lead to variations in what different researchers and research groups defined as a compatible blend. Thus, for lignin applications to nonwovens, it is difficult to formulate general compatibility rules due to the wide variation in lignin structure based on the lignin production process. As a result, it appears that the best method to determine compatibility is to perform lignin nonwoven processing techniques, such as electrospinning, at a bench-scale prior to scaling efforts. Due to the demonstrated heterogeneity of lignin, as the amount of lignin significantly increases within a composite, the probability for the occurrence of sufficiently different lignin structures also increases, and this could result in incompatibility issues. While the general compatibility trends discussed above will likely still hold, a few incompatible lignin fractions could severely impact a large-scale fiber production process. In processes that use spinnerets, the interruption of a single spinneret could necessitate halting the entire process to clear blockages and resume production.

As the demand for lignin increases, the availability of technical lignins will need to be considered to ensure an adequate supply is available. Consider the case of organosolv lignin: If a successful large-scale fiber production process is developed using a polymer that is only compatible with organosolv lignin, then the availability of organosolv lignin will play a major role in the ability to mass-produce the fiber. In contrast, if the compatible lignin is kraft lignin, then there will be much less concern about the lignin supply due to the abundance of kraft mills.

Lignin/PEO Nonwovens

A common lignin composite that shows promise for industrial applications is the combination of lignin and PEO. Lignin/PEO composites have shown potential applications in water filtration, carbonized nonwoven production, and air filtration. Nonwovens have been found to be rather efficient, since they are able to easily contain adsorbents and offer good efficiency when fabricated using electrospun, meltblown, and spunbond structures. The three primary design adjectives are immobilizing the adsorbents, controlling medium packing density, and improving the filtration capacity as a final composite structure (Amid *et al.* 2016). Dimethylformamide (DMF) was identified as a desirable solvent for lignin/PEO electrospinning (Schreiber 2012; Schreiber *et al.* 2014). In addition to DMF, water solutions with some added sodium hydroxide were also reported to result in successful electrospinning attempts (Poursorkhabi *et al.* 2015).

There is evidence that due to the nanoscale size of lignin/PEO nonwoven fibers produced *via* electrospinning, their filtration efficiency is improved, at similar pressure drop regimes, when compared to larger fibers (Graham *et al.* 2002; Chang and Chang 2016). This provides further evidence that lignin/PEO nonwovens have the potential to be used in filtration applications (Ding *et al.* 2016). It is also to be noted that filtration is not just limited to solids and liquids. In this respect lignin nonwovens have also been shown to be suitable for the filtration of gases to control odors and/or irritant vapors (Amid *et al.* 2016).

The state of entanglement determines the performance of PEO. The quantity of lignin heavily impacts the flocculation, as an increase in lignin correlates to a reduced flocculation (The North American Filter Market 2018). The key factors impacting lignin/PEO composites are lignin to PEO ratio, total polymer concentration, technical lignin source, and PEO molecular weight. Reported lignin to PEO ratios were between 85:15 and 99:1, with the most focus on 95:5 and 99:1 (Cho *et al.* 2020). The total polymer concentration investigated varied widely, from 5 to 50%, with most papers reporting successful electrospinning at concentrations between 20 and 40% in DMF (Schreiber 2012; Schreiber *et al.* 2014; Cho *et al.* 2020). However, aqueous electrospinning was reported to be successful between concentrations of 5 and 11%, which is significantly different from the efforts that used DMF (Poursorkhabi *et al.* 2015). The lignin type, pulping process, and plant were all shown to have significant impact on the electrospinning conditions required to produce smooth fibers. Dallmeyer *et al.* (2010) investigated the impact of pulping processes and found that softwood kraft lignin/PEO could be successfully electrospun at a 95:5 ratio with 30 wt% total polymer. In contrast, they determined that organosolv/PEO, hardwood kraft/PEO, and lignosulfonate/PEO composites required approximately 40 wt% total polymers, which is a significant difference (Dallmeyer *et al.* 2010). PEO molecular weight impacts the ability to be electrospun with low molecular weights, resulting in spraying rather than electrospinning, while high molecular weights were successful (Poursorkhabi *et al.* 2015).

The four key factors mentioned above may be manipulated to adjust the lignin/PEO membrane characteristics to meet a specific application. Carbonized nonwoven applications will have significantly different desired properties when compared to water filtration applications (Bahi *et al.* 2017; Cho *et al.* 2020). This versatility is an attractive component to lignin/PEO polymer blends. Some specific potential applications of lignin/PEO composites are discussed below.

Lignin/PEO - Water Filtration

For water purification purposes, zeolites were introduced to the lignin/PEO composite (Bahi *et al.* 2017), The addition of zeolites resulted in the surfaces of the composite fibers becoming coarser, which can be beneficial for trapping contaminants such as microorganisms or microplastics. In addition to the change in surface morphology, the properties of the electrospinning solutions and the fibers that are produced are significantly altered by the addition of zeolite (Bahi *et al.* 2017). In the cited work, a 25 to 30 wt% (total polymer) in DMF with a lignin to PEO ratio of 99:1 was used. Based on several experiments, the optimal zeolite concentration was determined to be 1%. The major concern for this composite membrane is durability, which was addressed through a post-spinning heat treatment process, resulting in a much stronger membrane. Retention of PS particles was used to measure membrane retention (Bahi *et al.* 2017). The lignin/PEO/zeolite composite achieved a retention percentage of 95% for particles larger than 1 micrometer, but particles smaller than 1 micrometer were not significantly removed. The 95% retention is important because a significant number of microorganisms and most microplastic particles are larger than 1 micrometer, indicating the potential for a lignin/PEO/zeolite membrane in water filtration (Bahi *et al.* 2017). The packing density of adsorbents in filter material depends on a number of conditions such as the presence of water - if water is present in hydrophilic housings; this leads to a substantial increase in back-swelling due to swelling in the fibers (Amid *et al.* 2016).

Lignin/PEO - Air Filtration

Air filtration testing has demonstrated that lignin membranes alone may not be sufficient for air filtration due to high penetration values. In addition, the lignin membranes showed cracking that was visible to the naked eye, providing pathways through the membrane. In contrast to the other lignin/PEO composites reported in several papers above (Dallmeyer *et al.* 2010; Poursorkhabi *et al.* 2015; Schreiber 2020; Schreiber *et al.* 2014; Bahi *et al.* 2017; Cho *et al.* 2020), where the lignin and PEO were electrospun together, this approach focused on electrospinning a lignosulfonate-based filter and then attaching PEO filters to either side. The composite filter was inserted into a surgical mask, and the resulting combination achieved a filtration efficiency equivalent to an N95 mask. However, the combination of so many layers resulted in an unacceptable pressure drop across the mask (Chang and Chang 2016). As a result, there is the potential for air filtration applications, but significant future work is needed to address the excessive pressure drop and reduce the number of layers.

Lignin/PEO - Carbonized Nonwovens

Significant research has gone into the preparation of carbonized nonwovens from several types of lignin (kraft, organosolv, Alcell, pyrolytic, *etc.*), but there is difficulty in achieving sufficient carbon content. In the carbonized nonwoven production process, the electrospun mats are first thermally stabilized and then carbonized. As discussed previously, the addition of PEO improves the ability of lignin to be electrospun. However, increasing the content of PEO has a negative effect on the quality of the carbonized nonwoven (Dallmeyer *et al.* 2010). As a result, the maximum PEO concentration reported for carbonized nonwoven-specific applications was 5% (Dallmeyer *et al.* 2010; Cho *et al.* 2020).

Lignin/PAN Nonwovens

A second common lignin nonwoven composite that shows promise is lignin with PAN. This has shown potential applications for battery separation membranes and in the production carbonized nonwovens. Similar to lignin/PEO composites, the main solvent identified for lignin/PAN electrospinning was DMF. In addition to DMF, dimethyl sulfoxide (DMSO) was also used for lignin/PAN electrospinning, and the ionic liquid, 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) was used for lignin/PAN dry-jet wet spinning (Al Aiti *et al.* 2020; Zhang *et al.* 2020b).

The primary factors affecting lignin/PAN composites were identified to be the lignin to PAN ratio and total polymer concentration. Unlike the lignin/PEO composites, which had similar desired properties for the end products, the desired characteristics of lignin/PAN composites are highly dependent on the end-use, resulting in a wider array of successful processing conditions. Carbonized nonwoven applications focus on carbon content and mechanical properties such as tensile strength, while battery applications focus on electrolyte uptake and porosity. In general, the total polymer solution concentration ranged from 10 to 25 wt%, while the ratios of lignin to PAN varied from 0:100 to 70:30. The most common successful electrospinning ratios were identified to be between 30:70 and 50:50 for DMF and below 30:70 for DMSO. In these ranges, the lignin/PAN fibers were found to be uniform, smooth, and bead-free (Zhao *et al.* 2015; Amid *et al.* 2016; Ding *et al.* 2016; Zhang *et al.* 2020b).

Lignin/PAN - Carbonized Nonwovens

Traditionally, carbon fiber processing begins with precursor production/isolation, then continues with fiber spinning, stabilization, carbonization, and finally, on occasions, fiber graphitization (de Avila Delucis *et al.* 2017). However, despite their excellent strength and performance characteristics, PAN carbon fibers are expensive and known to generate toxic byproducts, such as hydrogen cyanide (HCN). On the other hand, lignin is widely available, inexpensive, sustainable, and renewable material, and as such in theory it fulfills many of the requirements for ideal carbonized nonwoven production (de Avila Delucis *et al.* 2017). However, on their own, lignins lack the necessary carbon yields and associated mechanical strengths that pure PAN precursors offer (Sagues *et al.* 2019). For this reason, lignin/PAN polymer blends have been explored prior to carbonization (de Avila Delucis *et al.* 2017). Much of the lignin/PAN research has focused on carbonized nonwoven production (Ogale *et al.* 2016). For such lignin/PAN combinations, the lignin content was found to significantly impact both thermostabilization and carbonization (Zhang *et al.* 2020b), with documented associated efforts on the morphology of the fiber and the mechanical properties. Carbonization temperatures between 1000 and 1400 °C were found to be sufficient for lignin/PAN carbonization, with 1000 °C being the most commonly reported temperature (Ding *et al.* 2016; Park *et al.* 2017). The resulting carbonized nonwoven lignin/PAN mats have shown good elongation and strain at the breaking point with promise for carbonized nonwoven applications (Ding *et al.* 2016; Al Aiti *et al.* 2020).

To further explore this important area, lignin modification reactions have also been explored. One report discussed butyrated organosolv lignin (Ding *et al.* 2016), while another discussed a grafting approach of kraft lignin onto PAN (lignin-g-PAN) (Park *et al.* 2017). Both aimed to improve the compatibility of the two polymers prior to carbonization. The butyrated organosolv lignin was found to produce smooth fibers at lignin to PAN ratios below 60:40, with beads forming as the lignin content surpassed 60% of the total polymer weight (Ding *et al.* 2016). The addition of kraft lignin-g-PAN was shown to improve the tensile strength performance relative to lignin/PAN carbonized nonwovens. Surprisingly, it offered a higher tensile strength than neat PAN carbonized nonwovens, which is a key property for the utilization of carbonized nonwovens (Park *et al.* 2017).

Additional lignin modification efforts have been carried out by introducing propargyl groups on the phenolic groups of the lignin, which, upon subsequent thermal treatment (fiber formation and stabilization), have been shown to cyclize creating cyclic moieties similar to PAN cyclization chemistry that occurs during carbon fiber thermal regimes (Sen *et al.* 2013; Sadeghifar *et al.* 2016).

Lignin/PAN - Electrical applications

Lignin/PAN composites were found to work well as supercapacitors, batteries, and fuel cells (Nie *et al.* 2020). They are also ideal potential candidates as absorbers, filters, and electronic applications, where PAN-based carbon fibers and carbon fiber mats are already being used due to their high surface area (Go *et al.* 2018).

Zhao *et al.* (2015) investigated the potential for lignin/PAN membranes as replacements for commercial polypropylene (PP) battery separators. It was determined that an increase in lignin content led to an increase in membrane porosity, which is advantageous for electrolyte uptake, a key factor in battery separation membranes. The lignin/PAN showed better thermal and electrochemical stability, as well as faster electrolyte uptake when compared to commercial PP membranes. The lignin to PAN ratio of 3:7 was found to be the optimum ratio offering lignin/PAN membranes with superior C-rate and cycling performances. C-rate performance is a measure of discharge capacity relative to the discharge current density. For C-rate testing, desirable qualities include higher discharge capacities and lower capacity fading. Cycling performance is the ability for the electrochemical cell to retain its discharge capacity, with higher retention values corresponding to better cycling performance. Overall, the authors concluded that lignin/PAN membranes have the potential to replace the PP separators due to low costs and simple production methods (Zhao *et al.* 2015).

Electrodes are another lignin/PAN application in batteries, where they are used in carbonized PAN nonwoven composites produced *via* electrospinning. Carbonized nonwoven mats possess superior mechanical properties, as well as structural stability. Additionally, electrospun carbon fibers and carbonized nonwovens offer a large surface-to-volume ratio, 3D conductivity network, fast ion kinetics, and are simple to prepare. All of these are favorable qualities in electrode applications (Li *et al.* 2020).

In the past, carbon nanotubes, graphene, and 3D mesoporous carbon have all been used as supercapacitor flexible electrode materials. In one study, where a lignin/PAN-based carbonized nonwoven with hollow fibers was used as an electrode material, it was found that the composite exhibited excellent electrochemical properties (Yang *et al.* 2020). To produce the hollow nonwoven mats, coaxial electrospinning was used, followed by carbonization. The hydroxyl groups in lignin macromolecules and the low cost of lignin, as opposed to the PAN component, proved beneficial for a more sustainable mesoporous carbon synthesis. The heteroatoms in lignin were actually seen to be used to enhance the electrochemical performance of electrode material, and lignin-based carbonized nonwovens can help reduce the cost of electrodes while maintaining their flexibility (Yang *et al.* 2020).

Lignin/PAN - Challenges

While the primary challenge in pure lignin-based carbonized nonwovens is mechanical performance (Dallmeyer *et al.* 2014), additional complications arise from the use of lignin such as the extensive pre-processing required, including its isolation and purification from the various waste streams, as well as the inherent inconsistency in feedstock quality and the heterogeneity of properties across batches (Argyropoulos 2014; Nie *et al.* 2020). In general, work with kraft lignin indicates it is incompatible for use as a carbonized nonwoven precursors, since it is of rather low molecular weight and of a high phenolic content, resulting in excessive reactivity yet good antioxidant activity (de Avila Delucis *et al.* 2017). During the actual stabilization and carbonization steps in nonwoven processing, the use of lignin adds another level of complexity. It has been shown that during, even minor thermal treatments of completely non-derivatized lignin, extensive crosslinking occurs and its T_g dramatically increases, causing it to become a thermoset (Cui *et al.* 2013). If this happens too quickly, fiber quality is severely affected. Above 1500 °C, the tensile strength decreases, even though the modulus continues to increase. This can lead to structural fiber defects as a result of a high carbonization rate and a considerable loss of heteroatoms (de Avila Delucis *et al.* 2017).

In general, while a lot of progress has been made and the demand is continuously expanding, many improvements are still required with regards to the use of lignin in carbonized nonwovens. Processing optimization is a much-needed improvement that is still missing, beginning with lignin extraction, isolation, purification, fiber processing and finally, if solvents are to be used, with potentially costly solvent recovery operations. With regards to equipment, low-cost industrial scale electrospinning technologies are still unavailable (Nie *et al.* 2020). Lastly, homogeneity of properties across feedstock used and improved mechanical strengths are keys to bringing lignin carbonized nonwovens to scale (Argyropoulos 2014; de Avila Delucis *et al.* 2017).

Lignin/PVOH Nonwovens

Lignin/PVOH composites have shown potential for industrial applications in three major categories, namely; electrical, water purification, and antimicrobial. Most of the lignin/PVOH literature examined showed that an extra stabilization step is required for the creation of lignin/PVOH membranes, which are distinct from the lignin/PEO and lignin/PAN composites previously discussed. This is because if such composite membranes are not treated, they otherwise dissolve in water (Lee *et al.* 2019; Camiré *et al.* 2020). For carbonized nonwoven-based applications, this is not an issue since the thermostabilization and carbonization processes dramatically alter the structure of the polymers, eliminating water dissolution issues. However, for non-carbonized nonwoven-based applications, several methods have been examined to limit solubility in water. Thermostabilization alone is not enough to stabilize the lignin/PVOH composite. As a result, other methods were explored including acid treatment, photo-crosslinking, and steam treatment. The most successful stabilization methods were found to be (1) heat treatment followed by acid treatment with a citrate buffer and (2) a three-step process of steam, visible light, and heat treatments (Aadil *et al.* 2018; Lee *et al.* 2019).

Despite reports that lignin and PVOH intermolecularly interact, the lignin and PVOH are immiscible in bulk. Furthermore, the PVOH and lignin have different solubility parameters, which ultimately affect their compatibility (Zhao *et al.* 2018). Therefore, some treatment is necessary to overcome the immiscibility of lignin and PVOH. For example, Nair *et al.* (2014) applied high-shear homogenization to produce nanolignin. The nanolignin was blended with PVOH and exhibited improved thermal stability of the lignin/PVOH blending with a well-dispersed structure.

Similar to the lignin/PEO and lignin/PAN nonwoven composites, the key factors in lignin/PVOH electrospinning are both the lignin to PVOH ratio and total polymer content in the solvent. For lignin/PVOH, the ratio ranged from 0:100 to 90:10, and the total polymer content ranged from 5 to 25 wt%. The solvents examined included water (Lai *et al.* 2014a; Ago *et al.* 2016; Ma *et al.* 2016; Uddin *et al.* 2017; Lee *et al.* 2018; Lee *et al.* 2019; Perera Jayawickramage *et al.* 2019; Zhang *et al.* 2019), DMSO (Kwak *et al.* 2018; Roman *et al.* 2019; Hou *et al.* 2021), DMF (Beck *et al.* 2017), and a methanol-water mixture (Aadil *et al.* 2018), with water being the most common. Successful electrospinning conditions were reported with lignin to PVOH ratios below 50:50 and polymer concentrations near 10 wt%. Similar trends were observed for the lignin/PVOH system as the previously discussed systems. Increasing lignin content consistently reduced the viscosity of the electrospinning solution, consequently leading to a decrease in fiber diameter. Increasing lignin content was also found to increase porosity and specific surface area, which is highly advantageous for various applications (Beck *et al.* 2017; Zhang *et al.* 2019).

While the preceding lignin/PVOH discussion focused on electrospinning of lignin/PVOH composites, lignin/PVOH fibers were also reported to be created using a gel spinning process (Lu *et al.* 2017, 2018). The gel spinning was performed with varying ratios of methanol and acetone as the solvent. The addition of acetone to an excess of methanol was found to improve the fiber properties by inhibiting the diffusion of lignin from PVOH into the coagulation bath. Increasing lignin content was reported to increase the melting temperature and thus the fiber drawing temperature of the lignin/PVOH fibers. The best performing fibers were obtained from a 5:95 lignin to PVOH weight ratio using a 15:85 methanol to acetone volume ratio. These lignin/PVOH fibers were found to have superior mechanical properties when compared to commercially available PVOH fibers. Increasing the lignin to PVOH ratio to 50:50 resulted in a deterioration of the mechanical properties compared to the 5:95 fibers. However, the 50:50 fiber mechanical properties were still comparable to the commercial PVOH fibers, demonstrating the ability of lignin to replace some of the carbon sources for fibers (Lu *et al.* 2017).

Lignin/PVOH - Water purification membranes

Much of the research related to lignin/PVOH composite membranes has been carried out for water treatment and purification purposes. Camiré *et al.* (2020) reported that the optimal alkali lignin:PVOH ratio was 50:50 at a total polymer concentration of 15 wt% in water. A rather detailed table of electrospinning parameters was also provided by the authors. The produced alkali lignin/PVOH composite membrane was found to remove 70% of the fluoxetine (the representative pharmaceutical contaminant) from the solution (Camiré *et al.* 2020). For the same kraft lignin/PVOH composite membrane system, Hou *et al.* (2021) reported the optimal ratio was 60:40 with a total polymer concentration of 25 wt% in DMSO. In addition to the reported optimal ratio, this system contained a cobalt/iron bi-metal-organic-framework (bi-MOF) incorporated into the kraft lignin/PVOH membrane using *in-situ* solvothermal methods. Finally, peroxymonosulfate (PMS) was added to the system to increase the activity of the membrane. In the dark, the kraft lignin/PVOH/bi-MOF membrane with PMS degraded 60% of the perfluorooctanoic acid, the representative contaminant. The degradation value increased to 90% under solar irradiation and 100% under UV irradiation. The membrane was found to retain a 77% removal percentage after four adsorption/desorption cycles, indicating sufficient stability (Hou *et al.* 2021). In other efforts, Chen *et al*. (2021) reported an alkali lignin/PVOH composite intended for purification, pervaporation, and desalination of seawater. In this effort, thin-film composites were synthesized by casting alkali lignin/PVOH solutions (70 to 90 wt% of lignin content with the remaining being PVOH) supported and fabricated onto a polyester/PAN substrate. These composite membranes performed well with respect to pervaporation desalination of high salinity water, offering drinkable water.

Alternatively, carbonized nonwoven water purification systems utilize the adsorption characteristics of the nonwoven mat. In one such effort, Beck *et al.* (2017) compared alkali lignin/PVOH carbonized nonwoven membranes against PAN carbon fiber membranes and activated carbon for the adsorption of methylene blue (representative of a large molecule), iodine (representative of a small molecule), and tannic acid (representative of a major water contaminant). In all cases, the alkali lignin/PVOH carbonized nonwoven membranes exhibited significantly higher adsorption when compared to their PAN carbon fiber membrane counterparts. One unique aspect of this study was a sample economic impact calculation, which concluded that in a hypothetical water purification process the operating costs of the alkali lignin/PVOH carbonized nonwoven membrane would be approximately $340,000 cheaper than using activated carbon. This cost reduction was attributed to the increased adsorption capacity and faster binding of the adsorbent (Beck *et al.* 2017). This was further confirmed by another study, using a cationic dye; the study showed similar adsorption performance data with such carbonized nonwoven membranes. This effort also pointed to other important improvements for carbonized alkali lignin/PVOH characteristics such as better flexibility and stability during various adsorption/desorption cycles (Zhang *et al.* 2019). Finally, Kwak *et al.* (2018) examined wet-spun alkali lignin/PVOH blended fibers and demonstrated that the blended fibers had better stability, water-resistance, heavy metal absorption and regeneration abilities, especially through glutaraldehyde-induced crosslinking.

Lignin/PVOH - Electrical applications

In addition to the previously discussed battery membrane applications, lignin/PVOH composite membranes have been compared against commercially available PP membranes. It is important to note at this point that the most important factors for battery membrane applications are electrolyte uptake as well as thermal and chemical stability. Specifically, Uddin *et al*. (2017) compared the electrolyte uptake using common electrolytes for graphite, silicon, and lithium titanium oxide anodes and found that the alkali lignin/PVOH membranes showed faster electrolyte uptake profiles for all three electrolytes. In addition, the percent uptake of the alkali lignin/PVOH membranes was significantly higher than that of the PP membranes. These are desirable properties, as they allow the assembly time of the batteries to be reduced. Alkali lignin/PVOH membranes also showed better thermal stability (measured by shrinkage under thermal stress), shrinking only 15% versus 45% for the PP membranes. Finally, chemical performance and stability studies showed that for a single charge/discharge cycle, the PP and alkali lignin/PVOH membranes performed nearly identically. However, the alkali lignin/PVOH membrane showed a significantly better C-rate performance and resisted electrochemical side reactions. According to the authors in this field, future work needs to be focused on decreasing the membrane thickness since the functional alkali lignin/PVOH membranes needed to be significantly thicker than the industry standard (Uddin *et al*. 2017). Overall, however, the creation of lignin/PVOH composites as potential battery separation membranes appears promising.

Various publications have also described potential breakthroughs in using lignin/PVOH composites as carbonized nonwoven-based electrodes for supercapacitor applications (Lai *et al.* 2014a; Ago *et al.* 2016; Roman *et al.* 2019; Zhang *et al.* 2020c). In a manner similar to all other carbonized nonwoven applications, the lignin/PVOH mat needs to be thermally stabilized and carbonized to produce the carbonized nonwoven membrane. Ago *et al.* (2016) produced alkali lignin/PVOH carbonized nonwovens for use as conductive electrodes in supercapacitors. The performance of the examined electrode was notable despite the fact that only one a single sample range ratio (75/25 alkali lignin/PVOH) was examined. Lai *et al.* (2014) compared the alkali lignin/PVOH carbonized nonwovens against PVOH carbon nanofiber mats and concluded that the composite nonwoven mats had the potential to act as sustainable electrode materials in supercapacitors. They found that the optimal alkali lignin to PVOH ratio for this application was 70:30. The composite carbonized nonwovens were determined to lose only ten percent of their capacity over 6,000 charges/discharge cycles and performed well under high current situations (Lai *et al.* 2014a). Perera Jayawickramage and Ferraris (2019) also produced carbonized nonwovens with alkali lignin and PVOH. They used electrospinning followed by carbonization and activation of the fibers for supercapacitor electrodes. The resulting carbonized nonwovens showed a four-fold improvement compared to the neat ionic liquid coin cell supercapacitors with the blending ratio of 80:20, which is similar to the study done by Lai *et al.* (2014). Thus, there is a potential application for lignin/PVOH supercapacitor electrode applications.

It was reported that for a 70:30 ratio of alkali lignin to PVOH and a 1:1 ratio of alkali lignin/PVOH carbonized nonwoven to manganese (IV) oxide (MnO_2), the application of alkali lignin/PVOH composites as supercapacitor electrodes can be improved (Ma *et al.* 2016). The MnO_2 nanowhiskers were grown onto the alkali lignin/PVOH carbonized nonwoven mat using redox reactions. The 1:1 ratio displayed “excellent” supercapacitor behavior and performed better than 2:1 and 1:2 ratios as well as electrodes without MnO_2. The electrode without MnO_2 showed the best cycling stability (approximately 1% capacitance loss over 10,000 charges/discharge cycles), whereas the 1:1 ratio electrode demonstrated an 8% capacitance loss over the 10,000 cycles. Even with a larger loss in capacitance, it was concluded the 1:1 ratio was still the best due to its superior electrochemical properties (Ma *et al.* 2016).

Lignin/PVOH - Antimicrobial applications

Lignin has been shown to have antimicrobial properties, which carry through the electrospinning process. As a result, there is the potential to create nonwoven materials with antimicrobial characteristics (Aadil *et al.* 2018; Lee *et al.* 2018, 2019). The specifics of the lignin antimicrobial properties are further explained in the section of this review covering coatings and finishings. Various literature accounts describe that alkali lignin/PVOH composites were effective against Gram-positive bacteria *Staphylococcus aureus*, but ineffective against Gram-positive bacteria *Escherichia coli* (Lee *et al.* 2019). However, Aadil *et al.* (2018) found that incorporation of silver nanoparticles into acetone-extracted lignin/PVOH composites allowed the composite to be effective against *E. coli*. Overall, lignin/PVOH composite nonwovens have been proposed for potential applications in antimicrobial fabrics and biomedical applications such as wound dressings (Aadil *et al.* 2018; Lee *et al.* 2019). In other efforts, Lee *et al.* (2018) have discussed lignin/PVOH composites with antimicrobial properties. Their work involved the dispersion of thin multi-walled carbon nanotubes into the lignin/PVOH aqueous solution followed by electrospinning suspension into a fiber. These lignin/carbon nanotubes/PVOH fibers showed improved antimicrobial and mechanical properties, which are desirable appropriate characteristics for wound dressing purposes (Lee *et al.* 2018).

Lignin/PVOH - Other applications

Another application of lignin/PVOH electrospun nonwovens is air filtration (Cui *et al.* 2021). The cited authors prepared the air filter membrane by electrospinning PVOH with lignosulfonate on a nonwoven fabric. The hydrogen bonding capacity of the lignosulfonate offered a transparent filter with improved filtration efficiency, allowing the creation of PM2.5 filters. Such efforts demonstrate that lignin/PVOH composites offer high-performance filtration media with transparency, biodegradability, and excellent mechanical properties for personal use.

On another front, the phenolic hydroxyl group of lignin combined with PVOH in lignin composites have been shown to block UV light, and this effect has been documented in several studies (Fernandes *et al.* 2006; Xiong *et al.* 2018; Posoknistakul *et al.* 2020; Zhang *et al.* 2020c). For instance, using sugarcane bagasse and other organosolv lignins, lignin/PVOH composite films have been created by Posoknistakul *et al.* (2020). The UV absorbance of these composites was improved compared to pure PVOH. Additional advantages of lignin/PVOH composites are their thermal and photochemical stability. Fernandes and his colleagues obtained a kraft lignin derivative (KLD) by the reaction with p-aminobenzoic acid and phthalic anhydride, in blends with PVOH in DMSO (Fernandes *et al.* 2006). Compared to pure PVOH films, the thermal and photochemical stabilities of PVOH/KLD films were improved offering compelling antioxidant and photo-protective properties. Considering the aforementioned research, where it has been demonstrated that lignin-PVOH nonwovens can be manufactured, it is anticipated that thermally stable lignin-PVOH nonwovens with UV-absorbing characteristics can broaden the application areas of lignin/PVOH nonwovens.

The combination of lignin with PVOH has also been applied for the creation of natural fiber-reinforced polymer composites (Ko *et al.* 2018, 2020). Ko *et al.* (2018) developed an esterified alkali lignin/PVOH resin and applied it to natural fiber to create reinforced composites. In their effort, the authors mimicked the relationship between cellulose, lignin, and hemicellulose in wood by applying the alkali lignin/PVOH resin to natural fibers. The PVOH was introduced as a substitute for the role of hemicellulose in wood to address the issue of the otherwise low interfacial affinity of alkali lignin with cellulose. Furthermore, by invoking an esterification reaction of the system with maleic acid, they managed to improve the water repelling characteristics of the alkali lignin/PVOH resin (Ko *et al.* 2018). The esterified alkali lignin/PVOH resins showed enhanced thermal, mechanical, adhesive, and thermoset characteristics together with the aforementioned water repellant properties.

Other Lignin Composite Nonwovens

A few other lignin composites have been reported in the literature, including lignin-PMMA copolymers with PCL (lignin-PMMA/PCL), lignin/PLA, and lignin/TPU. Alkali lignin-PMMA/PCL has shown promising applications in the biomedical industry. Kai *et al.* (2015) reported the biocompatibility of alkali lignin-PMMA/PCL electrospun membranes with human dermal fibroblasts (HDFs), which can be used to determine and alleviate potential skin irritations. The HDFs attached and interacted favorably with the alkali lignin-PMMA/PCL membranes, demonstrating the potential for biomedical and personal care applications. Biocompatibility leads to one area of specific interest and promise is the use of alkali lignin-PMMA/PCL membranes as scaffolds for cell growth (Kai *et al.* 2015).

Furthermore, lignin/PLA blends were found to show potential applications in textiles and battery anodes (Cayla *et al.* 2016; Culebras *et al.* 2019) with fire-retardant characteristics. For example, a kraft lignin/PLA membrane that included 10 wt% of ammonium phosphate provided sufficient flame retardancy for a PLA fabric (Cayla *et al.* 2016). Furthermore, an organosolv lignin/PLA composite was thermally stabilized and carbonized, showing potential for battery anode applications. Carbonized nonwoven composite anodes of organosolv lignin/PLA with lignin to PLA ratios of 70:30 and 50:50 showed capacity values that were considered to be "beyond the state of the art" and were stable after 500 charges/discharge cycles (Culebras *et al.* 2019). The role of lignin as a fire-retardant will be further expanded and discussed in the coatings and finishings section of this review.

In addition, organosolv lignin/TPU composites were found to have potential battery anode applications. In a manner similar to lignin/PLA carbonized nonwoven composites, lignin/TPU anodes have also been manufactured, with the latter having a higher carbon content than the lignin/PLA anodes. However, the organosolv lignin/TPU anodes were found to have lower overall performance characteristics than the organosolv lignin/PLA anodes (Culebras *et al.* 2019).

DYESTUFF DISPERSANTS

Market Considerations

Since dye dispersants are not limited to nonwovens, they are considered to have a medium to large size market (Mandlekar *et al* 2018). Dispersants are used across many different industries for suspending colloidal particles in uses such as cosmetics, paints, pharmaceuticals, drilling mud, cement, ceramic applications, and dyes (Chen *et al.* 2018). In 2010, 1 million tons of dyes were produced globally (Yang *et al.* 2015). Demand for lignin-based products is expected to have around 6% compound annual growth rate (CAGR) between 2020 and 2026, as rising product demand and the demonstrated versatility of lignin as a dispersant is expected to continue (Global Market Insights 2021). When combined with worldwide nonwoven roll goods production worth $35.6 billion, as estimated by INDA in 2014, the industry finds itself at the crossroads between several industries including hygiene, wipes, medical, filtration, and construction (INDA). As a result, there is the potential to increase the use of renewable feedstocks in an industry that has been otherwise considered a major pollutant in addition to increasing performance and decreasing production costs.

The Science of Dispersion

Dispersants are used across a wide range of industries, such as cosmetics, cement, paints, and dying, to keep colloidal particles in suspension (Chen *et al.* 2018). Examples of dispersants include polyricinoleic acid, sodium polynaphthalene sulfonate, and lignosulfonates (Deckner 2018). When a solid dye is ground, a dispersing agent is added to assist the crushing of the granules and to prevent the particles from coalescing, thus ensuring that the dispersion is stable. In addition to their main role, dispersants also contribute to wetting of the dye, dilution, dye leveling, and dye intensity (Yang *et al.* 2015). Furthermore, many dispersants possess additional characteristics such as homogenizing and dye strength adjustment. Dispersants can also be surfactants of a cationic, nonionic, amphoteric, macromolecular, and/or anionic nature, with the anionic variety being the most common (Dispersant used for dye industry).

During the process of dyeing fibers, sorption and diffusion of the dye molecules at the surface of the fibers is critical. For this to occur, the dye molecules must first be transported from their solvated state close to the fiber surface so that sorption can take place. The rate of dye sorption mainly depends on the mass transfer considerations, while in the fluid phase, and it is influenced by convective diffusion. The latter mechanism can be best described as a combination of forced flow (convection) of the liquid and diffusion within the liquid phase (Burkinshaw *et al.* 2012). One dispersion mechanism that stabilizes particles in suspensions is the surface charge density effect. This effect promotes the development of repulsive forces between particles, stabilizing the suspension. Lignins with large amounts of charged groups, such as lignosulfonates, aid such processes because adsorption of lignin in a dispersant helps increase the surface charge density of the suspended particles (Chen *et al.* 2018). An additional mechanism that aids dispersion is based on the ability of high molecular weight lignins to reduce hydrophobic interactions between particles, thus preventing agglomeration. The presence of the adsorbed lignosulfonates in the formulation further improves the interaction of the particles with water molecules, thus promoting the overall hydrophilicity of the system offering the sought balance between hydrophobic and hydrophilic interactions (Chen *et al.* 2018).

Since dispersed dyes have little or no solubility in aqueous systems, the addition of dispersants also helps prevent the agglomeration of dye particles. To stabilize the dispersion, additives are used to control steric hindrance and electrostatic force among particles (Chen *et al.* 2018). Finally, it is to be noted that agglomeration of dye particles takes place when their size increases during a high-temperature dyeing process.

Disperse Dyes

Yang et al. estimated that in 2010, disperse dyes accounted for approximately 40 to 50% of the total production of dyes. Disperse dyes are mainly used for synthetic fibers in both dyeing and printing coloration techniques (Yang *et al.* 2015). They can be used in synthetic nonwovens, but not for PP (Aspland 2005). Disperse dyes have low water solubility, so in order to be used, they must be milled to very low particle size and dispersed in water using surfactants, dispersing agents, or *via* a carrier added during dyeing or printing (ILI).

The main advantages of disperse dyes are their excellent build-up and shade uniformity, as dye molecules are adsorbed and then diffused into amorphous regions of the fiber structure thanks to their substantivity (Shakoor *et al.* 2017). Substantivity, sometimes called affinity, is related to how dyes move from solutions to fibers (Textile Dying). The deposited dye can be removed from the surface by hot aqueous alkaline-reductive medium treatment. The diffusion of dye molecules depends on numerous factors, including the type of dye used, fiber structure, and process techniques. Nonwovens are known for their high surface area, so the dyeing rate is faster than with traditional textiles, but low fabric tension needs to be maintained to control structural integrity (Shakoor *et al.* 2017).

Current Lignin Use in Dye Dispersants

Some noteworthy lignin-based dyestuff dispersant producers include Borregaard LignoTech and Ingevity. While both companies are lignin-focused, lignin-based dye dispersants have also become incorporated into the usual offering of suppliers who sell petroleum-based dispersants. As an example, in addition to naphthalene monosulfonic acid formaldehyde condensate and sodium poly (naphthalene formaldehyde) sulfonate, Anyang

General Chemical Co., Ltd. also sells sodium lignosulfonate (in brown powder form, soluble in water, anionic type), which is used with disperse and VAT dyes and offers sanding speed, good dispersion, good thermal stability, high strength, the right light, and the ability to meet the requirements of high temperature and high-pressure dyeing (Dispersant used for dye industry).

The three earliest patents for lignin-based dye dispersants were filed by Lignotech (US) Inc., a Corp of Dryden Chemical Ltd, in 1972 (US3864276A –for the invention that relates to the "production of dispersing agents from mixtures of spent sulphite liquor solids and kraft liquor solids"), Westvaco Corp, also in 1972 (US3841887A -for "dyestuff compositions comprising an admixture of a dye cake, i.e., disperse dyes and vat dyes, and up to 75 percent by weight of an improved lignin surfactant"), and Reed Lignin Inc. in 1981 (US4492586A – for dispersants, "especially well-suited for use with insoluble dyes, that are produced by reacting hydroxyl benzyl alcohol compounds with sulfonated lignin derivatives").

Lignin Categories and Use for Dye Dispersants

The most common types of processed lignin used for dye dispersants are lignosulfonates, which are byproducts of the sulfite pulping process, and sulfonated kraft lignin from the kraft pulping process (Aro and Fatehi 2017). Lignosulfonates constitute up to 90% of commercially available lignin, with an annual production of close to 1.8 million tons (Chen *et al.* 2018). Lignosulfonates, also referred to as sulfonated lignins, are water-soluble anionic polyelectrolyte polymers, which are mainly recovered from the sulfite pulping of wood (brown liquor), or through sulfonation of alkali lignin (Xu and Ferdosian 2017).

Petroleum-based commercial dispersants that are mainly available include naphthalene-sulfonated formaldehyde and acid-phenol-formaldehyde condensates. The lignin-based alternative to the latter has been successful thanks to its plentiful and renewable raw material source, as well as due to its excellent performance. Lignosulfonate-based dye dispersants are commonly used in disperse, vat, reactive, and acid dyes, as well as some pigments (Chen *et al.* 2018). Disperse dyes, which are typically sold in paste (liquid) or powder form, are classified by energy level, and require a primary dispersant. Vat dyes are also typically offered in paste (liquid) and powder form, and reactive dyes, which were traditionally standardized with naphthalene sulfonates. Vat dyes can use lignin-based dye dispersants, whose major benefits are their purity and low staining properties (Borregaard LignoTech).

Highlighting the many advantages of lignin-based dispersants over petroleum-based dispersants, it was found that compared to naphthalene sulfonate dispersants, sulfomethylated alkali lignin and lignosulfonates possess better dispersing ability at high temperatures (Qin *et al.* 2020).

The benefits of lignin-based dispersants include reduction in milling time required to achieve the desired particle size. Reaching the desired particle size results in faster adsorption of the dispersant and greater repulsion between the particles. Proper sizing also helps decrease the azo bond reduction, further resulting in coloration improvement (Borregaard LignoTech). This claim was further supported by Yang *et al.* (2015), who described how azo dye is reduced as a result of lignosulfonate destroying the azo bonds, as well as by Qin *et al.* (2020), who advised that lignin dispersants can eliminate the (-N=N-) bond in azo dispersant dyes by reducing the hydrazo structure during milling and dyeing processes at high temperature. With regards to staining, which is the degree to which a dispersant stains fibers, light to moderately staining dispersants can be used as either primary or secondary dispersants. Adsorbent and solubility groups being present in dispersants also help improve the heat stability of a dyestuff at high temperatures (Borregaard LignoTech).

Lignin's structural versatility makes it an ideal raw material for dye dispersants, thanks to the variance in chemical composition, molecular weight, and solvent affinity that is obtained. This versatility will largely depend on its source and separation process (Bai *et al.* 2019).

Lignin is rich in aromatic compounds. Lignosulfonates are lypohydrophilic molecules, due to their hydrophobic aromatic structure and the presence of hydrophilic sulfonate groups. This unique combination within lignin structure makes it an effective dispersant (or surfactant), such that it is used in a wide range of industries, including dye dispersion (Xu and Ferdosian 2017). Aro and Fatehi (2017) also found that the increased hydrophobicity in lignosulfonates resulted in increased surface activity and decreased surface tension, adding to their dispersing performance. The molecular weight and degree of sulfonation in sulfonated lignin dye dispersants were crucial in determining their efficiency. Reduction of the sulfur content in lignosulfonates is important, as it helps to increase dispersion abilities by increasing hydrophobicity. It was shown that lower amounts of sulfonate groups create less interference in the hydrophobic adsorption between the hydrocarbon structure of lignins and the material to which it adsorbs. Therefore, high amounts of sulfur are counteractive to lignosulfonate dispersion performance. Despite this trend, the sulfur content of lignosulfonates is essential for their solubility and dispersion. Additionally, due to the presence of sulfonated groups, lignosulfonates are anionically charged and water-soluble (Aro and Fatehi 2017).

It is important for the selected dispersant to be able to retain dye particle separation in water, as the dye particle surface tends to have a lot of hydrophobic groups, which makes it easier for them to aggregate and precipitate in water. The presence of sulfonic groups makes the surface of a dye particle negatively charged, which builds the electrostatic effect on the particle surface and helps prevent aggregation (Zhang *et al.* 2018). As a result, sulfonic groups are a critical component to successful dye dispersants, further supporting the use of lignins in the technology.

Dispersants are one of the two major product groups that account for the widest use of lignosulfonates and sulfonated lignin. The presence of functional groups grants them their anionic charge density (0.1 to 0.9 meq g^{-1}) and appropriate molecular weight (10 000 to 50 000 g mol^{-1}). Increased molecular weight is proportional to increased viscosity in lignosulfonates and enhances its dye dispersant effectiveness. In a study referenced by Aro and Fatehi (2017), the increase in molecular weight to 14 000 g mol^{-1} improved heat stability, dispersibility of dye, and dye adsorption. Similarly, Tarasov *et al.* (2015) also concluded in their research that lignin with a large molecular weight may be used as a dispersant.

An apt description of lignosulfonates' behavior as dispersant in a dye-water system is provided by Yang *et al.* (2015), where they describe the hydrophobic group as the one that dyes, and the hydrophilic group as the one that inhibits the agglomeration of dye particles as well as stabilizes the dispersion through the formation of steric or electrostatic repulsion when the molecule is adsorbing on the surface of dye particles. They conducted an experiment in which the performance of three distinct sulfonated lignin (SL) fractions was compared. It was observed that with the increase in molecular weight, the content of phenolic hydroxyl groups, sulfonic acid groups, and carboxyl groups decreased, resulting in increased SL purity, color depth, and guaiacyl (G unit lignin) group content. They also found that this increase in molecular weight led to better dispersion and heat stability, supporting other claims found in the literature on this topic. Finally, increased molecular weight was correlated to an increase in the dyeing rate, and molecular weight above 2.5 kDa exhibited a minimum dye reduction degree. Dye reduction and fiber staining performance were also positively impacted by the increase in molecular weight and by the presence of phenolic hydroxyl content of SL (Yang *et al.* 2015).

The efficiency of lignosulfonates as dispersants was greatly affected by their molecular weight and amount of sulfonate groups, amongst other factors described above. Modifying lignosulfonates with hydroxy benzyl alcohol triggered an increase in the molecular weight, phenolic hydroxyl content, and sulfonation, which in turn allowed for better dye dispersion capabilities. Additionally, an increase in molecular weight and hydroxyl content increased the adsorption of lignosulfonates onto dye, whereas the sulfonate groups resulted in stabilization through strong repulsive charges (Aro and Fatehi 2017).

In the past, to design polymers with different polarities and solubilities, polymerization reactions were performed. Polarity had the potential to influence the polymer's hydrogen bonding and electrostatic interaction with other colloidal particles (Sabaghi and Fatehi 2020). However, as lignin contains both hydrophobic and hydrophilic groups, it has intrinsic multi-polarity (ILI). Studies suggest that the polarities of polymers may directly affect their performance in interacting with other particles in suspensions (Sabaghi and Fatehi 2020).

A study conducted by Zhang *et al.* (2018) reconfirmed that dispersibility and stain resistance were necessary traits of an effective dye dispersant. Surprisingly, however, there were opposing results on the impact of molecular weight. As sulfonated lignin is hydrophilic and dissolves in water, it is an ideal dye dispersant. Their experiment compared two post-sulfonated fractions, SD (with the insoluble part, higher molecular weight) and SX (with the soluble part and lower molecular weight and higher hydroxyl content). Both fractions presented high brightness values due to the phenolic hydroxyl blocking of 1,4–BS and the postprocessing with sodium borohydride, but SX seemed to have performed better in all aspects. It had the highest brightness value and showed high stain resistance on a variety of textile samples. The SX fraction also scored higher on dispersibility rating, achieving the highest grade of 5. The SX had higher SO_3H content than SD, pointing to more negative charges, creating a stronger electrostatic effect, which might explain the higher dispersibility rating. The fractionation of lignin described in the experiment might be the source of variation in findings with regards to molecular weight (Zhang *et al.* 2018).

Studies by Aro and Fatehi (2017) addressed the factors controlling the state of dispersion, finding that the nature of colloidal particles, as well as the conditions of the surrounding medium, have the greatest impact. Like its synthetically originated counterparts, lignin-based particles can be produced as non-fibrillar, spherical, and nano- and microparticles, which result in the same level of interaction at the oil/water interface. On the other hand, the interaction of lignin macromolecules with a solvent depends on ionic strength, pH, temperature, solvent quality, and monolignol composition in the lignin. Of course, higher stability can be attributed to the smaller particles of lignin, most likely due to size polydispersity and number density.

Among some less prominent attributes, thermal stability observed in lignosulfonates is also an important dye dispersant performance indicator (Aro and Fatehi 2017). Chen *et al.* (2018) supported this claim, adding hydrophobicity, water solubility, and negative charge density to the list, which are all attributes discussed earlier. Lastly, but also just as important, lignosulfonate contains aliphatic groups, which facilitate attachment to the dye particle surface (Zhang *et al.* 2018).

Lignin Use in Dye Dispersants: Challenges

As lignin use in dye dispersants for the nonwovens market is a relatively specialized area, perhaps lignin's function can also help address such challenges, as the difficulties in PP nonwoven dyeing, which is currently done through mass-pigmentation in a limited number of colors (Aspland 2005). On a similar topic, the application of pigments along with binders, which is considered the most versatile and accepted coloration method currently in nonwovens, struggles with some color migration problems and color non-uniformities. When solvents are evaporated from a solution or a dispersion, there is always a migration of the dispersed and dissolved material toward the source of heat and evaporation front, but there is a clear need for further research to provide more uniformity and allow for better control in production (Aspland 2005).

Although lignosulfonate has been widely used as a dye dispersant, it still has some disadvantages. The colorless catecholic structure in lignin is easy to oxidize to the quinonoid structure during lignin isolation and pulping processes, resulting in a dark color of lignin. As lignosulfonate staining effect on fiber is high, the darker color, and sometimes lignosulfonate's chemical structure prevents it from scaling lignin's application to many industries (Yang *et al.* 2015). This sentiment was later also supported by the research of Xu and Ferdosian (2017).

Qin *et al*. (2020) anticipate that technical lignin derivatives will be significant in the future and might aim to substitute for lignosulfonates (Qin *et al.* 2020). However, the dark color of technical lignin is still the main obstacle for its high value-added use in several products, including dyestuff dispersants. The staining of lignosulfonate results in color distortion in the dyeing process and is hard to avoid. Sulfonated kraft or alkali lignins that were processed during pulping contain more chromophores, resulting in a darker color. Chromophores in the lignosulfonate cannot be completely eliminated, so the amount of staining has to be controlled when lignosulfonates are used (Zang *et al.* 2018).

Although there are promising results of modification and application of kraft lignin as a dispersant, the modification includes solvent-based applications, and performance seems to be dependent on the case. Accordingly, more research is needed on this topic (Chen *et al.* 2018). Unmodified kraft lignin has not been found to be suitable as a dispersant because of its low solubility in water (Qin *et al.* 2020).

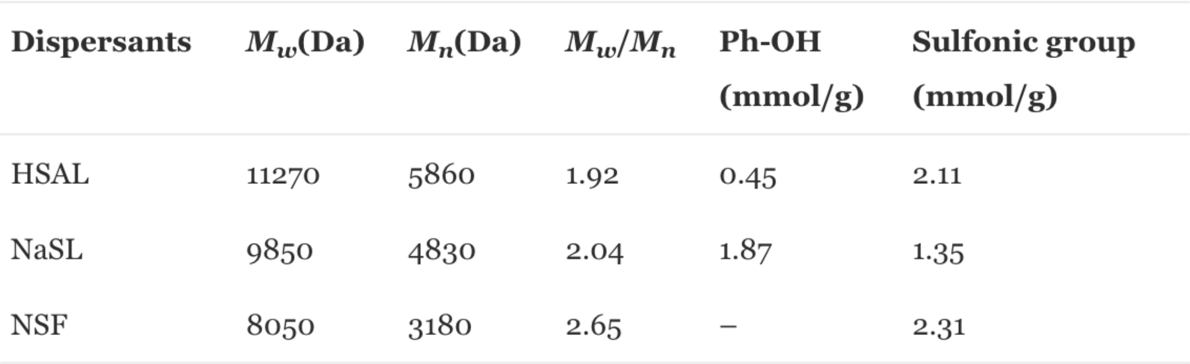
Lignin Use in Dye Dispersants: Future Opportunities

As an area of high potential growth, it is important to note that as of this writing the search for “lignin dispersant” has 146 patents filed, while a more specific search for “lignin dye dispersant” totals 33 filed patents, with 54% of them assigned to Westvaco Corp.

One promising study discusses the performance of nano-disperse dye with an average particle size of 94 nm using a hydroxypropyl sulfonated alkali lignin dispersant (HSAL). As the particle size of disperse dye severely affects dyeing quality, the utilization of such nano-disperse dye offers a promise of increased efficiency in lignin-based dispersant use in coloration. It is worth noting that commercial sodium lignosulfonate (NaLS) and sodium naphthalenesulfonate formaldehyde (NSF) dispersants proved unsuitable for the process. The study showed excellent dispersion and stability at high temperatures (130 °C). The dye uptake increased to 94.3%, and the reducing effect of nano dye (azo structure) was decreased to 5.4%. Additionally, the low reducing rate of HSAL guarantees the high dye content without being reduced by lignin dispersants in the dye bath during high-temperature dyeing (Qin *et al.* 2020).

It was found that the high content of sulfonic groups attached to the alkyl chain in HSAL molecules is capable of stretching out to the aqueous phase, providing a strong electrostatic repulsion to disperse dye particles, and forming the nano-disperse dye self-assembly. As a result, the adsorption layer of HSAL onto the dye was found to be thicker and more viscous compared with NaLS.

Table 2. Molecular Weight and Phenolic Hydroxyl Group Content of Dispersants (Reprinted with permission from Qin *et al.* 2020).



Dispersants	M_w(Da)	M_n(Da)	M_w/M_n	Ph-OH (mmol/g)	Sulfonic group (mmol/g)
HSAL	11270	5860	1.92	0.45	2.11
NaSL	9850	4830	2.04	1.87	1.35
NSF	8050	3180	2.65	–	2.31

This novel preparation method of nano-disperse dye has the potential to increase the efficiency and scalability of lignin in dyeing and printing (Qin *et al.* 2020).

LIGNIN-BASED COATINGS/FINISHINGS FOR NONWOVENS

In nonwoven industries, several kinds of coating/finishing technologies are used to modify the surface or web structure of nonwoven products for various industrial purposes. Among these purposes are wetting, flame retardant/protection, electrical, and antimicrobial properties, *etc*. (Wei *et al.* 2008; Zimniewska *et al.* 2008; Reti *et al.* 2009; Xiao *et al.* 2009; Indi *et al.* 2019). Coating is one of the chemical finishing techniques in the nonwoven industry, and nonwoven coatings share the techniques of textile coatings (Vade 2015). In this section, literature on lignin-based coatings applied to nonwoven fabrics is investigated, where benefits and the possibility of incorporating lignins are discussed.

Coating Methodologies

In the coating process, the nonwoven fabric is treated with solution or dispersions, mainly aqueous-based dispersions composed of polymers. Several additives, such as chemicals, fibers, plasticizers, or fillers, are added with the dispersion (Indi *et al.* 2019). Various coating methods are used in nonwoven fields, including roll coating, rotogravure coating, rotary screen coating, and doctor coating, but roll coating is the primary technique used (Singha 2012; Stylios *et al.* 2013; Vade 2015; Indi *et al.* 2019).

There are other chemical finishing techniques to functionalize the nonwoven fabrics such as padding and printing (Indi *et al.* 2019). Padding is another method to apply liquid or foam to the nonwovens, but unlike in the coating process, nonwovens are impregnated with the liquid by squeeze rollers in the padding process. In printing, the chemicals or polymers are applied on top of nonwovens.

Lignin as an Anti-Microbial Coating

Lignin, with its carbon-rich nature, has a hydrophobic property that can naturally protect the wood from pathogens and help the wood structure transport water (Vermerris *et al.* 2010). As well as hydrophobicity, lignin has chemical properties that make lignin-based coatings available, such as relatively small particle size, solubility, thermal properties, and stability (Khan *et al.* 2019). Lignin-based coatings have been studied in various fields, including nonwoven, textile, wood products, and packaging. In addition, it has been reported that lignin has antimicrobial, antioxidant, and UV-absorbing properties as well as flame-retardant properties (Cruz *et al.* 2001; Toh *et al.* 2005; Pan *et al.* 2006; Reti *et al.* 2008, 2009; Ugartondo *et al.* 2008; Doherty *et al.* 2011). However, despite the possibility of lignin on the nonwoven coating, there have been only a limited number of studies on lignin-based coating/finishing on nonwoven fabrics.

Due to trends embracing the need for greater UV protection and anti-microbial behavior in textiles, there has been increased attention on the UV-absorbing and antibacterial properties of lignin as a textile coating (Zimniewska *et al.* 2008; Dong *et al.* 2011; Zimniewska 2012; Li and Peng 2015; Sunthornvarabhas *et al.* 2017). Zimniewska *et al.* (2008) investigated the nano-sized lignin coatings on nonwovens to make a natural fiber-based functional fabric (Zimniewska *et al.* 2008, 2012). They treated kraft lignin with ultrasonic treatment to obtain a nano-sized structure, which was applied using the padding method and by silicone emulsion or binding agents such as acrylic dispersion. By these methods, the nanoparticles were fixed. The study showed that the lignin coating had impacts on UV protection and bactericidal and antistatic properties (Zimniewska *et al.* 2008; Zimniewska 2012).

Sunthornvarabhas *et al*. (2017) investigated the antimicrobial effects of lignin coated on nonwovens. They extracted the lignin from sugarcane bagasse with alkali treatment. The solution of lignin in DMSO was mixed with ethanol and coated on nonwoven glass fiber sheets. The extracted lignin on nonwoven fabrics could effectively reduce the bacterial colonies in proportion to the concentration of lignin on the fabrics without significant pressure drop, suggesting the potential of lignin for nonwoven filters or antibacterial nonwoven applications (Sunthornvarabhas *et al*. 2017). Further, in a subsequent study, they demonstrated that a lignin-based coating was more economically efficient compared to an inorganic antimicrobial coating using silver nanoparticles (Sunthornvarabhas *et al*. 2019).

Lignin as a Flame Retardant Coating

Flame retardant coating is an application of lignin coating that is recently getting attention in the nonwoven and textile fields (Reti *et al.* 2009; Jiao and Wu 2013; Song *et al.* 2017; Łukawski *et al.* 2020). An intumescent flame-retardant (IFR) coating protects the fabrics by forming an intumescent charred layer, and this layer prevents the heat transfer and combustion of nonwoven fabrics (Fu *et al.* 2017; Lopez-Cuesta 2017). The IFRs are mainly composed of an acid source, a carbonizing agent, and a blowing agent. The carbonizing agent is the important component of IFR coating, since it is the main material to produce the charred layer, and its quality is determined by the number of carbon atoms in the carbonizing agent.

In most cases, synthetic polymers that can make a stable charred structure, are used as carbonizing agents for IFR (Fu *et al.* 2017; Lopez-Cuesta 2017). Lignin also can be used as a carbonizing agent, on account of its many carbon atoms in its structures. Ian and Wu used alkali lignin, obtained from alkaline pulping, as a carbonization agent for flame retardant coating. They did alkaline pulping and spray drying of the resulting waste liquor to obtain the alkaline lignin. Compared to the pentaerythritol, one of the traditional IFR carbonizing agents, lignin could improve the flame retardancy of the coating (Fu *et al.* 2017).

Reti *et al*. (2009) applied an IFR coating with lignin to nonwovens to develop flame-retardant nonwovens. They blended polyethylene glycol, PLA, and ammonium polyphosphate with kraft lignin and coated them on hemp and wool nonwovens by pressing the blended film with heat and pressure. The coating acted as a protective layer and prevented the combustion of nonwovens, while simultaneously enhancing the tensile properties and flexibility of the nonwovens.

Other Properties and Areas of Future Study

As well as the flame retardant and antimicrobial properties of lignin, other properties of lignin have been noted to functionalize the nonwoven fabrics. Lignin was also studied as an additive to the film membranes for both forward and reverse osmosis with nonwovens (Vilakati *et al.* 2013). The alkali lignin was dissolved in DMF and N-methyl pyrrolidone and coated on top of polyester nonwoven fabrics by using a casting knife. The performance of the nonwoven membrane was improved by the addition of lignin, as it increased the porosity of the membrane. However, the properties of nonwoven fabrics affected the performance of the membrane more significantly. Another probable application of the lignin-based coating is to manufacture waterproof-breathable fabrics such as tent fabrics where a lignin-based coating on polyester was reported to have high water vapor transmission rates, but low liquid water penetration (Zhang *et al.* 2020d).

Zhang *et al.* (2020d) added lignin to a waterborne polyurethane (WPU) coating as an antioxidant agent, and the lignin could enhance the aging resistance of the fabrics and the water vapor transmission, especially with a 2% addition to the WPU coating. This research was done with woven fabrics; however, considering that nonwoven fabrics are also used for tent fabrics, it may be said that this coating method also can be applied to the nonwoven fabrics (Zhang *et al.* 2020d). Another research study has also confirmed the possibility of lignin-based polyurethane fabrics. Cardamone (1992) applied the lignin polyurethane (LPU) to cotton fabrics by padding, showing improvement of strength and abrasion resistance retention of cotton fabrics (Cardamone 1992). However, since the experiment with only polyurethane was not done in the study, it is difficult to ascertain whether the improvement was caused by lignin.

With the distinctive characteristics of lignin, such as hydrophobicity, UV absorption, and antimicrobial properties, the range of lignin-based coatings/finishings is significant for various industries and applications. However, only a few studies have been done on lignin-based coatings/finishings on nonwoven fabrics, compared to the coating studies on woven textile materials. Nonwoven fabrics have similar properties to woven textile materials regarding their raw materials and bulk structure; however, the properties of nonwoven fabrics can be very different, depending on their manufacturing process. Thus, the effects of the coating can be different from the coatings on other textile materials. It is necessary to do more research on lignin-based coatings/finishings applied to the nonwoven fabrics in order to verify the possibility of lignin as a finishing material.

CONCLUSIONS

Importance of Lignin in the Nonwoven Industry

Lignin has garnered significant interest recently due to its standing as the second most abundant organic substance behind cellulose. If processed purposefully, it could become a replacement for numerous unsustainable polymers and chemicals. The nonwoven industry is an important industry that can often be overlooked. The significance of the products produced by nonwoven techniques means that the industry can expect considerable growth. Lignin is already present in some nonwoven products, but with both experiencing notable current and projected growth, the need for a complete review is apparent.

Lignin in Nonwoven Fabrication

Kraft lignin presents 85% of the market share of available lignin worldwide, and less than 5% of all 50 million tons of kraft lignin produced per year are committed to use in value-added products. Chemically, kraft lignin may be fractionated into unique groups that demonstrate strong antioxidative qualities and high molecular weight. Kraft lignin is an especially thermally stable source for nonwoven fibers. Kraft lignin is easily separated into acid-soluble and acid-insoluble portions, making processing of fractions fairly simple. Finally, kraft lignin may be refined to high lignin purity and sulfonated to a higher degree than lignosulfonates. As a result, kraft lignin is a cheap source of lignin and an exciting avenue for the nonwoven industry as a fiber precursor.

The addition of lignin into nonwoven processing does not significantly alter the methodology or techniques used for fiber fabrication. Processing can be broken down into three major steps: web formation, web bonding, and finishing. There are numerous ways to produce nonwovens, with electrospinning offering the most promise. Electrospinning offers desirable properties and versatility that cannot be easily matched by other techniques. Other techniques include drylaid, wetlaid, and meltblown.

Lignin/polymer composites show promise for lignin in the nonwoven industry, especially for water treatment and battery membrane applications. When compatible lignin/polymer solutions are prepared, fiber production has been demonstrated to improve processability and fiber properties. The three most common lignin/polymer composites reported in the literature were lignin/PEO, lignin/PAN, and lignin/PVOH. These have been shown to have a wide range of applications and demonstrate the promising future for lignin composites in the nonwoven industry.

Lignin-based dyestuff dispersants have a proven performance record and an increasing range in applications. Recent studies show that lignosulfonate-based dye dispersants can serve their function better than synthetic dye dispersants in some applications. Although lignin-based dyestuff dispersants are not specific to nonwovens or raw materials, they show a lot of promise in synthetic fiber/filament coloration in nonwovens. Noteworthy research includes lignin use in disperse dyes for PP coloration, addressing the un-dyeability of PP in nonwovens, and use of hydroxypropyl sulfonated alkali lignin dispersant in nano disperse dyes for increased efficiency. However, the most promising and immediate focus in the industry is on further development of technical lignin as a sustainable, abundant, and inexpensive feedstock for lignin-based dye dispersion agents with comparable performance to the contemporary medium.

Nonwoven products have been treated with several finishing techniques, including coating and padding. Lignin is one of the promising materials for nonwoven coatings/finishings due to its chemical properties, such as carbon-based structure, hydrophobicity, thermal properties, and solubility. It has been reported that lignin can give nonwovens various functions through coating applications. For instance, flame-retardant, antimicrobial, and UV protecting nonwovens can be made by lignin-based coatings/finishings. However, only a few studies have been performed on lignin-based coatings/finishings on nonwoven fabrics compared to more numerous studies on woven textile materials. Further studies focused on the nonwoven field are required.

Future Developments and Directions

This review aimed to encompass the incorporation of lignin into the nonwoven industry from fibers and processing to dyeing and coating. Both the lignin and the nonwoven industries are experiencing significant interest and projected growth; thus, a review is appropriate to discuss the integration potential of lignin across the nonwoven industry. As the growth of lignin composites continues, the already comparable performance is also expected to improve and expedite growth in the market. As processing techniques improve, processing lignin may be done more reliably and efficiently. The coloration of finished nonwoven products has shown promise with lignin as a sustainable dispersion agent, but the subject must be further studied to be able to displace current unsustainable options. Coating and other finishing techniques show promising fire-retardation and anti-microbial properties but require further study. Overall, lignin demonstrates vertical integration with its compatibility with polymeric composites and current processing techniques as well as efficacy in numerous applications (fibers, dye dispersion, coatings, *etc.*) such that it should no longer be ignored. Instead, lignin should be viewed as a sustainable, versatile, financially viable source of carbon for the entire manufacturing chain of the nonwoven industry.

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REFERENCES CITED

Aadil, K. R., Mussatto, S. I., and Jha, H. (2018). “Synthesis and characterization of silver nanoparticles loaded poly(vinyl alcohol)-lignin electrospun nanofibers and their antimicrobial activity,” *International Journal of Biological Macromolecules* 120, 763-767. DOI: 10.1016/j.ijbiomac.2018.08.109.

About Nonwovens, https://www.inda.org/about-nonwovens/ (accessed 2021 -06 -14).

Ago, M., Borghei, M., Haataja, J. S., and Rojas, O. J. (2016). “Mesoporous carbon soft-templated from lignin nanofiber networks: Microphase separation boosts supercapacitance in conductive electrodes,” *RSC Adv.* 6(89), 85802-85810. DOI: 10.1039/C6RA17536H.

Al Aiti, M., Das, A., Kanerva, M., Järventausta, M., Johansson, P., Scheffler, C., Göbel, M., Jehnichen, D., Brünig, H., Wulff, L., Boye, S., Arnhold, K., Kuusipalo, J., and Heinrich, G. (2020). “Dry-jet wet spinning of thermally stable lignin-textile grade polyacrylonitrile fibers regenerated from chloride-based ionic liquids compounds,” *Materials* 13(17), 3687. DOI: 10.3390/ma13173687.

Alekhina, M., Erdmann, J., Ebert, A., Stepan, A. M., and Sixta, H. (2015). "Physico-chemical properties of fractionated softwood kraft lignin and its potential use as a bio-based component in blends with polyethylene," *J. Mater. Sci.* 50(19), 6395-6406. DOI: 10.1007/s10853-015-9192-9.

Amid, H., Mazé, B., Flickinger, M. C., and Pourdeyhimi, B. (2016). "Hybrid adsorbent nonwoven structures: A review of current technologies," *J. Mater. Sci.* 51(9), 4173-4200. DOI: 10.1007/s10853-016-9741-x.

Argyropoulos, D. S. (2013). "Towards thermoplastic lignin polymers: Progress in the utilization of kraft lignin for the synthesis of heat stable polymer melts," *J. Biotechnol. Biomater.* 03(03). DOI: 10.4172/2155-952X.1000e123.

Argyropoulos, D. S. (2014). "The emerging bio-refinery industry needs to refine lignin prior to use," *J. Biotechnol. Biomaterial*. S6 (001). DOI:10.4172/2155-952X.S6-e001.

Aro, T., and Fatehi, P. (2017). "Production and application of lignosulfonates and sulfonated lignin," *ChemSusChem* 10(9), 1861-1877. DOI: 10.1002/cssc.201700082.

Aslanzadeh, S., Ahvazi, B., Boluk, Y., and Ayranci, C. (2017). "Carbon fiber production from electrospun sulfur free softwood lignin precursors," *J. Eng. Fabr. Fibers* 12(4), 33-34. DOI: 10.1177/155892501701200405

Asmatulu, R., and Khan, W. S. (2019). "Historical background of the electrospinning process," in: *Synthesis and Applications of Electrospun Nanofibers*, Elsevier, pp. 17-39. DOI: 10.1016/B978-0-12-813914-1.00002-X.

Aspland, J. R. (2005). "The coloration and finishing of nonwoven fabrics," *Nonwoven Enhancements* 28.

ASTM International. (2019). "Standard terminology relating to textiles," ASTM International. DOI: 10.1520/D0123-19.

Bahi, A., Shao, J., Mohseni, M., and Ko, F. K. (2017). "Membranes based on electrospun lignin-zeolite composite nanofibers," *Separation and Purification Technology* 187, 207-213. DOI: 10.1016/j.seppur.2017.06.015.

Bai, L., Greca, L. G., Xiang, W., Lehtonen, J., Huan, S., Nugroho, R. W. N., Tardy, B. L., and Rojas, O. J. (2019). "Adsorption and assembly of cellulosic and lignin colloids at oil/water interfaces," *Langmuir* 35(3), 571-588. DOI: 10.1021/acs.langmuir.8b01288.

Batra, S. K., and Pourdeyhimi, B. (2012). *Introduction to Nonwovens Technology*, DEStech Publications, Inc.

Beck, R. J., Zhao, Y., Fong, H., and Menkhaus, T. J. (2017). "Electrospun lignin carbon nanofiber membranes with large pores for highly efficient adsorptive water treatment applications," *Journal of Water Process Engineering* 16, 240-248. DOI: 10.1016/j.jwpe.2017.02.002.

Borregaard LignoTech. (2021). Dyestuff Dispersants.

Burkinshaw, S. M., Hewitt, A. D., Blackburn, R. S., and Russell, S. J. (2012). "The dyeing of nonwoven fabrics. Part 1: Initial studies," *Dyes and Pigments* 94(3), 592-598. DOI: 10.1016/j.dyepig.2011.09.011.

Camiré, A., Espinasse, J., Chabot, B., and Lajeunesse, A. (2020). "Development of electrospun lignin nanofibers for the adsorption of pharmaceutical contaminants in wastewater," *Environ. Sci. Pollut. Res*. 27(4), 3560-3573. DOI: 10.1007/s11356-018-3333-z.

Cardamone, J. M. (1992). "Reacting cotton cellulose with lignin-based polyurethane," *Textile Research Journal* 62(7), 371-381. DOI: 10.1177/004051759206200702.

Cayla, A., Rault, F., Giraud, S., Salaün, F., Fierro, V., and Celzard, A. (2016). "PLA with intumescent system containing lignin and ammonium polyphosphate for flame retardant textile," *Polymers* 8(9), 331. DOI: 10.3390/polym8090331.

Chang, C.-Y., and Chang, F.-C. (2016). "Development of electrospun lignin-based fibrous materials for filtration applications," *BioResources* 11(1), 2202-2213. DOI: 10.15376/biores.11.1.2202-2213.

Chen, J., Eraghi Kazzaz, A., AlipoorMazandarani, N., Hosseinpour Feizi, Z., and Fatehi, P. (2018). "Production of flocculants, adsorbents, and dispersants from lignin," *Molecules* 23(4), 868. DOI: 10.3390/molecules23040868.

Chen, H. (2015) "Lignocellulose biorefinery feedstock engineering," in: *Lignocellulose Biorefinery Engineering*, Elsevier, pp. 37-86. DOI: 10.1016/B978-0-08-100135-6.00003-X.

Chen, Y.-T., Sun, Y.-M., Hu, C.-C., Lai, J.-Y., and Liu, Y.-L. (2021). "Employing lignin in the formation of the selective layer of thin-film composite membranes for pervaporation desalination," *Mater. Adv.* 2(9), 3099-3106. DOI: 10.1039/D1MA00150G.

Cho, M., Ji, L., Liu, L.-Y., M. Johnson, A., Potter, S., Mansfield, S. D., and Renneckar, S. (2020). "High performance electrospun carbon nanofiber mats derived from flax lignin," *Industrial Crops and Products* 155, article no. 112833. DOI: 10.1016/j.indcrop.2020.112833.

Crestini, C., Lange, H., Sette, M., and Argyropoulos, D. S. (2017). "On the structure of softwood kraft lignin," *Green Chem.* 19(17), 4104-4121. DOI:10.1039/C7GC01812F.

Cruz, J. M., Domínguez, J. M., Domínguez, H., and Parajó, J. C. (2001). "Antioxidant and antimicrobial effects of extracts from hydrolysates of lignocellulosic materials," *J. Agric. Food Chem.* 49(5), 2459-2464. DOI: 10.1021/jf001237h.

Cui, C., Sadeghifar, H., Sen, S., and Argyropoulos, D. S. (2013). "Toward thermoplastic lignin polymers; Part II: Thermal & polymer characteristics of kraft lignin & derivatives," *BioResources* 8(1), 864-886.

Cui, C., Sun, R., and Argyropoulos, D. S. (2014). "Fractional precipitation of softwood kraft lignin: Isolation of narrow fractions common to a variety of lignins," *ACS Sustainable Chem. Eng.* 2(4), 959-968. DOI: 10.1021/sc400545d.

Cui, J., Lu, T., Li, F., Wang, Y., Lei, J., Ma, W., Zou, Y., and Huang, C. (2021). "Flexible and transparent composite nanofibre membrane that was fabricated *via* a 'green' electrospinning method for efficient particulate matter 2.5 capture," *Journal of Colloid and Interface Science* 582, 506-514. DOI: 10.1016/j.jcis.2020.08.075.

Culebras, M., Geaney, H., Beaucamp, A., Upadhyaya, P., Dalton, E., and Collins, M. N. (2019). "Bio-derived carbon nanofibers from lignin as high performance li-ion anode materials," *ChemSusChem*12, 1-7.

Dallmeyer, J. I. (2013). "Preparation and characterization of lignin nanofibre-based materials obtained by electrostatic spinning," DOI: 10.14288/1.0073787.

Dallmeyer, I., Chowdhury, S., and Kadla, J. F. (2013). "Preparation and characterization of kraft lignin-based moisture-responsive films with reversible shape-change capability," *Biomacromolecules* 14(7), 2354-2363. DOI: 10.1021/bm400465p.

Dallmeyer, I., Ko, F., and Kadla, J. F. (2010). "Electrospinning of technical lignins for the production of fibrous networks," *Journal of Wood Chemistry and Technology* 30(4), 315-329. DOI: 10.1080/02773813.2010.527782.

Dallmeyer, I., Lin, L. T., Li, Y., Ko, F., and Kadla, J. F. (2014). "Preparation and characterization of interconnected, kraft lignin-based carbon fibrous materials by electrospinning," *Macromol. Mater. Eng.* 299(5), 540-551. DOI: 10.1002/mame.201300148.

Das, P., Ojah, N., Kandimall, R., Mohan, K. Gogo, I. D., Dolui, S. K., and Choudhury, A. J. (2018). "Surface modification of electrospun PVA/chitosan nanofibers by dielectric barrier discharge plasma at atmospheric pressure and studies of their mechanical properties and biocompatibility," *Int. J. Biol. Macromol.* 114. 1026-1032. DOI: 10.1016/j.ijbiomac.2018.03.115

de Avila Delucis, R., de Araujo Calado, V. M., Moraes d'Almeida, J. R., and Amico, S. C. (2017). "Carbon fibers from sustainable resources," in: *Handbook of Composites from Renewable Materials*, V. K. Thakur, M. K. Thakur, and M. R. Kessler, M. R. (eds.), John Wiley & Sons, Inc., Hoboken, NJ, USA, pp. 1-23. DOI: 10.1002/9781119441632.ch1.

Deckner, G. (2018). "Mixing Things Up: Formulating with Dispersants," *Prospector Knowledge Center*. https://knowledge.ulprospector.com/8805/pcc-mixing-things-up-formulating-with-dispersants/ (accessed 2022 -02 -23).

Ding, R., Wu, H., Thunga, M., Bowler, N., and Kessler, M. R. (2016). "Processing and characterization of low-cost electrospun carbon fibers from organosolv lignin/polyacrylonitrile blends," *Carbon* 100, 126-136. DOI: 10.1016/j.carbon.2015.12.078.

Dispersant used for dye industry http://www.offerchems.com/dispersant-used-dye-industry/ (accessed 2021 -06 -14).

Doherty, W. O. S., Mousavioun, P., and Fellows, C. M. (2011). "Value-adding to cellulosic ethanol: Lignin polymers," *Industrial Crops and Products* 33(2), 259-276. DOI: 10.1016/j.indcrop.2010.10.022.

Dong, X., Dong, M., Lu, Y., Turley, A., Jin, T., and Wu, C. (2011). "Antimicrobial and antioxidant activities of lignin from residue of corn stover to ethanol production," *Industrial Crops and Products* 34(3), 1629-1634. DOI: 10.1016/j.indcrop.2011.06.002.

Eucaliva https://eucaliva.eu/ (accessed 2021 -06 -14).

Fernandes, D. M., Winkler Hechenleitner, A. A., Job, A. E., Radovanocic, E., and Gómez Pineda, E. A. (2006). "Thermal and photochemical stability of poly(vinyl alcohol)/modified lignin blends," *Polymer Degradation and Stability* 91(5), 1192-1201. DOI: 10.1016/j.polymdegradstab.2005.05.024.

Fu, S., Song, P., and Liu, X. (2017). "Thermal and flame retardancy properties of thermoplastics/natural fiber biocomposites," in: *Advanced High Strength Natural Fibre Composites in Construction*, Elsevier, pp. 479-508. DOI: 10.1016/B978-0-08-100411-1.00019-4.

Global Market Insights, Inc. (2021). "Lignin market revenue to hit $1 billion by 2026, says Global Market Insights, Inc. June 14, 2021.

Go, D., Opitz, M., Lott, P., Rahimi, K., Stollenwerk, J., Thomas, H., Möller, M., Roling, B., and Kuehne, A. J. C. (2018). "Electrochemical characterization of laser-carbonized polyacrylonitrile nanofiber nonwovens," *J. Appl. Polym. Sci.* 135(25), 46398. DOI: 10.1002/app.46398.

Graham, K., Ouyang, M., Raether, T., Grafe, T., McDonald, B., Knauf, P., and Co, D. (2002). *Polymeric Nanofibers in Air Filtration Applications*, Galveston, Texas, p. 18.

Han, C. D., and Chuang, H.-K. (1985). "Criteria for rheological compatibility of polymer blends," *J. Appl. Polym. Sci.* 30(11), 4431-4454. DOI: 10.1002/app.1985.070301118.

Hou, C., Chen, W., Fu, L., Zhang, S., Liang, C., and Wang, Y. (2021). "Efficient degradation of perfluorooctanoic acid by electrospun lignin-based bimetallic MOFs nanofibers composite membranes with peroxymonosulfate under solar light irradiation," *International Journal of Biological Macromolecules* 174, 319-329. DOI: 10.1016/j.ijbiomac.2021.01.184.

Hutten, I. M. (2016). “Introduction to nonwoven filter media,” in: *Handbook of Nonwoven Filter Media*, Elsevier, pp. 1-52. DOI: 10.1016/B978-0-08-098301-1.00001-0.

ILI - International Lignin Institute https://www.ili-lignin.com/ (accessed 2021 -06 -14).

INDA, About INDA https://www.inda.org/ (accessed 2021 -06 -14).

Indi, Y. M., Deshpande, R. H., and Patil, P. D. (2019). “New trends in finishing of nonwovens,” *Asian Textile Journal* 2019, 61-67.

Inkwood research, Global PP Nonwoven Fabrics Market | Growth, Share, Size https://www.inkwoodresearch.com/reports/pp-nonwoven-fabrics-market (accessed 2021 -06 -14).

Introduction to Nonwovens. (2004). In: *Nonwoven Fabrics*, W. Albrecht, H. Fuchs, and W. Kittelmann (eds.), Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, FRG, pp. 1-12. DOI: 10.1002/3527603344.ch0.

Jiao, L. Y., and Wu, Z. J. (2013). “Alkali lignin as a carbonization agent on the thermal degradation and flame retardancy of intumescent flame retardant coating,” *AMR* 750–752, 1385-1388. DOI: 10.4028/www.scientific.net/AMR.750-752.1385.

Kai, D., Jiang, S., Low, Z. W., and Loh, X. J. (2015). “Engineering highly stretchable lignin-based electrospun nanofibers for potential biomedical applications,” *J. Mater. Chem. B* 3(30), 6194-6204. DOI: 10.1039/C5TB00765H

Kakoria, A., and Sinha-Ray, S. (2018). “A review on biopolymer-based fibers *via* electrospinning and solution blowing and their applications,” *Fibers* 6(3), 45. DOI: 10.3390/fib6030045

Karaaslan, M. A., Cho, M., Liu, L.-Y., Wang, H., Renneckar, S. (2021). “Refining the properties of softwood kraft lignin with acetone: Effect of solvent fractionation on the thermomechanical behavior of electrospun fibers,” *ACS Sustainable Chem. Eng*. 9(1), 458-470. DOI: 10.1021/acssuschemeng.0c07634

Khan, T. A., Lee, J.-H., and Kim, H.-J. (2019). “Lignin-based adhesives and coatings,” in: *Lignocellulose for Future Bioeconomy*, Elsevier, pp. 153-206. DOI: 10.1016/B978-0-12-816354-2.00009-8

Kittelmann, W., Dilo, J. P., Gupta, V. P., Kunath, P., Schreiber, J., Wegner, A., Zäh, W., Münstermann, U., Möschler, W., Watzl, A., and Böttcher, P. (2004). “Web bonding,” in: *Nonwoven Fabrics*. W. Albrecht, H. Fuchs, and W. Kittelmann (eds.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, pp. 269-408. DOI: 10.1002/3527603344.ch6

Ko, H., Kim, J. W., Kim, H. C., Zhai, L., and Kim, J. (2020). “Esterified PVA-lignin resin by maleic acid applicable for natural fiber reinforced composites,” *J. Appl. Polym. Sci.* 137(26), article no. 48836. DOI: 10.1002/app.48836.

Ko, H.-U., Zhai, L., Park, J. H., Lee, J. Y., Kim, D., and Kim, J. (2018). “Poly(vinyl alcohol)-lignin blended resin for cellulose-based composites,” *J. Appl. Polym. Sci*. 135(34), article no. 46655. DOI: 10.1002/app.46655.

Kubo, S., and Kadla, J. F. (2003). “The formation of strong intermolecular interactions in immiscible blends of poly(vinyl alcohol) (PVA) and lignin,” *Biomacromolecules* 4(3), 561-567. DOI: 10.1021/bm025727p.

Kun, D., and Pukánszky, B. (2017). “Polymer/lignin blends: interactions, properties, applications,” *European Polymer Journal* 93, 618-641. DOI: 10.1016/j.eurpolymj.2017.04.035.

Kwak, H. W., Woo, H., Kim, E. H., and Lee, K. H. (2018). “Water-resistant lignin/poly(vinyl alcohol) blend fibers for removal of hexavalent chromium,” *Fibers Polym.* 19(6), 1175-1183. DOI: 10.1007/s12221-018-8052-z.

Lai, C., Zhou, Z., Zhang, L., Wang, X., Zhou, Q., Zhao, Y., Wang, Y., Wu, X.-F., Zhu, Z., and Fong, H. (2014a). "Free-standing and mechanically flexible mats consisting of electrospun carbon nanofibers made from a natural product of alkali lignin as binder-free electrodes for high-performance supercapacitors," *Journal of Power Sources* 247, 134-141. DOI: 10.1016/j.jpowsour.2013.08.082.

Lai, C., Kolla, P., Zhao, Y., Fong, H., and Smirnova, A. L. (2014b). "Lignin-derived electrospun carbon nanofiber mats with supercritically deposited Ag nanoparticles for oxygen reduction reaction in alkaline fuel cells," *Electrochimica Acta* 130, 431-438. DOI: 10.1016/j.electacta.2014.03.006

Lee, E., Song, Y., and Lee, S. (2019). "Crosslinking of lignin/poly(vinyl alcohol) nanocomposite fiber webs and their antimicrobial and ultraviolet-protective properties," *Textile Research Journal* 89 (1), 3-12. DOI: 10.1177/0040517517736468.

Lee, E.-S., Kim, Y.-O., Ha, Y.-M., Lim, D., Hwang, J. Y., Kim, J., Park, M., Cho, J. W., and Jung, Y. C. (2018). "Antimicrobial properties of lignin-decorated thin multi-walled carbon nanotubes in poly(vinyl alcohol) nanocomposites," *European Polymer Journal* 105, 79-84. DOI: 10.1016/j.eurpolymj.2018.05.014.

Leifeld, F., Kittelmann, W., Bernhardt, S., Schäffler, M., Paschen, A., Wulfhorst, B., Krčma, R., and Blechschmidt, D. (2004). "Dry-law process," in: *Nonwoven Fabrics*, W. Albrecht, H. Fuchs, and W. Kittelmann (eds.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, pp, 141-236. DOI: 10.1002/3527603344.ch4.

Li, H., and Peng, L. (2015). "Antimicrobial and antioxidant surface modification of cellulose fibers using layer-by-layer deposition of chitosan and lignosulfonates," *Carbohydrate Polymers* 124, 35-42. DOI: 10.1016/j.carbpol.2015.01.071.

Li, Q., Xie, S., Serem, W. K., Naik, M. T., Liu, L., and Yuan, J. S. (2017). "Quality carbon fibers from fractionated lignin," *Green Chem.* 19(7), 1628-1634. DOI: 10.1039/C6GC03555H.

Li, X., Sun, N., Tian, X., Yang, T., Song, Y., Xu, B., and Liu, Z. (2020). "Electrospun coal liquefaction residues/polyacrylonitrile composite carbon nanofiber nonwoven fabrics as high-performance electrodes for lithium/potassium batteries," *Energy Fuels* 34(2), 2445-2451. DOI: 10.1021/acs.energyfuels.9b03637.

Li, Y., Li, F., Yang, Y., Ge, B., and Meng, F. (2021). "Research and application progress of lignin-based composite membrane," *Journal of Polymer Engineering* 41(4), 245-258. DOI: 10.1515/polyeng-2020-0268.

LigniMatch. (2010). "Future use of lignin in value added products—A roadmap for possible Nordic/Baltic innovation.

Lopez-Cuesta, J.-M. (2017). "Flame retardancy properties of clay–polymer nanocomposites," in: *Clay-Polymer Nanocomposites*, Elsevier, pp. 443-473. DOI: 10.1016/B978-0-323-46153-5.00013-6.

Lu, C., Blackwell, C., Ren, Q., and Ford, E. (2017). "Effect of the coagulation bath on the structure and mechanical properties of gel-spun lignin/poly(vinyl alcohol) fibers," *ACS Sustainable Chem. Eng*. 5(4), 2949-2959. DOI: 10.1021/acssuschemeng.6b02423.

Lu, C., Rawat, P., Louder, N., and Ford, E. (2018). "Properties and structural anisotropy of gel-spun lignin/poly(vinyl alcohol) fibers due to gel aging," *ACS Sustainable Chem. Eng.* 6(1), 679-689. DOI: 10.1021/acssuschemeng.7b03028.

Łukawski, D., Grześkowiak, W., Lekawa-Raus, A., Widelicka, M., Lisiecki, F., and Dudkowiak, A. (2020). "Flame retardant effect of lignin/carbon nanotubes/potassium carbonate composite coatings on cotton roving," *Cellulose* 27(12), 7271-7281. DOI: 10.1007/s10570-020-03270-y.

Luo, Y., Nartker, S., Miller, H., Hochhalter, D., Wiederoder, M., Wiederoder, S., Stterington, E., Drzal, L. T., and Alocilja, E. C. (2010). "Surface functionalization of electrospun nanofibers for detecting *E. coli* O157: H7 and BVDV cells in a direst-charge transfer biosensor," *Biosens. Bioelectron.* 26(4), 1612-1617. DOI: 10.1016/j.bios.2010.08.028

Ma, X., Kolla, P., Zhao, Y., Smirnova, A. L., and Fong, H. (2016). "Electrospun lignin-derived carbon nanofiber mats surface-decorated with MnO_2 nanowhiskers as binder-free supercapacitor electrodes with high performance," *Journal of Power Sources* 325, 541-548. DOI: 10.1016/j.jpowsour.2016.06.073.

Mandlekar, N., Cayla, A., Rault, F., Giraud, S., Salaün, F., Malucelli, G., and Guan, J.-P. (2018). "An overview on the use of lignin and its derivatives in fire retardant polymer systems," in: *Lignin: Trends and Applications*, InTech, Croatia, p. 231.

Nair, S. S., Sharma, S., Pu, Y., Sun, Q., Pan, S., Zhu, J. Y., Deng, Y., and Ragauskas, A. J. (2014). "High shear homogenization of lignin to nanolignin and thermal stability of nanolignin-polyvinyl alcohol blends," *ChemSusChem* 7(12), 3513-3520. DOI: 10.1002/cssc.201402314.

Nanoscience instruments. Electrospinning - Nanoscience Instruments https://www.nanoscience.com/techniques/electrospin/ (accessed 2021 -06 -14).

New Cloth Market. (2021). "Nonwoven manufacturing process, nonwoven fabric making process," *Technical Textiles*, June 14, 2021.

Nie, G., Zhao, X., Luan, Y., Jiang, J., Kou, Z., and Wang, J. (2020). "Key issues facing electrospun carbon nanofibers in energy applications: On-going approaches and challenges," *Nanoscale* 12(25), 13225-13248. DOI: 10.1039/D0NR03425H.

Nonwoven Bonding Techniques (2016), in: *Nonwovens: Process, Structure, Properties and Applictions*, T. Karthik, P. Karam C., and R. Rathinamoorthy (eds.), WPI Publishing.

Ogale, A. A., Zhang, M., and Jin, J. (2016). "Recent advances in carbon fibers derived from biobased precursors," *J. Appl. Polym. Sci.* 133(45). DOI: 10.1002/app.43794.

Pan, X., Kadla, J. F., Ehara, K., Gilkes, N., and Saddler, J. N. (2006). "Organosolv ethanol lignin from hybrid poplar as a radical scavenger: Relationship between lignin structure, extraction conditions, and antioxidant activity," *J. Agric. Food Chem.* 54(16), 5806-5813. DOI: 10.1021/jf0605392.

Park, C.-W., Youe, W.-J., Han, S.-Y., Kim, Y. S., and Lee, S.-H. (2017). "Characteristics of carbon nanofibers produced from lignin/polyacrylonitrile (PAN)/kraft lignin-g-PAN copolymer blends electrospun nanofibers," *Holzforschung* 71(9), 743-750. DOI: 10.1515/hf-2017-0024.

Perera Jayawickramage, R. A., and Ferraris, J. P. (2019). "High performance supercapacitors using lignin based electrospun carbon nanofiber electrodes in ionic liquid electrolytes," *Nanotechnology* 30(15), article no. 155402. DOI: 10.1088/1361-6528/aafe95.

Pill, H., and Afflerbach, K. (2004). "Wet lay method," in: *Nonwoven Fabrics*, W. Albrecht, H. Fuchs, and W. Kittelmann (eds.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, pp, 237-267. DOI: 10.1002/3527603344.ch5.

Posoknistakul, P., Tangkrakul, C., Chaosuanphae, P., Deepentham, S., Techasawong, W., Phonphirunrot, N., Bairak, S., Sakdaronnarong, C., and Laosiripojana, N. (2020). "Fabrication and characterization of lignin particles and their ultraviolet protection ability in PVA composite film," *ACS Omega* 5(33), 20976-20982. DOI: 10.1021/acsomega.0c02443.

Poursorkhabi, V., Mohanty, A. K., and Misra, M. (2015). "Electrospinning of aqueous lignin/poly(ethylene oxide) complexes," *J. Appl. Polym. Sci.* 132(2), app.41260. DOI: 10.1002/app.41260.

Pouteau, C., Baumberger, S., Cathala, B., and Dole, P. (2004). "Lignin–polymer blends: Evaluation of compatibility by image analysis," *Comptes Rendus Biologies* 327(9–10), 935-943. https://doi.org/10.1016/j.crvi.2004.08.008.

Prisma Renewable Composites https://prismacomposites.com/ (accessed 2021 -06 -14).

Qin, Y., Yuan, M., Hu, Y., Lu, Y., Lin, W., Ma, Y., Lin, X., and Wang, T. (2020). "Preparation and interaction mechanism of nano disperse dye using hydroxypropyl sulfonated lignin," *International Journal of Biological Macromolecules* 152, 280-287. DOI: 10.1016/j.ijbiomac.2020.02.261

Réti, C., Casetta, M., Duquesne, S., Bourbigot, S., and Delobel, R. (2008). "Flammability properties of intumescent PLA including starch and lignin," *Polym. Adv. Technol.* 19(6), 628-635. DOI: 10.1002/pat.1130.

Reti, C., Casetta, M., Duquesne, S., Delobel, R., Soulestin, J., and Bourbigot, S. (2009). "Intumescent biobased-polylactide films to flame retard nonwovens," *Journal of Engineered Fibers and Fabrics* 4(2), article no. 155892500900400. DOI: 10.1177/155892500900400206.

Roman, J., Neri, W., Derré, A., and Poulin, P. (2019). "Electrospun lignin-based twisted carbon nanofibers for potential microelectrodes applications," *Carbon* 145, 556-564. DOI: 10.1016/j.carbon.2019.01.036.

Sabaghi, S., and Fatehi, P. (2020). "Polarity of cationic lignin polymers: Physicochemical behavior in aqueous solutions and suspensions," *ChemSusChem* 13(17), 4722-4734. DOI: 10.1002/cssc.202000897.

Sadeghifar, H., and Argyropoulos, D. S. (2015). "Correlations of the antioxidant properties of softwood kraft lignin fractions with the thermal stability of its blends with polyethylene," *ACS Sustainable Chem. Eng*. 3(2), 349-356. DOI: 10.1021/sc500756n.

Sadeghifar, H., and Argyropoulos, D. S. (2016). "Macroscopic behavior of kraft lignin fractions: melt stability considerations for lignin–polyethylene blends," *ACS Sustainable Chem. Eng.* 4(10), 5160-5166. DOI: 10.1021/acssuschemeng.6b00636.

Sadeghifar, H., Sen, S., Patil, S. V., and Argyropoulos, D. S. (2016). "Toward carbon fibers from single component kraft lignin systems: Optimization of chain extension chemistry," *ACS Sustainable Chem. Eng*. 4(10), 5230-5237. DOI: 10.1021/acssuschemeng.6b00848.

Sadeghifar, H., Wells, T., Le, R. K., Sadeghifar, F., Yuan, J. S., Ragauskas, A. J. (2017). "Fractionation of organosolv lignin using acetone:water and properties of the obtained fractions," *ACS Sustainable Chem. Eng*. 5(1), 580-587. DOI: 10.1021/acssuschemeng.6b01955.

Sagues, W. J., Jain, A., Brown, D., Aggarwal, S., Suarez, A., Kollman, M., Park, S., and Argyropoulos, D. S. (2019). "Are lignin-derived carbon fibers graphitic enough?" *Green Chem*. 21(16), 4253-4265. DOI: 10.1039/C9GC01806A.

Schreiber, M. (2012). "A study on the electrospinning behaviour and nanofibre morphology of anionically charged lignin," *AML* 3(6), 476-480. DOI: 10.5185/amlett.2012.icnano.336.

Schreiber, M., Vivekanandhan, S., Cooke, P., Mohanty, A. K., and Misra, M. (2014). "Electrospun green fibres from lignin and chitosan: A novel polycomplexation process for the production of lignin-based fibres," *J. Mater. Sci.* 49(23), 7949-7958. DOI: 10.1007/s10853-014-8481-z.

Sen, S., Sadeghifar, H., and Argyropoulos, D. S. (2013). "Kraft lignin chain extension chemistry *via* propargylation, oxidative coupling, and Claisen rearrangement," *Biomacromolecules* 14(10), 3399-3408. DOI: 10.1021/bm4010172.

Seo, D. K., Jeun, J. P., Kim, H. B., and Kang, P. H. (2011). "Preparation and characterization of the carbon nanofiber mat produced from electrospun PAN/lignin precursors by electron beam irradiation," *Rev. Adv. Mater. Sci.* 28, 31-34.

Shakoor, A., Baig, G. A., Tausif, M., and Gilani, S. Q. Z. (2017). "Pigment and disperse printing of needlepunched polyethylene terephthalate nonwovens," *Dyes and Pigments* 136, 865-872. DOI: 10.1016/j.dyepig.2016.09.052.

Shi, X., Wang, X., Tang, B., Dai, Z., Chen, K., and Zhou, J. (2018). "Impact of lignin extraction methods on microstructure and mechanical properties of lignin-based carbon fibers," *J. Appl. Polym. Sci* 135(10), article no. 45580. DOI: 10.1002/app.45580

Singha, K. (2012). "A review on coating & lamination in textiles: Processes and applications," *AJPS* 2(3), 39-49. DOI: 10.5923/j.ajps.20120203.04.

Song, K., Ganguly, I., Eastin, I., and Dichiara, A. (2017). "Lignin-modified carbon nanotube/graphene hybrid coating as efficient flame retardant," *IJMS* 18(11), 2368. DOI: 10.3390/ijms18112368.

Stukenbrock, K.-H. (2004a). "Mechanical finishing," in: *Nonwoven Fabrics*, W. Albrecht, H. Fuchs, and W. Kittelmann (eds.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, pp 411-420. DOI: 10.1002/3527603344.ch7.

Stukenbrock, K.-H. (2004b). "Chemical finishing," in: *Nonwoven Fabrics*, W. Albrecht, H. Fuchs, and W. Kittelmann (eds.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, pp. 421-459. DOI: 10.1002/3527603344.ch8.

Stylios, G. K., and Jones, I. (2013). *Joining of Textiles; Principles and Applications*, Woodhead Publishing Series in Textiles No. 110, Woodhead Publishing.

Suhas, Carrott, P. J. M., and Ribeiro Carrott, M. M. L. (2007). "Lignin – from natural adsorbent to activated carbon: A review," *Bioresource Technology* 98(12), 2301-2312. DOI: 10.1016/j.biortech.2006.08.008.

Sunthornvarabhas, J., Liengprayoon, S., Lerksamran, T., Buratcharin, C., Suwonsichon, T., Vanichsriratana, W., and Sriroth, K. (2019). "Utilization of lignin extracts from sugarcane bagasse as bio-based antimicrobial fabrics," *Sugar Tech.* 21(2), 355-363. DOI: 10.1007/s12355-018-0683-2.

Sunthornvarabhas, J., Liengprayoon, S., and Suwonsichon, T. (2017). "Antimicrobial kinetic activities of lignin from sugarcane bagasse for textile product," *Industrial Crops and Products* 109, 857-861. DOI: 10.1016/j.indcrop.2017.09.059.

Tarasov, D., Leitch, M., and Fatehi, P. (2015). "Production of lignosulfonate in NSSC-based biorefinery," *Biotechnol Progress* 31(6), 1508-1514. DOI: 10.1002/btpr

Textile Chemicals | Auxiliary, Finishing & Dye Chemicals| Ingevity - Ingevity https://www.ingevity.com/markets/textiles/ (accessed 2021 -06 -14).

Textile Dyeing- Common Terms Used and Dyes Classification.

The North American Nonwovens Filter Market (2018). Textile World.

Toh, K., Nakano, S., Yokoyama, H., Ebe, K., Gotoh, K., and Noda, H. (2005). "Anti-deterioration effect of lignin as an ultraviolet absorbent in polypropylene and polyethylene," *Polym. J.* 37(8), 633-635. DOI: 10.1295/polymj.37.633.

Uddin, M.-J., Alaboina, P. K., Zhang, L., and Cho, S.-J. (2017). "A low-cost, environment-friendly lignin-polyvinyl alcohol nanofiber separator using a water-based method for safer and faster lithium-ion batteries," *Materials Science and Engineering: B* 223, 84-90. DOI: 10.1016/j.mseb.2017.05.004.

Ugartondo, V., Mitjans, M., and Vinardell, M. (2008). "Comparative antioxidant and cytotoxic effects of lignins from different sources," *Bioresource Technology* 99(14), 6683-6687. DOI: 10.1016/j.biortech.2007.11.038.

Vade, A. (2015). "Coating and lamination of non-wovens," *Dye Chem. Pharma. Business News* 2015, 54-57.

Vermerris, W., Sherman, D. M., and McIntyre, L. M. (2010). "Phenotypic plasticity in cell walls of maize brown midrib mutants is limited by lignin composition," *Journal of Experimental Botany* 61(9), 2479-2490. DOI: 10.1093/jxb/erq093.

Vilakati, G. D., Wong, M. C. Y., Hoek, E. M. V., and Mamba, B. B. (2014). "Relating thin film composite membrane performance to support membrane morphology fabricated using lignin additive," *Journal of Membrane Science* 469, 216-224. DOI: 10.1016/j.memsci.2014.06.018.

Wang, S. X., Yang, L., Stubbs, L. P., Li, X., and He, C. (2013). "Lignin-derived fused electrospun carbon fibrous mats as high-performance anode materials for lithium ion batteries," *ACS Appl. Mater. Interfaces* 5, 12275-12282. DOI: 10.1021/am4043867

Wei, Q., Xiao, X., Hou, D., Ye, H., and Huang, F. (2008). "Characterization of nonwoven material functionalized by sputter coating of copper," *Surface and Coatings Technology* 202(12), 2535-2539. DOI: 10.1016/j.surfcoat.2007.09.022.

Xiang, P., Kuznetsov, A. V., and Seyam, A. M. (2006). "Modeling of the hydroentanglement process," *Journal of Engineered Fibers and Fabrics* 1(2), article no. 155892500600100. DOI: 10.1177/155892500600100201.

Xiao, X., Chen, F., Wei, Q., and Wu, N. (2009). "Surface modification of polyester nonwoven fabrics by Al_2O_3 sol–gel coating," *J. Coat. Technol. Res.* 6(4), 537-541. DOI: 10.1007/s11998-008-9157-x.

Xiong, F., Wu, Y., Li, G., Han, Y., and Chu, F. (2018). "Transparent nanocomposite films of lignin nanospheres and poly(vinyl alcohol) for UV-absorbing," *Ind. Eng. Chem. Res.* 57(4), 1207-1212. DOI: 10.1021/acs.iecr.7b04108.

Xu, C., and Ferdosian, F. (2017). "Utilization of lignosulfonate as dispersants or surfactants," in: *Conversion of Lignin into Bio-Based Chemicals and Materials; Green Chemistry and Sustainable Technology*, Springer, Berlin, Heidelberg, pp. 81-90. DOI: 10.1007/978-3-662-54959-9_5.

Yang, D., Li, H., Qin, Y., Zhong, R., Bai, M., and Qiu, X. (2015). "Structure and properties of sodium lignosulfonate with different molecular weight used as dye dispersant," *Journal of Dispersion Science and Technology* 36(4), 532-539. DOI: 10.1080/01932691.2014.916221.

Yang, J., Ching, Y., and Chuah, C. (2019). "Applications of lignocellulosic fibers and lignin in bioplastics: A review," *Polymers* 11(5), 751. DOI: 10.3390/polym11050751.

Yang, X., Mao, L., Peng, W., Jin, J., Yang, S., and Li, G. (2020). "Synthesis of double-layered $NiCo_2O_4$-nanosheet-loaded PAN/lignin-based hollow carbon nanofibers for high-performance supercapacitor," *ChemistrySelect* 5(8), 2602-2609. DOI: 10.1002/slct.201904546.

Yu, Q., Bahi, A., and Ko, F. (2015). "Influence of poly(ethylene oxide) (PEO) percent and lignin type on the properties of lignin/PEO blend filament: Influence of poly(ethylene oxide) (PEO) percent," *Macromol. Mater. Eng*. 300(10), 1023-1032. DOI: 10.1002/mame.201500045.

Zhang, H., Yu, B., Zhou, W., Liu, X., and Chen, F. (2018). "High-value utilization of *Eucalyptus* kraft lignin: Preparation and characterization as efficient dye dispersant," *International Journal of Biological Macromolecules* 109, 1232-1238. DOI: 10.1016/j.ijbiomac.2017.11.118.

Zhang, R., Maltari, R., Guo, M., Kontro, J., Eronen, A., and Repo, T. (2020a). "Facile synthesis of vanillin from fractionated kraft lignin," *Industrial Crops and Products* 145, article no. 112095. DOI: 10.1016/j.indcrop.2020.112095.

Zhang, X., Dong, S., Wu, W., Yang, J., Li, J., Shi, K., and Liu, H. (2020b). "Influence of lignin units on the properties of lignin/ PAN -derived carbon fibers," *J. Appl. Polym. Sci.* 137(42), article no. 49274. DOI: 10.1002/app.49274.

Zhang, X., Liu, W., Liu, W., and Qiu, X. (2020c). "High performance PVA/lignin nanocomposite films with excellent water vapor barrier and UV-shielding properties," *International Journal of Biological Macromolecules* 142, 551-558. DOI: 10.1016/j.ijbiomac.2019.09.129.

Zhang, W., Yang, P., Li, X., Zhu, Z., Chen, M., and Zhou, X. (2019). "Electrospun lignin-based composite nanofiber membrane as high-performance absorbent for water purification," *International Journal of Biological Macromolecules* 141, 747-755. DOI: 10.1016/j.ijbiomac.2019.08.221.

Zhang, Y., Li, T.-T., Lou, C.-W., and Lin, J.-H. (2020d). "Facile method for tent fabrics with eco-friendly/durable properties using waterborne polyurethane/lignin: Preparation and evaluation," *Journal of Industrial Textiles* 2020, article no. 152808372093188. DOI: 10.1177/1528083720931884.

Zhao, G., Ni, H., Ren, S., and Fang, G. (2018). "Correlation between solubility parameters and properties of alkali lignin/PVA composites," *Polymers* 10(3), 290. DOI: 10.3390/polym10030290.

Zhao, M., Wang, J., Chong, C., Yu, X., Wang, L., and Shi, Z. (2015). "An electrospun lignin/polyacrylonitrile nonwoven composite separator with high porosity and thermal stability for lithium-ion batteries," *RSC Adv*. 5(122), 101115-101120. DOI: 10.1039/C5RA19371K.

Zimniewska, M. (2012). "Functionalization of natural fibres textiles by improvement of nanoparticles fixation on their surface," *JFBI* 5(3), 321-339. DOI: 10.3993/jfbi09201210.

Zimniewska, M., Kozłowski, R., and Batog, J. (2008). "Nanolignin modified linen fabric as a multifunctional product," *Molecular Crystals and Liquid Crystals* 484 (1), 43/[409]-50/[416]. DOI: 10.1080/15421400801903395.

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