

Molecular Structure of Sodium Lignosulfonate from Different Sources and their Properties as Dispersant of TiO₂ Slurry

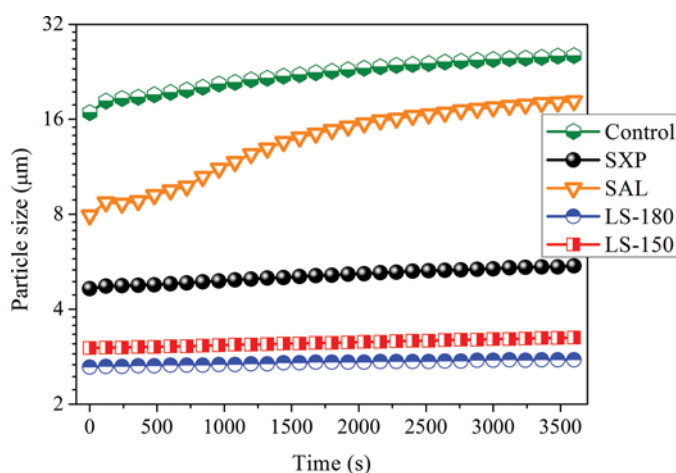
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GRAPHICAL ABSTRACT



The molecular structure and properties of four sodium lignosulfonates (LSs) derived from pulping or bioethanol production were evaluated and compared. SXP and SAL were produced by sulfite pulping and sulfonation reaction of lignin from alkali pulping of poplar, respectively. LS-180 and LS-150 were from sulfite pretreatment to overcome recalcitrance of lignocelluloses (SPORL) pretreatment of lodgepole pine for bioethanol production. The molecular weights of the two LSs from SPORL were much smaller than those from pulping. However, LS-180 and LS-150 had higher sulfur content, especially LS-180. UV–Vis absorption spectra of LS-180 and SXP showed redshift, indicating increased amount of guaiacyl units or conjugated structures. The infrared spectra showed that LS-180 and SXP had more conjugated structures. LS-150 had the highest methoxyl group content, while SAL and LS-180 had lowest. The ¹H-NMR was used to further investigate the difference of molecular linkages within each LS. LS-150 had more β-O-4' structures than the others, while SXP had more β-β' structures. When used as dispersant for TiO₂ slurry, LS-180, LS-150, and SXP all had excellent dispersibility, but not SAL, suggesting LS from bioethanol production is an excellent source of LS and lignin sulfonation of alkali lignin is not sufficient for dispersion applications.

Keywords Dispersion properties, lignin co-product, molecular structure, sodium lignosulfonate, SPORL pretreatment

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INTRODUCTION

Lignin is a biopolymer naturally present on earth in large quantities.^[1] Approximately five millions of metric tons of technical lignin is produced annually by the pulp and paper industry.^[2] The structure of lignin is very

complex and amorphous, which is based on the phenyl propane derivate. They are linked by a multitude of inter-unit bonds including β -O-4', β - β' , β -5', and α -O-4'.^[3] Technical lignin mostly has not been used for high value products other than burnt for combined heating and power.^[4] With appropriate modification, technical lignin can be widely used in rubber reinforcing agent,^[5] oilfield chemicals,^[6] building materials additives,^[7] dyes,^[8] and pesticides dispersant.^[9]

Although the basic structure of lignin is almost the same, including *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) propane,^[3] the composition and structure of technical lignin is highly dependent on the sources of the plant and the industrial processes.^[10]

Pulping, including alkali and sulfite processes, produces two kinds of technical lignin, alkali lignin and lignosulfonate (LS), respectively. Alkali lignin accounted for almost 85% of all technical lignin produced. However, alkali lignin has low molecular weight and is water insoluble.^[11] Through modifications, such as sulfonation, sulfomethylation, alkali lignin could be converted to LS. The introduction of sulfonic acid groups can enhance the water solubility and improves the utility of alkali lignin.

Biorefining of lignocelluloses for producing biofuel and bioproducts can reduce our reliance on fossil fuel, mitigate climate change, and help sustainable development.^[12,13] The three major components of lignocelluloses are cellulose, hemicellulose, and lignin. Developing value-added lignin-coproducts holds the key to economical biofuel production. Among all the biorefining processes, sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL) is the most robust and efficient process for bioconversion of woody biomass, especially for softwoods.^[14–17] SPORL produced LS with direct market potential. Therefore, the molecular structure and dispersion properties of LS from SPORL need to be evaluated and compared with those from sulfite pulping processes. This study evaluated two hardwood LSs from sulfite and alkali (with subsequent sulfonation) pulping of a polar wood, and two softwood (lodgepole pine) LSs produced by SPORL.

MATERIALS AND METHODS

Materials

A commercial sodium LS (SXP) was a by-product from sulfite pulping of poplar wood from Shixian Papermaking Co. Ltd. (Jilin, China). It consists of approximately 70% LS, 11% reductive substances (mainly sugar acids), low molecular weight organic compounds, inorganic salts, and other impurities. SXP used for molecular structure characterization was ion-exchanged to remove the impurities. Another commercial sulfonated alkali lignin (SAL),

from alkali pulping of poplar wood followed by a sulfonation, was supplied by Tongdao Papermaking Co. Ltd. (Hunan, China).

Another two LSs were from pretreatment of beetle-killed lodgepole pine wood chips using SPORL at 180°C and 150°C for 25 and 135 minutes, respectively, as described previously.^[18] After the pretreatment, the spent liquor was first filtered using Whatman filter paper to remove water insolubles. LS was then separated and purified by ultrafiltration (142-mm Millipore Hazardous Waste Filtration System, Millipore, Ireland) using ultrafiltration membranes (Ultracel® 1 KDa Ultrafiltration Discs, Millipore Corporation, Billerica, MA) with cutoff molecular weight of 1000 Da, which allowed the removal of the impurities, such as glucose, mannose, furfural, hydroxymethylfurfural (HMF), and acetic acid. The conductivity of the filtrate was monitored using a YSI Conductance Meter (Model 35, YSI Inc., Yellow Springs, OH, USA). The glucose content of the purified LS and the effluent was monitored using a commercial glucose analyzer (YSI 2700S, YSI Inc., Yellow Springs, OH, USA). The ultrafiltration was terminated when the conductance and the glucose content of the effluent was below 1.0 mS/cm and 0.2 g/L, respectively.

High purity sodium LS (D748) from sulfite pulping of softwood was donated by LignoTech USA (Rothschild, WI). The data about D748 were from our previous publications.^[18,19]

TiO₂ powder was purchased from Kermel Chemistry Co. Ltd. (Tianjin, China) with purity of 99%. An EyeTech Laser particle size analyzer (Ankersmid Co. Ltd., Holland) was used to analysis TiO₂ particle size in aqueous suspensions. The average particle diameter of TiO₂ was 5.43 μ m. All other chemicals including sulfuric acid, sodium bisulfite were ACS reagent grade and purchased from Sigma-Aldrich (St. Louis, MO).

Gel Permeation Chromatography (GPC)

Aqueous GPC was conducted using Ultrahydrogel™ 120 and Ultrahydrogel™ 250 columns and measured with a Waters UV detector 2487 at 280 nm (Waters Co., USA). Polystyrene sulfonates with molecular weights ranging from 500 to 10,000 g/mol were used for calibration. A 0.10 M NaNO₃ solution was used as eluent at 0.50 mL/min. All samples used for GPC analysis were filtered by a 0.22 μ m membrane.

Elemental Analysis

The elemental analysis was determined by the vario EL III Element Analyzer (Elementar Analysensysteme GmbH, Hanau, Germany).

Spectroscopy Analyses

The IR spectra of LSs were recorded by a Nexus spectrometer (Thermo Nicolet Corp., USA) with a range from

4000 to 400 cm^{-1} . The ^1H -NMR spectra of 30 mg LSs were obtained on a Bruker DRX-400 spectrometer (Bruker Corp., Germany).

Turbiscan Lab Expert Stability Analysis

TiO_2 aqueous suspension of 100 g was prepared using 3 g of TiO_2 powder suspended in 100 mL deionized water. LS of 0.015 g was slowly mixed with the TiO_2 suspension and stirred at 300 rpm for 15 minutes before measurement. A pulsed near infrared light was used to characterize the dispersion properties of LSs (Turbiscan Lab Expert, Formulaction, France). Light transmitted and back-scattered were recorded along the tube height (~ 40 mm) of aqueous TiO_2 suspension (20 mL) as functions of time (1 hour), which allows suspension stability kinetics to be measured.

Through using the TLAB EXPERT software, the variations of TiO_2 particle diameter in the opacity zone can be calculated. The delta backscattering variations as functions of time and the global stability index of the whole slurry can be calculated by the EASYSOFT software, which can be used to characterize the global stability.^[20]

RESULTS AND DISCUSSION

Molecular Weight Distribution and Elemental Analysis

The weight average (M_w), number average (M_n), and polydispersity (M_w/M_n) of the four LSs were shown in Table 1. SXP, purified from sulfite pulping process, had the largest molecular weight with M_w approximately 7800 Da. It is well known that alkaline pulping process highly fragments lignin. Hence, the M_w of SAL was only 2500 Da, three times lower than that of SXP. The molecular weight of ligosulfonates from SPORL, LS-180, and LS-150 was much smaller than those from pulping and papermaking process, especially for the higher temperature SPORL. The M_w of LS-180 was only 840 Da. This is due to the facts that SPORL only produces partial delignification through lignin sulfonation and the low molecular weight lignin is always first solubilized before dissolving large molecular weight lignin. D748, from sulfite pulping of softwood, was supplied by LignoTech USA, the M_w of which was 14,000 Da, almost 14-fold of LSs from SPORL. SXP, SAL, and LS-150 had a normal curve with a small

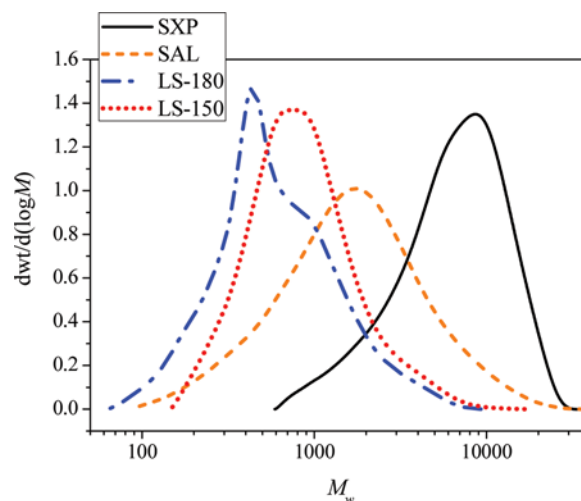


FIG. 1. Molecular weight distribution of LSs.

fraction of low molecular weight oligomers as shown in Figure 1. Compared with SXP and LS-150, the curve of SAL was much broader to result in a greater polydispersity. The curve of LS-180 looked like a bimodal curve, which showed that there were two LS fractions with different amounts and different molecular weights.

Elemental analysis indicated that SAL and LS-150 had higher carbon content than other LSs (Table 1). For instance, the carbon content of LS-150 was 39.14% compared with 23.53% for SXP. This might be due to the dehydration of LS-150 in the industrial production process.^[21] Sulfur content is a very important parameter. It not only affects LS water solubility but also physicochemical properties. Our earlier studies^[22,23] demonstrated that LS with higher sulfur content was a better dispersant for cement and coal-water slurry. LSs from SPORL had higher sulfur content (Table 1). The sulfur content of LS-180 and LS-150 was 11.33% and 6.67%, respectively. The sulfur content of SXP and D748 was 4.96% and 6.01%, respectively. D748 had larger molecular weight and sulfur content than SXP, which might be due to the higher purity of D748. SAL, modified by the sulfonation, had the lowest sulfur content, only 3.87%, perhaps due to the low reactivity of alkali lignin.

TABLE 1
Molecular weight distribution and elemental analysis of LSs

	M_n (Da)	M_w (Da)	M_w/M_n	N (%)	C (%)	H (%)	S (%)
SXP	4600	7800	1.69	0.20 ± 0.013	23.53 ± 0.894	4.22 ± 0.028	4.96 ± 0.009
SAL	990	2500	2.54	0.22 ± 0.016	36.12 ± 2.782	5.19 ± 0.181	3.87 ± 0.121
LS-180	440	840	1.90	<0.14	24.99 ± 0.050	3.44 ± 0.003	11.33 ± 0.320
LS-150	670	1110	1.66	0.26 ± 0.026	39.14 ± 0.107	4.91 ± 0.013	6.67 ± 0.114

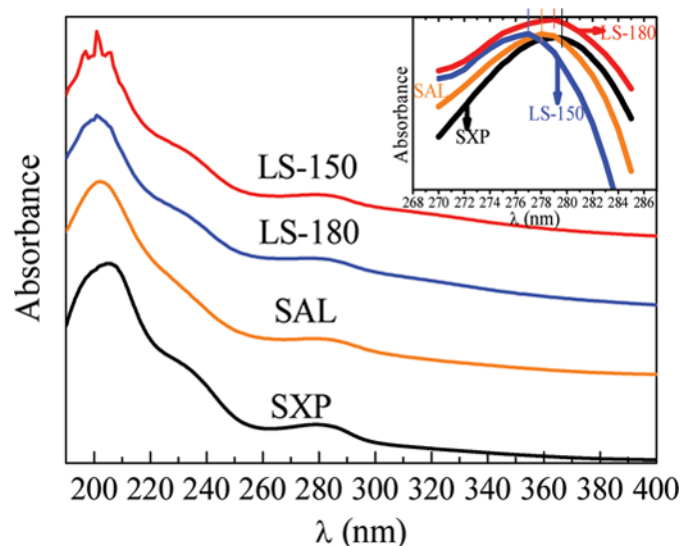


FIG. 2. UV-Vis spectra of LSs.

UV-Vis Spectra

Lignin is an irregular aromatic biopolymer composed by phenylpropane units of H, G, and S. These monomeric units are linked in lignin macromolecule by various ether and C–C bonds.^[24] The structures of technical lignins are even more heterogeneous than those of native lignin. Degradation of lignin during pulping or pretreatment results in a notable decrease in the amounts of original lignin moieties, particularly β -O-4' units, and the formation of a large variety of new structures.^[25]

The aromatic ring structure and chromophoric groups in LS could absorb ultraviolet light strongly, therefore forming characteristic absorption peaks at 210 and 280 nm.^[8] The UV-Vis spectra of LS of 60 mg/L were recorded (Figure 2). Each LS sample had two characteristic absorption peaks at 210 and 280 nm. When there are more G units or more conjugated structures in lignin, redshift will occur at the peak around 280 nm. Generally, the

maximum absorption intensity of hardwood lignin is near 280 nm, while that of softwood lignin is around 275–277 nm.^[26] However, after the industrial process, such as pulping, this no longer holds true. The maximum absorption intensity of SXP and LS-180 was near 280 nm (Insert in Figure 2), indicating there were more G units or more conjugated structures.

IR Analysis

In order to study the difference in functional groups content, the semi-quantitative method of IR was used to analyze the molecular structure of four LSs.^[1,27] The areas of bands at 1420 and 1512 cm^{-1} , attributing to aromatic ring stretching vibrations,^[28] were calculated. The ratios of A_{1420}/A_{1512} of four LSs were all around 1.00. Hence, 1512 cm^{-1} peak could be used as the reference peak. The assignments and the ratios of characteristic peaks and 1512 cm^{-1} were shown in Table 2. All LSs showed a broad band around 3436 cm^{-1} , due to the OH stretching in phenolic and aliphatic structures, and the bands at 2941 and 2846 cm^{-1} , predominantly attributed to C–H vibration in methyl and methylene groups of side chains and aromatic methoxyl groups in LSs.^[29] Compared with the other LSs, LS-180 showed a weak band at 3436 cm^{-1} , while SAL showed weak bands at 2941 and 2846 cm^{-1} . In the carbonyl/carboxyl region, only LS-180 had a very weak band around 1720 cm^{-1} , arising from unconjugated ketone, carbonyl, and ester groups (not shown in Table 2), while all LSs had a shoulder around 1645 cm^{-1} , originated from C=O vibration in conjugated *p*-subst, aryl ketones. The ratio of A_{1645}/A_{1512} in LS-180 and SXP was greater, meaning that there were more conjugated structures. This might be the reason of the redshift of their UV-Vis spectra (Figure 3). The spectral region below 1400 is very difficult to analyze, because most bands are complex with various vibrations contributions.^[29] Nevertheless, there are specific lignin units in this region. All LSs showed the C–H vibrations in G units plus C–O

TABLE 2
IR bands assignment of LSs and the ratios of characteristic peak and 1512 cm^{-1}

Wavenumber	Assignment	SXP	SAL	LS-180	LS-150
A_{3436}/A_{1512}	OH stretching in phenolic and aliphatic structures	2.300	2.269	1.794	2.021
A_{2941}/A_{1512}	C–H vibration in $-\text{CH}_3$ and $-\text{CH}_2$	1.562	0.708	1.045	1.135
A_{2846}/A_{1512}	C–H vibration in $\text{CH}_3\text{O}-$	2.368	1.567	1.723	2.807
A_{1645}/A_{1512}	C=O vibration in conjugated <i>p</i> -subst, aryl ketones	1.978	1.792	2.268	1.588
A_{1462}/A_{1512}	C–H deformations band of asymmetric methyl and methylene	1.397	1.618	1.036	1.021
A_{1420}/A_{1512}	Aromatic skeleton vibrations combined with C–H in plane deformations	0.974	0.975	1.000	1.045
A_{1142}/A_{1512}	G ring plus C–O stretching	1.741	1.731	0.503	1.544
A_{1086}/A_{1512}	S ring and C–O stretching	2.047	1.794	1.864	2.544
A_{1046}/A_{1512}	S=O stretching	2.159	1.672	4.130	2.875

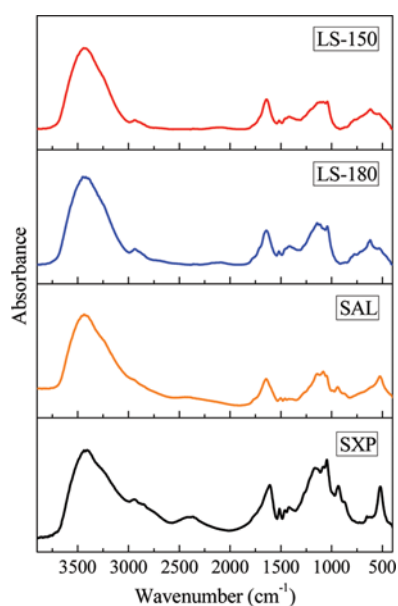


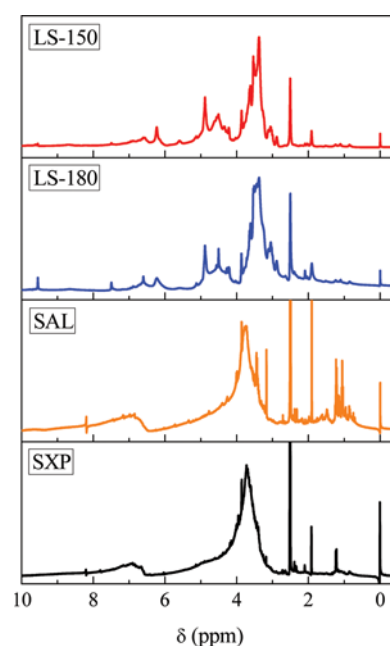
FIG. 3. IR spectra of LSs.

stretching (1142 cm^{-1}) and S units plus C–O stretching (1086 cm^{-1})^[30] but the intensities of the bands varied substantially among samples. The band around 1046 cm^{-1} was due to S=O stretching.^[31] LS-180 had the highest intensity at 1046 cm^{-1} , while that of SAL was lowest. This was in agreement with the result from elemental analysis.

¹H-NMR Analysis

For the in-depth elucidation of structural features, the four LSs were also subjected to ¹H-NMR analysis (Figure 4). As observed, the structure of LSs from SPORL was very different from those from pulping processes, especially for the signals between 5.00 and 4.00 ppm. The ¹H-NMR spectra were obtained from 30 mg LSs in 0.5 mL DMSO-*d*₆. Therefore, the signal intensity of DMSO-*d*₆ ($2.56\sim 2.44\text{ ppm}$) was used as reference. The intensities of specific signals were calculated in Table 3. The resonance between 7.20 and 6.80 ppm was attributed to aromatic protons in G units, and that between 6.80 and 6.20 ppm was attributed to S units, indicating the presence of relative contents of S and G units in the lignin.^[32] The content of G in LS-180 was lowest, while the content of S in LS-150 was highest. It was suggested that the molecular structure of LS was highly affected by the pretreatment temperature. In terms of poplar LS, the G and S content in SXP and SAL did not vary too much.

The signal at $6.20\sim 5.75\text{ ppm}$ was assigned to the H_α in $\beta\text{-O-}4'$ and $\beta\text{-}1'$ structures. The signal between $5.75\sim 5.45\text{ ppm}$ was attributed to H_α , H_β in $\beta\text{-}5'$ substructures. As shown in Table 3, LS-150 had more $\beta\text{-}5'$ linkages. The signals at $5.00\sim 4.75$ and $4.75\sim 4.35\text{ ppm}$ were assigned

FIG. 4. ¹H-NMR spectra of LSs.

to the H_α and H_β in $\beta\text{-O-}4'$ units,^[33] respectively. Comparing with SAL, SXP had a little more $\beta\text{-O-}4'$ structures. LS-180 had less $\beta\text{-O-}4'$ structures than LS-150, suggesting higher temperature made more $\beta\text{-O-}4'$ linkages cleaved. Although the cleavage of $\alpha\text{-aryl}$ ether bonds was mainly responsible for the lignin fragmentation, acid-induced hydrolysis of arylglycerol- $\beta\text{-arylether}$ substructures also exists during sulfite pulping,^[34,35] so did SPORL pretreatment. The signals at $4.35\sim 4.00$, and $3.20\sim 2.90\text{ ppm}$ were attributed to H_α in $\beta\text{-}\beta'$ structures and H in xylan residues, and H_β in $\beta\text{-}\beta'$ structures, respectively, which varied significantly between different LSs. During acid sulfite pulping, other than sulfonation, lignin condensation also occurred competing with sulfonation and counteracting degradation of lignin.^[36] The condensation reactions could result in the formation of diphenylmethane substructures involving C-1 or C-6 and C-5 of aromatic nuclei, while some substructures in lignin could also undergo internal condensation to form a cyclohexene ring, such as $\beta\text{-O-}4'$ and $\beta\text{-}\beta'$ units.^[37] SXP had the highest $\beta\text{-}\beta'$ structures. In addition, the molecular weight of SXP was also the biggest. It was suggested that there were more condensation during poplar sulfite pulping than lodgepole pine SPORL pretreatment. SPORL was similar to acid sulfite pulping. The cleavage of $\alpha\text{-aryl}$ ether and $\beta\text{-aryl}$ ether bonds and sulfonation facilitated lignin fragmentation and dissolution. The degradation and sulfonation of lignin was much more prominent in SPORL than in acid sulfite pulping.

The signals at $4.00\sim 3.50\text{ ppm}$ was originated from the protons in methoxyls. LS-150 had much higher methoxyl groups, while SAL and LS-180 had lower methoxyl groups.

TABLE 3
Signal assignment and intensity of ^1H -NMR spectra of LSs

Signal (ppm)	Assignment	SXP	SAL	LS-180	LS-150
7.80 ~ 7.20	Aromatic protons in positions C-2 and C-6 with C=O group	1.14	1.25	0.04	0.97
7.20 ~ 6.80	H ₂ , H ₅ , H ₆ in guaiacyl (G) units	1.00	1.01	0.10	1.00
6.80 ~ 6.20	H ₂ , H ₆ in syringyl (S) units	0.91	0.89	0.83	2.19
6.20 ~ 5.75	H _α of β-O-4' and β-1' structures	0.61	0.60	0.30	0.91
5.75 ~ 5.45	H _α , H _β in β-5' substructures	0.50	0.50	0.07	0.69
5.20 ~ 5.00	H in xylan residues	0.48	0.44	0.23	0.91
5.00 ~ 4.75	H _α in β-O-4' structures	0.73	0.66	1.84	2.54
4.75 ~ 4.35	H _β in β-O-4' structures	1.38	1.30	1.52	3.95
4.35 ~ 4.00	H _γ in β-β' structures and H in xylan residues	1.85	1.59	1.15	1.83
4.00 ~ 3.50	H in methoxyls	5.66	4.28	4.36	7.19
3.20 ~ 2.90	H _β in β-β' structures	2.81	2.30	1.68	1.98
2.56 ~ 2.44	DMSO	1.00	1.00	1.00	1.00
2.30 ~ 2.00	H in aromatic acetates	0.47	0.60	0.88	0.40
2.00 ~ 1.70	H in aliphatic acetates	0.46	0.70	0.85	0.50
1.70 ~ 0.75	Aliphatic H	1.42	2.58	1.75	0.98

Dispersion Properties of LS from Different Sources

TiO₂ is widely used in paints, plastics, and inks.^[38,39] In general, TiO₂ particles must be dispersed in a liquid medium. However, due to the large surface area and surface properties, TiO₂ particles are easy to form agglomerates. It is therefore essential to study which kind of dispersant is more efficient for the dispersion stability of TiO₂ slurry.

In this work, we used Turbiscan Lab Expert to study the dispersion properties of four LSs from different sources. Compared with classic methods, Turbiscan Lab Expert can not only measure the long-term stability of opaque and concentrated colloidal dispersion, but also detect the instability phenomena much easier and earlier than that with naked eyes.^[40] The variations of TiO₂ particle diameter in the opacity zone were recorded as a function of standing time (Figure 5a). A linear increase of particle diameter was found in control TiO₂ suspension (from 16.8 μm at time zero to 25.4 μm at 60 minutes, or an increase of around 50%), which suggested some agglomerates formed. When adding LS as dispersant, the dispersion stability of TiO₂ suspension improved significantly. The initial particle diameter was only 4.7, 7.9, 2.6, and 3.0 μm with the addition of SXP, SAL, LS-180, and LS-150, respectively. In the same 60 minutes period, the particle size increased by 17%, 132%, 8%, and 10% (5.5, 18.3, 2.8, and 3.3 μm at 60 minutes, respectively) for SXP, SAL, LS-180, and LS-150, respectively. As for the increase, the addition of SAL was worse than that of no dispersant. However, the particle diameter was still smaller than that of no dispersant (18.3 and 25.4 μm at 60 minutes, respectively). When we used D748 as dispersant, the initial particle

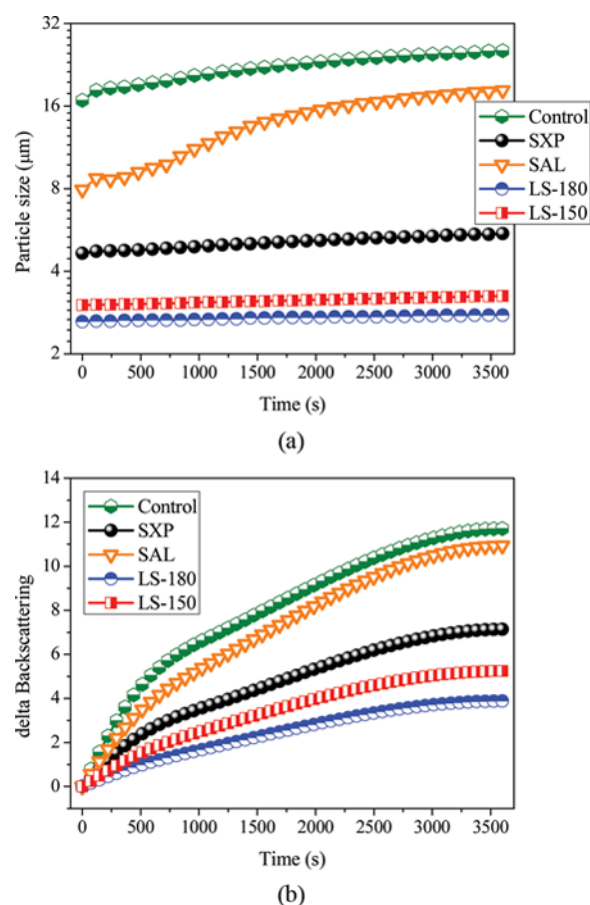


FIG. 5. Dispersion properties of LSs used as a dispersant for TiO₂ slurry. a) Particle size; b) delta Backscattering.

size was 4.5 μm ,^[19] better than LS from pulping process, however, which still could not beat LS from SPORL.

Figure 5b showed the global dispersion stability of TiO_2 suspension. The smaller the changes of the delta Backscattering was, the better the dispersion stability of suspension was. After the addition of LS, the dispersion stability of TiO_2 suspension enhanced obviously except for SAL. We also calculated the global stability index according to the EASYSOFT software. The stability index of Control, SXP, SAL, LS-180, and LS-150 was 8.05, 4.66, 7.12, 2.41, and 3.40, respectively. The smaller stability index means the much more stable suspension. Therefore, among all these four LSs, SAL was the worst dispersant for TiO_2 suspension. All the other three LSs were efficient dispersant for TiO_2 slurry, especially the LS from SPORL pretreatment. This might be due to the higher sulfur content in LS-180 and LS-150, resulting in the stronger electrostatic repulsion between TiO_2 particles.

CONCLUSIONS

This study demonstrated that LSs from bioethanol production is an excellent dispersant for TiO_2 slurry. The molecular structure and dispersion properties of four LSs were compared in this work. SXP, originated from poplar sulfite pulping process, had the largest molecular weight. LS-180 and LS-150, produced from SPORL pretreatment of lodgepole pine for bioethanol production through subsequent enzymatic saccharification and fermentation, had very small molecular weight, only around 1000 Da. The molecular weight of SAL, by-products from poplar alkali pulping followed by sulfonation, was medium. The sulfonic content of LS-180 and LS-150 was much higher than that of the two LSs from pulping process. SXP and LS-180 contained more guaiacyl units and conjugated structures, resulting in the redshift of their UV-Vis spectra. In terms of the linkages, LS-150 had more $\beta\text{-O-4'}$ structures than the others, while SXP had more $\beta\text{-}\beta'$ structures. When used as dispersant, all these LSs could enhance the dispersion stability of TiO_2 suspension. Especially LS-180, after the 60 minutes standing, the particle diameter of TiO_2 particle was only 11% of no dispersant TiO_2 suspension.

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REFERENCES

- [1] Tejado, A., Pena, C., Labidi, J., Echeverria, J., and Mondragon, I. (2007) *Bioresour. Technol.*, 98: 1655–1663.
- [2] Mai, C., Milstein, O., and Hüttermann, A. (2000) *J. Biotechnol.*, 79: 173–183.
- [3] Ralph, J., Hatfield, R.D., Piquemal, J., Yahiaoui, N., Pean, M., Lapierre, C., and Boudet, A.M. (1998) *Proc. Natl. Acad. Sci. U. S. A.*, 95: 12803–12808.
- [4] Gouveia, S., Fernández-Costas, C., Sanromán, M., and Moldes, D. (2012) *Bioresour. Technol.*, 121: 131–138.
- [5] Gregorová, A., Košíková, B., and Moravčík, R. (2006) *Polym. Degrad. Stab.*, 91: 229–233.
- [6] Li, Z. and Liu, H. (2004) *Adv. Fine Petrochem.*, 7: 6–9.
- [7] Arshanitsa, A., Ponomarenko, J., Dizhbite, T., Andersone, A., Gosselink, R.J., van der Putten, J., Lauberts, M., and Telysheva, G. (2013) *J. Anal. Appl. Pyrolysis*, 103: 78–85.
- [8] Yang, D., Li, H., Qin, Y., Zhong, R., Bai, M., and Qiu, X. (2015) *J. Dispersion Sci. Technol.*, 36: 532–539.
- [9] Pang, Y., Gao, W., Lou, H., Zhou, M., and Qiu, X. (2014) *Colloids Surf. A Physicochem. Eng. Aspects*, 441: 664–668.
- [10] Tejado, A., Pena, C., Labidi, J., Echeverria, J., and Mondragon, I. (2007) *Bioresour. Technol.*, 98: 1655–1663.
- [11] Gan, L., Zhou, M., Yang, D., and Qiu, X. (2013) *J. Dispersion Sci. Technol.*, 34: 644–650.
- [12] Zhu, J. and Pan, X. (2010) *Bioresour. Technol.*, 101: 4992–5002.
- [13] Perlack, R.D. and Stokes, B.J. (2011) *U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry*; Oak Ridge: Oakridge National Laboratory; pp. 1–194.
- [14] Zhu, J., Pan, X., Wang, G., and Gleisner, R. (2009) *Bioresour. Technol.*, 100: 2411–2418.
- [15] Zhu, W., Zhu, J., Gleisner, R., and Pan, X. (2010) *Bioresour. Technol.*, 101: 2782–2792.
- [16] Tian, S., Luo, X., Yang, X., and Zhu, J. (2010) *Bioresour. Technol.*, 101: 8678–8685.
- [17] Zhu, J., Zhu, W., OBryan, P., Dien, B.S., Tian, S., Gleisner, R., and Pan, X. (2010) *Appl. Microbiol. Biotechnol.*, 86: 1355–1365.
- [18] Zhou, H., Leu, S.-Y., Wu, X., Zhu, J., Gleisner, R., Yang, D., Qiu, X., and Horn, E. (2014) *RSC Adv.*, 4: 27030–27038.
- [19] Zhou, H., Zhu, J., Luo, X., Leu, S.-Y., Wu, X., Gleisner, R., Dien, B.S., Hector, R.E., Yang, D., and Qiu, X. (2013) *Ind. Eng. Chem. Res.*, 52: 16057–16065.
- [20] Li, P., Yang, D., Lou, H., and Qiu, X. (2008) *J. Fuel Chem. Technol.*, 36: 524–529.
- [21] Mansouri, N.-E.E. and Salvadó, J. (2006) *Ind. Crops Prod.*, 24: 8–16.
- [22] Ouyang, X., Ke, L., Qiu, X., Guo, Y., and Pang, Y. (2009) *J. Dispersion Sci. Technol.*, 30: 1–6.
- [23] Yang, D., Qiu, X., Zhou, M., and Lou, H. (2007) *Energy Convers. Manage.*, 48: 2433–2438.
- [24] Ralph, J., Lundquist, K., Brunow, G., Lu, F., Kim, H., Schatz, P.F., Marita, J.M., Hatfield, R.D., Ralph, S.A., and Christensen, J.H. (2004) *Phytochem. Rev.*, 3: 29–60.
- [25] Balakshin, M.Y., Capanema, E.A., and Chang, H.M. (2009) *Charact. Lignocellulosic Mater.*, 9: 148–170.

- [26] Nakano, J. (1989) *Chemistry of Lignin: Basic and Application*; Tokyo: Uni Shuppan.
- [27] Pandey, K. and Pitman, A. (2003) *Int. Biodeterior. Biodegrad.*, 52: 151–160.
- [28] Sun, R., Mott, L., and Bolton, J. (1998) *J. Agric. Food Chem.*, 46: 718–723.
- [29] Boeriu, C.G., Bravo, D., Gosselink, R.J.A., and Van Dam, J.E.G. (2004) *Ind. Crops Prod.*, 20: 205–218.
- [30] Lawther, J.M., Sun, R.C., and Banks, W. (1996) *Ind. Crops Prod.*, 5: 97–105.
- [31] Shao, L., Qiu, J.H., Feng, H.X., Liu, M.Z., Zhang, G.H., An, J.B., Gao, C.M., and Liu, H.L. (2009) *Synth. Met.*, 159: 1761–1766.
- [32] Toledano, A., Serrano, L., Garcia, A., Mondragon, I., and Labidi, J. (2010) *Chem. Eng. J.*, 157: 93–99.
- [33] Kubo, S. and Kadla, J.F. (2004) *Macromolecules*, 37: 6904–6911.
- [34] Glasser, W.G., Northey, R.A., and Schultz, T.P. (2000) *Lignin: Historical, Biological, and Materials Perspectives*; Washington, DC: American Chemical Society.
- [35] Marques, A., Evtuguin, D., Magina, S., Amado, F., and Prates, A. (2009) *J. Wood Chem. Technol.*, 29: 337–357.
- [36] Gellerstedt, G. and Gierer, J. (1971) *Svensk Papperstidn*, 74: 117–127.
- [37] Gellerstedt, G. (1976) *Svensk Papperstidn*, 79: 537–543.
- [38] Boisvert, J.-P., Persello, J., Castaing, J.-C., and Cabane, B. (2001) *Colloids Surf. A Physicochem. Eng. Aspects*, 178: 187–198.
- [39] Farrokhpay, S., Morris, G.E., Fornasiero, D., and Self, P. (2004) *J. Colloid Interface Sci.*, 274: 33–40.
- [40] Celia, C., Trapasso, E., Cosco, D., Paolino, D., and Fresta, M. (2009) *Colloids Surf. B Biointerfaces*, 72: 155–160.