

Accelerated Polymerization of Ammonium Lignosulfonate from Loblolly Pine

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Abstract

Lignin bioproducts derived from pulping of woody biomass find utility in multiple industrial applications. Ammonium lignosulfonates have historically displayed unique polymerization characteristics relative to other lignin materials and show promise as sustainable adhesives for the panel industry. To further understand the system's chemistry, polymerization reactions were observed through the lens of viscosity build-up using high temperature rheological measurements. It was found that highly controllable lignosulfonate properties like cooking temperature, pH, and percentage dissolved solids each significantly contribute to gelation behavior. The concept of thermal priming to shorten gelation time was also introduced and demonstrated. Finally, possible applications for this technology are postulated.

Borregaard LignoTech is the world's leading producer of commercial lignosulfonate products from woody biomass, a business that continues to grow as sustainability comes to the forefront of industry and society. Lignosulfonates exhibit a variety of valuable properties and functions that enables their implementation across a multitude of applications (Lauten et al. 2010). Some examples of current lignosulfonate applications include dispersing and binding pesticide formulations, water-reducing concrete admixtures, dispersing carbon black, performance additives in lead acid batteries, and extending resin in various adhesive systems. As demand for sustainable products rises, Borregaard has invested in expanding its production of lignosulfonates in North America through formation of a business venture with Rayonier Advanced Materials. LignoTech Florida (LTF) came online in June 2018 and brought with it an annual production capacity of 100,000 metric tons of various softwood lignosulfonate products. The products offered by LTF include a range of ammonium and sodium lignosulfonates modified to match a number of application technologies mentioned above.

Ammonium lignosulfonates (Am-LS) offered by LTF are derived from the softwood ammonium sulfite lye, which is in turn produced from acid sulfite pulping of loblolly pine. A unique property noted over the years for most Am-LS materials is their strong proclivity to undergo polymerization reactions under increasingly acidic conditions, resulting in liquid products with continually elevating viscosities and levels of insoluble matter (Felber et al. 1977, Shen and Fung

1981, Philippou et al. 1982, Bialski et al. 1986, Popova et al. 1991, Alonso et al. 2005). Figure 1 is an example that helps demonstrate ammonium lignosulfonate's polymerization reactivity. Polymerization is manifested in the graph as an increase to viscosity during storage at elevated temperatures. In a similar demonstration, Figure 2 demonstrates how the solids content of ammonium lignosulfonate influences its viscosity build-up after prolonged heating.

This unique behavior also presents an opportunity to generate products with novel hydrophobic characteristics. This change is likely induced through a mechanism of considerable molecular weight buildup toward eventual point insolubility. If a better understanding of the controllable factors contributing to the polymerization effect could be developed, then it will be possible to take control of this reactivity and render hydrophobic yet still soluble Am-LS products. This would be a significant development, as pronounced hydrophobicity is not conventionally associated with lignosulfonates. It is possible

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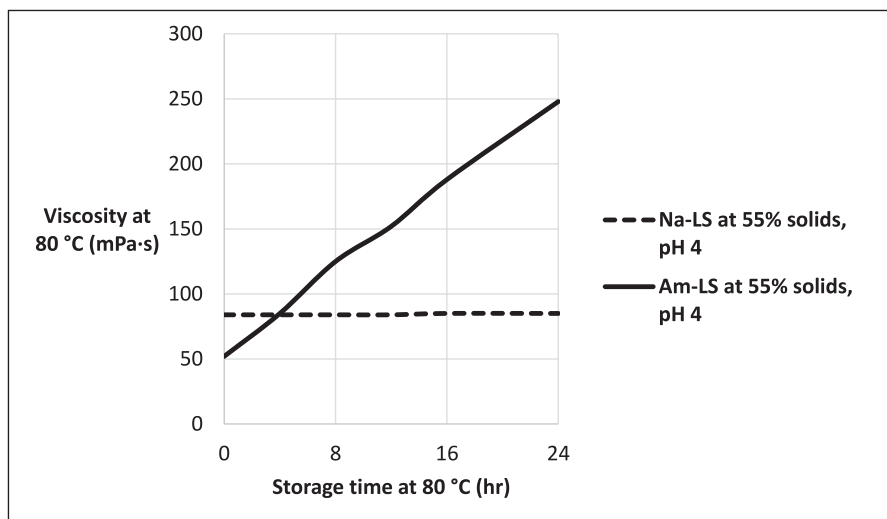


Figure 1.—High temperature increase in viscosity of ammonium lignosulfonate (Am-LS) versus sodium lignosulfonate (Na-LS).

that an Am-LS with elevated hydrophobic properties could potentially be used as water-resistant aquaculture binders or as synergistic extenders for urea-formaldehyde, phenol-formaldehyde, and methylene diphenyl diisocyanate (MDI) adhesives (Philippou et al. 1982, Janowiak and Carlson 1998, Alonso et al. 2005).

A rheological approach was adopted to study the polymerization behavior of LTF Am-LS. This method involves use of a sealed pressure vessel rheometer configuration, allowing for real-time measurement of sample viscosities over the course of customizable cooking regimes. The benefit to this approach is the ability to observe the time course of the polymerization reactions with a clear instrument response. A typical instrument response is displayed in Figure 3. The rheological change noted by this instrument is an exponential increase in viscosity; however, the time and rate at which this occurrence takes place is a function of several analyte properties (e.g., pH, weight percent [wt%] dissolved solids, temperature, etc.). The ability to modify these properties opens up a robust new technique for furthering our understanding of Am-LS polymerization chemistry.

The goal of this report is to demonstrate the current state of Borregaard LignoTech's efforts to better comprehend Am-LS's polymerization proclivity, with intent to exact control over it and allow for production of novel products capable of entering into new applications and markets. The rheological approach for analyzing the phenomenon will be extensively detailed alongside traditional analytical techniques associated with lignosulfonates. Furthermore, we will detail a statistically significant model developed to quantify and predict the factors contributing to polymerization by way of rheology. It is believed that our findings will help to innovate in the field of lignosulfonates, further contributing toward the effort to establish a globally sustainable bioeconomy based on renewable resources.

Materials and Methods

Raw material and rheology sample preparation

Am-LS lye material (~4 liters) was sampled at LTF and immediately cooled on ice for shipment to LignoTech USA (Rothschild, Wisconsin). Materials were kept refrigerated (~10°C) prior to sample preparation. The thick Am-LS lye

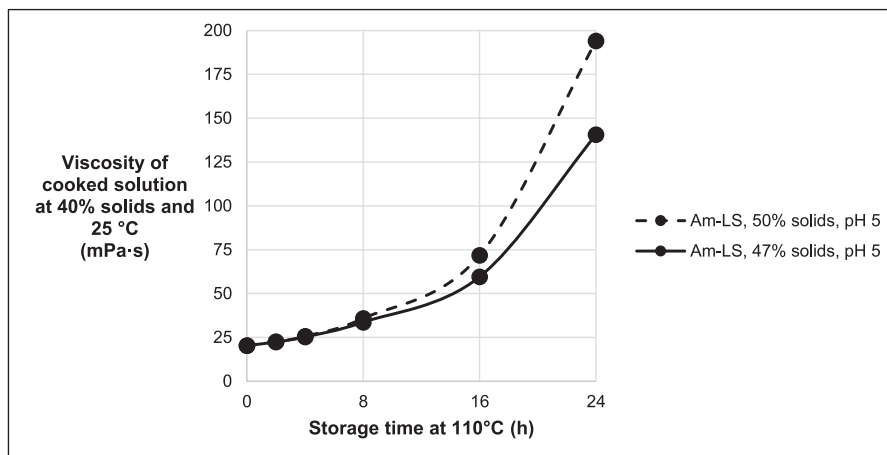


Figure 2.—Increased reactant concentration results in more ammonium lignosulfonate (Am-LS) polymerization.

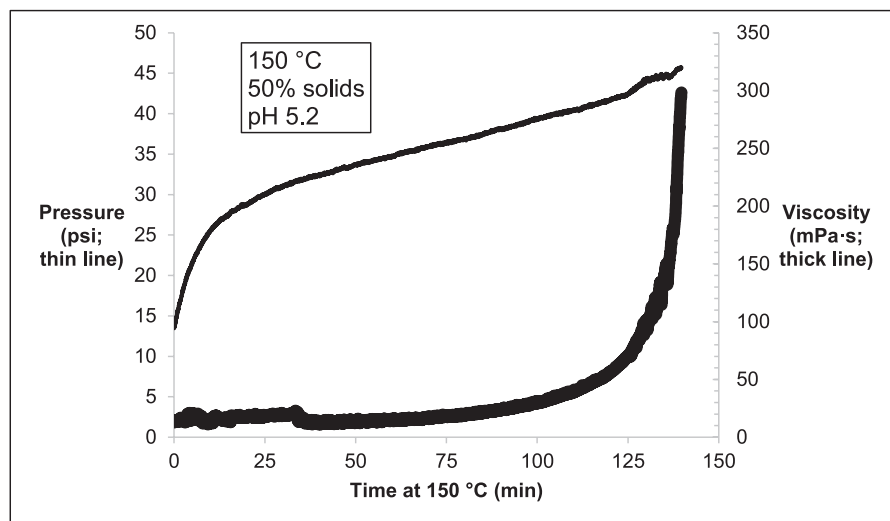


Figure 3.—Rheological observation of ammonium lignosulfonate polymerization.

had a pH of ~ 1.8 to 2.2 and a dissolved solids content of ~ 61 to 62 wt%.

To prepare samples for rheological analysis, thick liquor was heated to $\sim 50^\circ\text{C}$ and neutralized with aqua ammonia (28% NH_3 in H_2O) to a desired pH. Following neutralization, the dissolved solids content was gravimetrically measured by drying a sample in an oven at 110°C for 1 hour. Dissolved solids results were considered prior to further addition of water to dilute the material to the desired levels. For the samples that included a cross-linking agent (glyoxal [40 wt% aqueous solution], Sigma-Aldrich), glyoxal was added after neutralization but prior to additional dilution due to its water content.

Polymerization rheology

Analytical equipment.—To perform rheological analysis, an Anton Paar (Ashland, Virginia) modular compact rheometer (model 102) was equipped with a pressure cell system (CC32.2/XL/PR150/SS/A1) heated by a cylinder electrical temperature device (C-ETD 200/XL). Pressure cell components were forged of stainless steel. Preformulated lignin samples (25 mL or ~ 30 g, depending on specific gravity) were weighed directly into the pressure cell cup, which was then sealed and inserted into the heater. Viscosity measurements were acquired using concentric cylinder geometry (CC32.2/Pr/Ti-A1). Pressure in the cell was measured in tandem with viscosity through an attached meter piped into the vessel. The pressures recorded were exclusively produced by the lignosulfonate sample, primarily through generation of steam but also due to gaseous byproducts emitted over the course of heating. Anton Paar RheoCompass software (version 1.23) was used to drive the instrument.

Polymerization assay.—A standard test was developed for the rheometer to measure the amount of time taken for a given sample to begin undergoing polymerization in a manner that is both observable and reproducibly quantifiable. The test involves frequent viscosity acquisition over time at a preselected constant temperature. Samples were sheared at 100 reciprocal seconds with viscosity measurements taken every 2 seconds. All measured viscosities were

averaged over one revolution by the software. Data were recorded during the time taken for the apparatus to reach the selected temperature, but these measurements were segregated from the measurements taken once target temperature was reached. Warm-up times were entirely consistent: 20.7 ± 0.1 , 22.6 ± 0.0 , and 25.4 ± 0.1 min for 135°C , 142.5°C , and 150°C , respectively. The experiment halted measurement upon recording a viscosity ≥ 150 mPa s at the test temperature. Once this defined endpoint was reached, the rheometer automatically ceased heating the cylinder. External cooling water lines were also manually applied at this time. After the equipment was able to be safely handled, each element of the equipment was entirely disassembled and exhaustively washed with hot water, pipe cleaners, and microfiber cloths.

The polymerization assay served as a basis for conducting a designed experiment, constructed with assistance of Design Expert v.11 (Stat-Ease, Minneapolis, Minnesota). The software was capable of interpreting assay results and generated a corresponding response surface model capable of predicting gel time and gel rate of Am-LS (as defined in this work). In addition, we are provided analyses of variance (ANOVAs), graphs of one- and two-factor interactions, as well as customizable two- and three-dimensional contour plots.

Further rheological demonstrations.—Apart from the gel testing, thermal priming demonstrations were performed using the rheometer configuration previously described. A specific sample formulation was subjected to cooking times lasting for predefined fractions of its gel time (pH 3, 55% dry matter, 135°C , 0% cross-linker). At the conclusion of the defined analysis time, the rheometer was rapidly cooled to 70°C and held for ~ 1 hour to monitor viscosity stability. After observation time, the rheometer was then cooled to ambient temperature. Cooled liquid samples were next withdrawn from the cylinder for characterization. Fractional gel time cooks were configured to last 3/8, 1/2, 5/8, and 3/4 of the gel time required for the analyzed sample. Prior to the fractional cooks, the gel time of the tested material was measured using the assay described in the “Polymerization assay” section.

Additional analytical techniques

Quantities of monomeric sugars and molecular weights of progressively cooked Am-LS samples were measured using an ion chromatography system calibrated with commercial standard monosaccharides. Molecular weight analysis was performed as described in the literature (Fredheim et al. 2002, 2003). Dissolved solids content, as indicated in the “Raw material and rheology sample preparation” section, were measured using the 1-hour oven-drying method. Finally, sample pH values were monitored using a standard electrode pH meter calibrated immediately prior to reading with valid pH 4, 7, and 10 calibration standards.

Results and Discussion

Rheological observation of polymerization

Rheology was employed to quantify the polymerization behavior of Am-LS, which enabled real-time observation and quantification of the polymerization reactions in the form of a viscosity response. The rheometer setup forces an Am-LS sample to polymerize in a closed and controlled environment that can be cleaned afterward and reset for analysis of additional samples. This rheometer configuration essentially serves as a pressurized reaction vessel with the added capability of being able to “look inside” through the lens of accurate viscosity readings, beyond only recording temperature and pressure.

As Figure 3 showed, the onset of polymerization is observed on the rheometer as an increase in measured viscosity at an exponential rate. Description of the polymerization behavior observed using the rheometer is hereafter interchangeably referred to as gelling. Use of exchangeable vocabulary is founded upon the physical nature of the lignosulfonate in the measuring system after cooling, since it has physically gelled as a function of lignin polymerization. A collage of images of gelled Am-LS withdrawn from the measurement system after having cooled is compiled in Figure 4. The black lignin gel is a nonflowing and moldable semisolid. Of the gelled material after cooling, only a small (yet unknown) portion remains soluble. The remainder of the mass can be described as

flakes and globular agglomerates. Future work will seek to better describe the gelled material; however, no further analyses of its properties are included in this work.

It became crucial to identify a time point on the Am-LS exponential viscosity curve that is able to quantify the onset of polymerization, but early enough to avoid formation of a cooked material that might problematically befoul the measuring apparatus. For this reason, a standard test was programmed that halted measurement of viscosity at the analysis temperature once recording a viscosity reading ≥ 150 mPa s. By defining a cutoff point, it became possible to define two time-based responses. The simplest response involves the time taken for a sample to reach said cutoff point (150 mPa s), defined as the “gel time.” All materials withdrawn from the cylinder at this point appear similar to what is shown in Figure 4. A second response intended to quantify the rate of gelation was also defined. Specifically, the “gel rate” was defined as the time taken for a sample to reach 150 mPa s subtracted from the time taken to reach 100 mPa s. It is thought that this gap in time could provide insight into the rate at which polymerization proceeds.

It is important to note that the defined points on the viscosity curve were not adjusted according to varying analysis temperature. In reality, the gel time endpoint of a sample at 150°C would translate to a higher viscosity than a sample that reaches the same endpoint at a lower temperature. However, this was deemed negligible on account of the minor difference in measured viscosity once temperatures rose above $\sim 120^\circ\text{C}$. For instance, a sample at 52 percent dissolved solids saw its viscosity decrease from 10.5 to 9.8 mPa s, while the cylinder temperature ramped from 135°C to 150°C. This minor difference (0.7 mPa s) suggests that the difference between 150 mPa s as measured at 135°C and 150°C is likely within the instrument’s range of error; thus, it is not required to be corrected for.

Designed experiment and the predictive models rendered

After gaining an understanding of how polymerization translates to responses from the rheometer, the next task was to develop and perform a designed experiment capable of

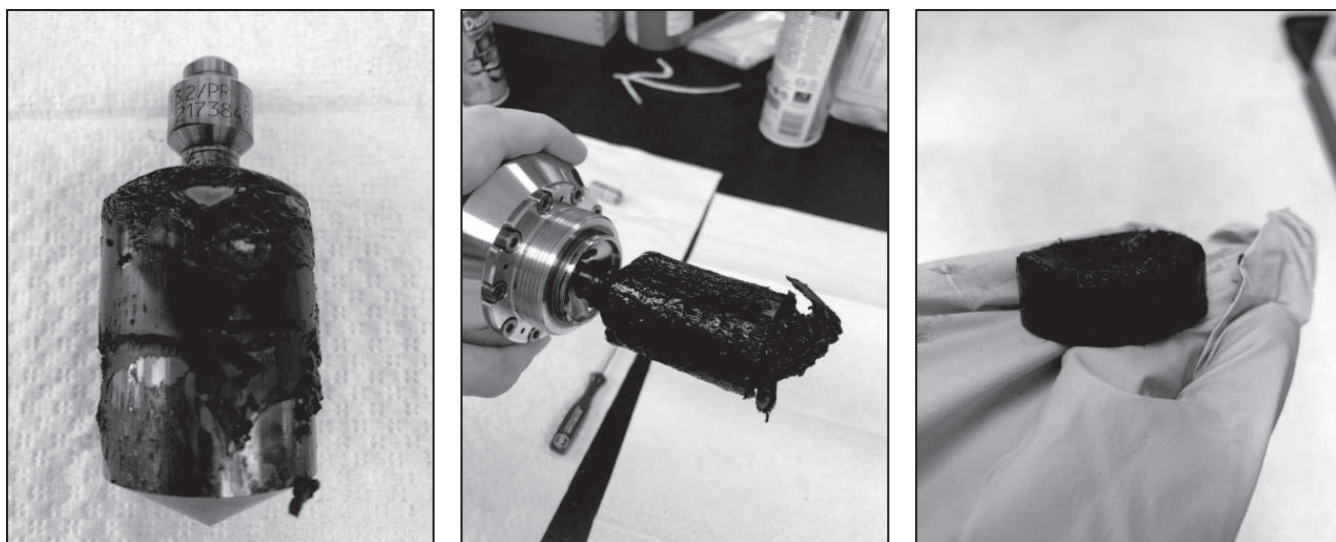


Figure 4.—Images of gelled ammonium lignosulfonates.

quantifying the influence of key parameters upon Am-LS gelation. The factors included were pH, percent dry matter, temperature, and addition of glyoxal (cross-linking agent). The assay responses were the previously discussed gel time (defined as time to 150 mPa s in h) and gel rate (defined as [time to 150 mPa s – time to 100 mPa s] in h). Table 1 details the experimental layout as well as the parameters of the factors studied in the designed experiment. Four identical center point samples were also analyzed to estimate for response surface curvature.

The effect of glyoxal addition was integrated into the design in an effort to identify the contribution of potential cross-linking agents. Glyoxal itself is a di-aldehyde that can facilitate acid-catalyzed cross-linking through a mechanism similar to formaldehyde (Bialski et al. 1986). Glyoxal was used as a cross-linker in place of formaldehyde, taking into consideration laboratory handling safety with respect to our rheometer configuration. In the event that Am-LS is to be implemented as a gelling component in formaldehyde-free systems, then the results from glyoxal addition will be demonstrative of implementation of cross-linking agents not subject to stringent regulation. Some examples of these types of cross-linkers include glutaraldehyde, succinaldehyde, and 2,5-diformylfuran.

After completing the schedule of rheology analyses across the 20 samples designated by the experiment, the analytical software was able to generate statistically significant models for predicting the two analyzed responses. Prior to presenting any results, it is first important to note that no significant response curvature was found for either response (data not shown). In addition, the software advised that certain mathematical transformations to the data would improve the model accuracy for both responses. Based on these suggestions, gel time responses underwent an inverse data transformation, while gel rate responses were treated with a log₁₀ data transformation. Highlights from the software-provided ANOVAs for both responses are shown in Table 2. Both models computed by the software were significant; however, the amount of significant two-factor interactions differs between both responses.

Understanding the gel time response

Table 2 shows that all four primary factors significantly contribute to gel time. Temperature was revealed to be involved in significant two-factor interactions with every other factor: higher temperature and lower pH decreases gel time, higher temperature and higher dry matter decreases gel time, and higher temperatures plus the addition of cross-linker decreases gel time. These relationships indicate that the most influential factor promoting polymerization of Am-LS is the temperature at which it is held, since it significantly interacts with every other controllable parameter of a given Am-LS material. For instance, gel time

Table 1.—Randomized two-level factorial experiment for evaluating ammonium lignosulfonate polymerization.^a

Factor label	Name	Minimum	Maximum
A	Temperature (°C)	135.0	150.0
B	pH	3.0	6.0
C	% dry matter	52.0	58.0
D	% glyoxal (wt% on dry matter)	0.0	3.9

^a Runs included 16 design points and four center points.

Table 2.—Analysis of variance for gel time and gel rate.

Source	Response <i>P</i>	
	Gel time	Gel rate
Model	<0.0001	0.0003
A: Temperature	<0.0001	<0.0001
B: pH	<0.0001	0.0004
C: % solids	<0.0001	0.9401
D: % glyoxal	0.0002	0.0002
A–B	0.0004	0.1067
A–C	0.0034	0.2737
A–D	0.0221	0.0375
B–C	0.2433	0.4218
B–D	0.0075	0.3393
C–D	0.1521	0.2851

decreases by ~5.5 hours when moving from 135°C to 150°C at 58 percent dry matter, pH 6, and no added cross-linking agent. In comparison, gel time only decreases by ~4 hours when changing glyoxal addition from 0 up to 3.9 percent at 135°C, 58 percent dry matter, and pH 6.

A significant two-factor interaction was also identified between pH and glyoxal dosage. This was expected, since cross-linking reactions involving glyoxal require protonation of the carbonyl oxygen. After protonation, the partially positive carbonyl carbon can then undergo electrophilic aromatic substitution with a nearby free aromatic carbon. Given that the pKa of protonated aldehydes is ~–8, it is logical that lower pH correlates with greater response influence by aldehyde-bearing cross-linkers. It is also worth noting that greater amounts of hydronium ions are auto-ionized in the aqueous system at increasing temperatures, which provides an explanation for the significance of the temperature-glyoxal interaction (A to D, *P* = 0.0221).

The results obtained were not surprising, but rather demonstrative of the significance of each of the tested variables around controlling the time required for Am-LS to undergo gelation-inducing polymerization. This information should prove valuable for: (1) future product development, (2) future technologies for creating specialty products, and (3) the necessary process parameters for avoiding Am-LS gelation.

Understanding the gel rate response

The gel rate response was defined with intent to describe the rapidity with which polymerization takes place as it begins. Gel rate's crude definition (time to 150 mPa s minus time to 100 mPa s in h) likely contributed to the model containing only a single significant two-factor interaction. In addition, a strong level of deviation was recorded for the four identical center point samples (average center point gel rate measured in quadruplicate: 0.12 ± 0.05 h). Nevertheless, the model predicting the defined gel rate is considered to be statistically significant (*P* = 0.0003) but it is driven by fewer factors than the model for gel time.

The primary takeaways regarding gel rate found in Table 2 include the revelation that the only critical factors are temperature, pH, and addition of glyoxal. Percentage dry matter was shown to have virtually no contribution to gel rate (*P* = 0.9401). Only a single two-factor interaction was found to be significant: the interaction between temperature and glyoxal addition. This information shows that the rate at which gelling proceeds is controlled by higher temperatures,

lower pH levels, and levels of cross-linking agent addition (should they be added).

Gel rates ranged from 0.02 hour (1.2 min) to 0.73 hour (43.8 min). From a practical perspective, the extended gelation rates and the samples they were exhibited by could prove useful in instances where gelation is welcome, but a level of control on its speed is important. For example, enhanced oil recovery involving gel-prone Am-LS requires extended gel rates to allow for an Am-LS liquid product to be delivered to the destination where it is intended to fully gel (Felber et al. 1977; Lawrence and Felber 1981a, 1981b). This sort of requirement means use of an Am-LS that has been sequentially treated to lower gel time (a thermal priming step) and then modified (cooled and/or neutralized) to ensure the gel rate is slow enough to prevent the product from setting in unintended locations.

Thermal priming demonstration and investigation

After successfully constructing a predictive model for describing the gelation behavior of Am-LS, it next became necessary to further investigate the concept of priming Am-LS to create a stable material with a shortened gel time. This approach would be necessary for delivering Am-LS materials into applications that are not capable of inducing gelation from a standard Am-LS product by their own process dynamics. Furthermore, a priming step could potentially be implemented into an industrial process.

The rheometer was again used to demonstrate the concept of thermal priming. This demonstration involved thermally treating Am-LS samples from a master batch for fractions of the studied sample's gel time. After the predetermined time had passed, samples were cooled to monitor for viscosity stability. In addition, cooked liquid samples were analyzed for molecular weight, sugar content, and pH. The Am-LS makeup chosen for this analysis was customized to be as follows: pH 3, 55 percent dissolved solids, no added cross-linker, cooked at 135°C. This Am-LS formulation was chosen to be approximately "medium" in terms of reactivity toward polymerization, based off the predicted gel times and rates defined obtained from the response surface models. Importantly, the rheometer was programmed for these experiments to have a temperature ramp-up rate that was identical in time to what was manually recorded for a 2-liter Parr reactor vessel loaded with the same Am-LS: 20°C to 135°C in 1.43 hours, 80.4°C/h. The intent behind programming the rheometer to more accurately simulate a larger scale reactor was to move toward scaled-up production of thermally primed prototypes.

It was found that the gel time for the formulated Am-LS was 4.95 hours, a timespan that includes 1.43 hours of abated ramp-up. From this information, samples were cooked for fractions of this time: 3/8, 1/2, 5/8, and 3/4 of the gel time. These fractional times translate to 1.86, 2.47, 3.09, and 3.71 hours, respectively. After cooking, the samples were first analyzed for viscosity stability. This evaluation was intended to gauge whether simply cooling Am-LS after thermal priming was capable of stifling further polymerization of the material. It would also be possible to limit further reactions by means of dilution or neutralization. However, the rheometer is not configured in a manner that makes such demonstrations possible. Spray drying

thermally primed Am-LS into powder could also serve as a means for halting further reactivity.

Figure 5 displays the rheology of the materials cooked for various fractions of their gel time. Inclusion of the temperature data on the secondary vertical axis is intended to explain that the sudden elevation in viscosity observed at specific times was solely induced by cooling the instrument, as opposed to a sudden onset of polymerization. The key takeaway from this demonstration is twofold: first, the viscosity of thermally primed samples at 70°C does increase in line with extended cooking times, as expected. The second and more critical conclusion is that despite the elevations in viscosity, these viscosities remain relatively constant over an hour after thermal priming. Average viscosity over the holding period is also listed in Table 3. Specifically, the viscosity of the solutions increased from 70 mPa s at 70°C for the uncooked material up to 2270 mPa s at 70°C for the material cooked for 3.7 hours. Results suggest that heating a material short of its gelation period can indeed produce a material with a newly shortened gel time as indicated by the drastic build-ups in viscosity that are beginning to be observed as cooking time extends. Furthermore, polymerization reactions can be stifled during storage and transit assuming the material was not too severely cooked and appropriate actions are taken to halt further reaction (e.g., dilution, cooling, neutralization, spray drying). Therefore, delivering products with a shortened gel time is indeed a feasible concept that warrants study at larger scales of production. It will also be important to take samples that have been primed and prove that their gelation can be reactivated in short time through additional heating.

After demonstrating viscosity stability, the samples were subjected to further characterization in an effort to better understand the effects of thermal priming. Some conventional methods of lignosulfonate characterization were applied, including measuring pH, lignosulfonate molecular weight, and monomeric sugar content. First, it was found that the pH of the sample progressively dropped as cooking time was extended, with the most significant drop occurring between the uncooked sample and the sample cooked for 1.9 hours (0.6 pH units). pH decline appeared to level out at pH 1.9 once the samples reached ~3 hours of cooking. These results suggest that acidic compounds are being generated during the cook, and we conjecture that this effect is derived from degradation of the monosaccharides present. To confirm, the monosaccharide contents in each sample were also considered. Because this is a softwood lignosulfonate, the prevailing carbohydrates in the material are the hexoses glucose and mannose derived from glucomannan hemicelluloses. Xylose was next in abundance, followed by minor (<1.0 wt% on dry matter) quantities of rhamnose, galactose, and arabinose. Quantities of all of these sugars were also found to decline as cooking time progresses, with the most significant decrease taking place between the uncooked sample and the sample cooked for 1.9 hours. This trend matches up with what was observed for pH decline, possibly indicating that the sugars rapidly react to form a variety of pH-lowering byproducts. The most reactive sugar was xylose, which experienced a relative decrease of ~72 percent over the first 1.9 hours of cooking. Furthermore, xylose content was decreased by ~94 percent over the course of the cooks. All other sugars only saw their abundances reduced by ~65 to 75 percent in the sample

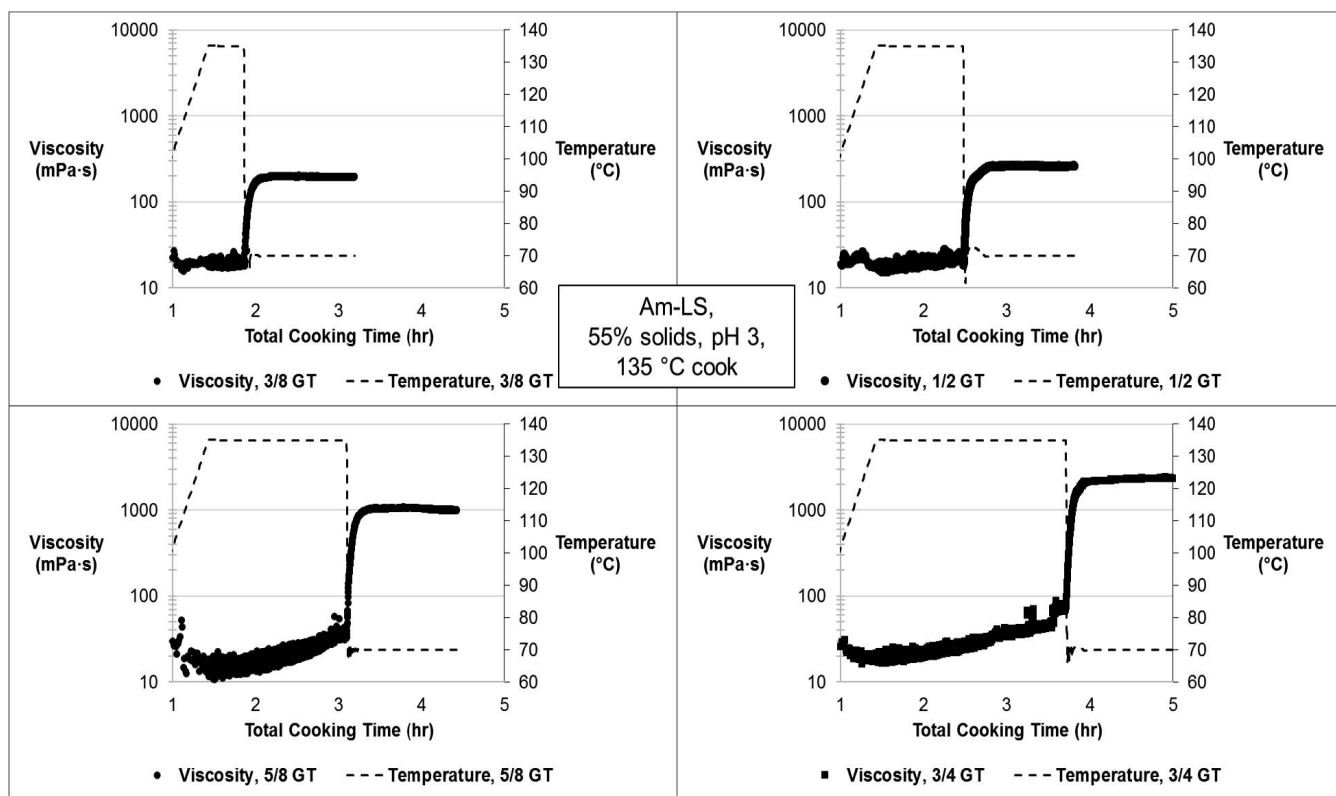


Figure 5.—Demonstration of viscosity increase and stability after thermal priming. Am-LS = ammonium lignosulfonate.

cooked the longest time. These changes suggest that the generation of furfural from dehydration of xylose is likely a major reaction taking place, presenting a chemical species into the system that may be reacting with lignin as a hydrophobic cross-linker. Future work should seek to characterize some of these sugar-derived byproducts, including the presence of sugar-derived furans.

It is important to note that while the sugar contents are greatly diminished at the conclusion of the longest cook conducted, they are not completely removed. Instead, it could be that at a certain point the majority of the reactivity taking place occurs around the lignosulfonate molecules. Understanding changes to lignosulfonate molecular weight can help identify at which point the lignin begins undergoing significant polymerization, whether it be interlignin polymerization, lignin reacting with the previously discussed sugar byproducts, or a combination of the two. Table 3 shows that the molecular weight certainly increases over prolonged cooking times; however, the

greatest increases are observed in the final intervals of cooking time (3.1 vs. 3.7 h). This finding is in agreement with previous conjecture concerning the order in which the components of Am-LS react: first the sugars followed by the lignosulfonates. A plot comparing $M_{w,w}$ and total sugar content over cooking time is included as Figure 6, which clearly demonstrates the rapid increase in lignosulfonate's molecular weight beginning once sugar content was decreased by ~50 percent.

In all, a significant amount of elucidative information was obtained through the thermal priming exercise. First, a proof of concept was demonstrated for thermal priming along the basis of sample rheology, where it was found that reactivity can be induced in Am-LS materials and then stifled by cooling. Next, insight was gained into the interplay between sample pH, sugar content, and lignosulfonate molecular weight over the time course of a cook. It was found that these three properties are likely interrelated and therefore warrant further investigation.

Table 3.—Changes to ammonium lignosulfonate properties over the time course of thermal priming.

Cooking time (h)	Avg. viscosity at 70°C over 1 h after cook (mPa s)	pH after cook	wt% on dry matter					$M_{w,w}$ (kDa)	$M_{w,n}$ (kDa)
			Glucose	Mannose	Xylose	Minor sugars ^a	Total sugar		
0	70 ^b	3.0	3.1	9.7	3.6	3.0	19.4	26.7	2.1
1.9	200	2.4	2.1	5.7	1.0	2.1	10.9	34.7	2.1
2.5	260	2.2	1.7	4.0	0.5	1.7	7.9	50.1	2.1
3.1	1030	1.9	1.3	2.8	0.3	1.4	5.8	92.0	2.3
3.7	2270	1.9	1.1	2.3	0.2	1.0	4.6	150.0	2.4

^a Σ Rhamnose, galactose, and arabinose.

^b Uncooked sample.

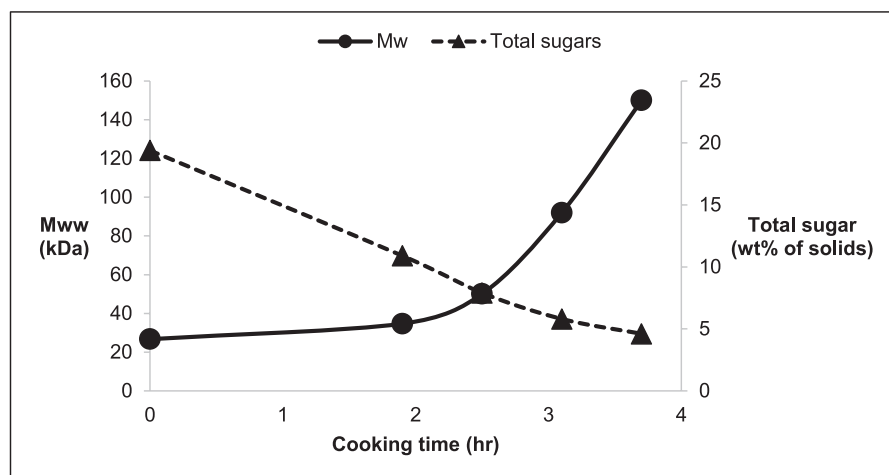


Figure 6.—Relationship between loss in ammonium lignosulfonate sugar content and increase in Mw_w with increasing thermal priming times.

Commercial applications of interest

It is most important to translate the findings of this work into applications where this chemistry can be manipulated into performing functions that the existing lignosulfonate products are unable to perform. The first conceivable application where this phenomenon could prove beneficial is as a hydrophobic pellet or agglomerate binder. Specifically, Am-LS could be subjected to a predetermined thermal priming regime at a low pH (and possibly with an added cross-linker) to reach a point short of initiating polymerization. Through cooling, pH elevation, dilution, and/or spray drying, this product could then be implemented into a pelleting or agglomeration process, upon which the heat of the process would immediately restart the polymerization process. Some of the industries where hydrophobic pellet or agglomerate binders would prove advantageous include aquaculture, agrochemicals, wood, and metallurgy wastes (Blackmore 1986, Buzulukov et al. 2000, Komarov and Fomin 2002).

Another application for this technology is enhanced oil recovery. This is an application where Am-LS has been used in the past (Felber et al. 1977; Lawrence and Felber 1981a, 1981b; Mickus et al. 1988; Hornof 1990; Popova et al. 1991; Gasumov et al. 2009). Specifically, a certain formulation of Am-LS product is piped down into the porous earth and allowed to gel within and effectively seal the subterranean fractures that contribute to lower levels of crude oil recovery. An Am-LS product for this application would have to be formulated to not be prone to gelation during downward piping but have enough polymerization-inducing properties to allow for gelation to occur at the temperatures and pressures experienced underground.

It is also worth investigating whether a gel-prone Am-LS could serve as a sustainable alternative to low-grade adhesives. It is possible that adhesives not intended to be long-lived and/or remarkably strong could be substituted with a well-formulated Am-LS product. This sort of compromise could allow for Am-LS products to enter into new markets, mostly as environmentally friendly alternatives to higher-performing synthetic adhesives. Single-use products in particular come to mind, especially those produced by the papermaking industry. Furthermore, it is

also possible that novel Am-LS products could be implemented as resin extenders in the adhesive systems used for wood board products like fiberboard, waferboard, oriented strand board, and particleboard (Philippou et al. 1982, Peng and Riedl 1994, Snopkov et al. 1995, Janowiak and Carlson 1998, Alonso et al. 2004, Yuan et al. 2014). These adhesive systems, typically involving urea-formaldehyde, phenol-formaldehyde, or pMDI systems, could warrant a lower dosage if a gel-prone Am-LS product is introduced to the fiber either prior to adhesive application or during adhesive application.

Conclusions

Ammonium lignosulfonate from loblolly pine was subjected to rigorous analysis intended to further explain its particular proclivity for undergoing polymerization chemistry that results in its behavior as a hydrophobic lignosulfonate. Two statistically significant models were constructed to predict the gel time and gel rate for this material by way of a rheological approach, paving the way for guided product development. A scheme for creating a gel-prone ammonium lignosulfonate material was introduced and demonstrated in the form of thermal priming, resulting in thicker liquid products that require less energy to initiate the exponential stage of polymerization. Valuable information concerning the track of sample pH, molecular weight, and sugar content revealed the initial chemistry to involve sugar degradation followed by rapid lignin polymerization, although it is unclear how much of the lignin polymerization includes inter-lignin polymerization versus linking between lignin and sugar byproducts. Finally, several potential commercial applications for these materials were conjectured upon in an effort to inspire further innovation using the chemistry. This work should pave the way for new applications in which lignosulfonate, a remarkably sustainable resource, can further benefit society as a renewable performance chemical.

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