

Lignin-g-poly(acrylamide)-g-poly(diallyldimethylammonium chloride): Synthesis, Characterization and Applications

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The search for a renewable substitute to petroleum-based products has fueled increasing research on lignin, an under-utilized product from pulping processes. In this work, lignin was copolymerized with acrylamide (AM) and diallyldimethylammonium chloride (DADMAC) under acidic conditions with Na₂S₂O₈ as an initiator, generating a cationic water-soluble lignin-g-P(AM)-g-P(DADMAC) copolymer. The optimal reaction conditions, using a 5×4 factorial design experiment, were determined to be an AM/DADMAC/lignin molar ratio of 5.5:2.4:1, 90 °C, 0.26 mol L⁻¹ of lignin, and pH 2. Under the optimal reaction conditions, the resulting lignin-g-P(AM)-g-P(DADMAC) co-

polymer was 83% soluble in an aqueous solution (at 10 g L⁻¹) and at neutral pH. The copolymer had a charge density of 1.27 meq g⁻¹, molecular weight of (1.33 ± 0.08) × 10⁶, an AM grafting ratio of 112 wt%, and a DADMAC grafting ratio of 20 wt%. In addition, the activation energy for producing this copolymer as well as the thermal and rheological properties of the copolymer were determined. The flocculation performance of lignin-g-P(AM)-g-P(DADMAC) copolymer was evaluated in a kaolin suspension, which showed that the lignin copolymer had a comparable flocculation efficiency with the synthetic analogue of P(AM)-g-P(DADMAC) at pH 6.

1. Introduction

The search for renewable alternatives to petroleum-based products has become a very active area of research as a result of the increasing environmental impact and economic volatility of crude oil. Lignin, a byproduct of pulping processes, has emerged as a primary source of renewable aromatic feedstock.^[1] Lignin is a highly abundant biopolymeric material that is produced in large quantities in the pulping and cellulosic ethanol industries.^[2] It currently represents 30% of all non-fossil organic carbon on earth and its availability would exceed by 20 billion tons each year.^[3] Despite an estimated 50 million tons of lignin extracted annually, only 2% of lignin is converted into value-added commodities including dispersants, adhesives, and surfactants.^[3,4] In addition to the high abundance, lignin has many desirable physiochemical characteristics including a large number of functional groups. As lignin has such a wide variety of reactive units arising from its monomer-

ic structure including phenol, ether, carboxylic acid, and -OH functional groups,^[5] one can render lignin functionalized for specific applications, such as flocculants,^[6] dispersants,^[7,8] binders,^[9,10] adhesives,^[11] hydrogels,^[12] and composites.^[13]

Owing to its biodegradability, its antioxidant and antimicrobial properties, as well as its reinforcing capabilities, lignin can be an excellent candidate for new polymer composite materials. However, its poor thermal stability and difficulties in melting performance mean its direct use in composite production is not preferred. For these reasons, most lignin applications focus on modified lignins rather than unmodified lignin produced in pulping processes.^[14] Although there are many different ways to modify lignin, the focus of this work is on graft copolymerization, where lignin acts as the macro-initiator for the polymerization, and the polymer is built from the lignin core. Lignin's hydroxyl groups can initiate ring-opening polymerization (ROP) of ε-caprolactone, yielding lignin-poly(caprolactone).^[15] Lignin copolymers can also be generated using free radical polymerization, grafting vinylic monomers onto the lignin backbone using a chemical initiator.^[16-19] This technique has been used to generate lignin-polystyrene,^[20] lignin-polyacrylamide,^[21] lignin-poly(acrylic acid),^[19] and lignin-poly(vinyl acetate).^[20] Both lignin-poly(acrylic acid) and lignin-poly(acrylamide) are water soluble products, whereas lignin-poly(styrene) is water insoluble and has been used as a biodegradable wood coating to reduce water sensitivity and increase the binding strength of poly(1-phenylethylene) plastic coatings on wood.^[19,22,23] The thermal properties of these copolymers were reported to depend on the length of the poly(caprolactone) chain. Lignin-poly(lactic acid) (PLA) copolymers were synthesized in the presence of an organic catalyst with the thermal proper-

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ties of the copolymer improving with the weight fraction of lignin in the copolymer.^[16] The first objective of this study was to investigate the rheological and thermal properties to understand if the lignin copolymer can be used in composites.

Wastewater treatment systems are integrated parts of many chemical processes and municipalities. The current technology relies heavily on either inorganic salts (i.e. alum, FeCl_3) or petroleum-based synthetic polymers including poly(acrylamide) (PAM), cationic poly(acrylamide) (CPAM), and anionic poly(acrylamide) (APAM).^[24] Although these systems are efficient, inorganic salts are toxic and produce large quantities of sludge, and synthetic polymers are nonbiodegradable and their respective monomers can be toxic.^[24]

Lignin can be incorporated in flocculant production for wastewater treatment systems. A highly cationic organosolv lignin was produced by grafting glycidyltrimethylammonium chloride (GTMAC) on hardwood lignin, and the product was found suitable for sulfate removal and kaolin settling.^[25] Lou and co-workers prepared an ecofriendly flocculant by synthesizing chitosan, acrylamide, and lignin, and the copolymer showed promising results for dye removal.^[26] In another study, lignin-based coagulant was produced by grafting diallyldimethylammonium chloride (DADMAC) and acrylamide (AM) onto lignin collected from papermaking sludge, and the product was successfully used along with polyferric chloride and polyaluminum chloride for the removal of humic acid in a coagulation/ultrafiltration process.^[27] Kraft lignin can also be used in the production of flocculants; however, kraft lignin is only soluble in aqueous solutions at a pH higher than 11. Kraft lignin can be converted to water-soluble flocculants through chemical modification (oxidation, sulfomethylation, carboxymethylation and co-polymerization).^[7, 19, 28, 29] The cationic modification of kraft lignin by epoxide ring-opening using GTMAC^[28] and the Mannich^[30] reaction has been studied extensively in both organic and aqueous media (alkaline pH). The graft copolymerization of kraft lignin with AM, methacryloxyethyl trimethylammonium chloride (DMC) and DADMAC has also been assessed in organic solvents for their potential use as a flocculant in wastewater treatment.^[20] However, the copolymerization of kraft lignin under aqueous conditions has yet to be studied.^[31] The second objective of this study was to produce a triblock copolymer of kraft lignin, AM, and DADMAC in an aqueous medium, yielding a cationic water-soluble polymer.

The main novelty of this work was the copolymerization of kraft lignin, acrylamide, and DADMAC, in which the reaction conditions were optimized in aqueous media using a 5×4 factorial design methodology. The structural, thermal, and rheological properties of the produced copolymer were compared with those of synthetic copolymer of AM and DADMAC. In addition, the flocculation efficiency of the lignin copolymer was compared with that of the synthetic copolymers. In this work, the synthesis and characterization of a green chemical, kraft lignin-based copolymer, was comprehensively discussed.

2. Results

2.1. Reaction Mechanism

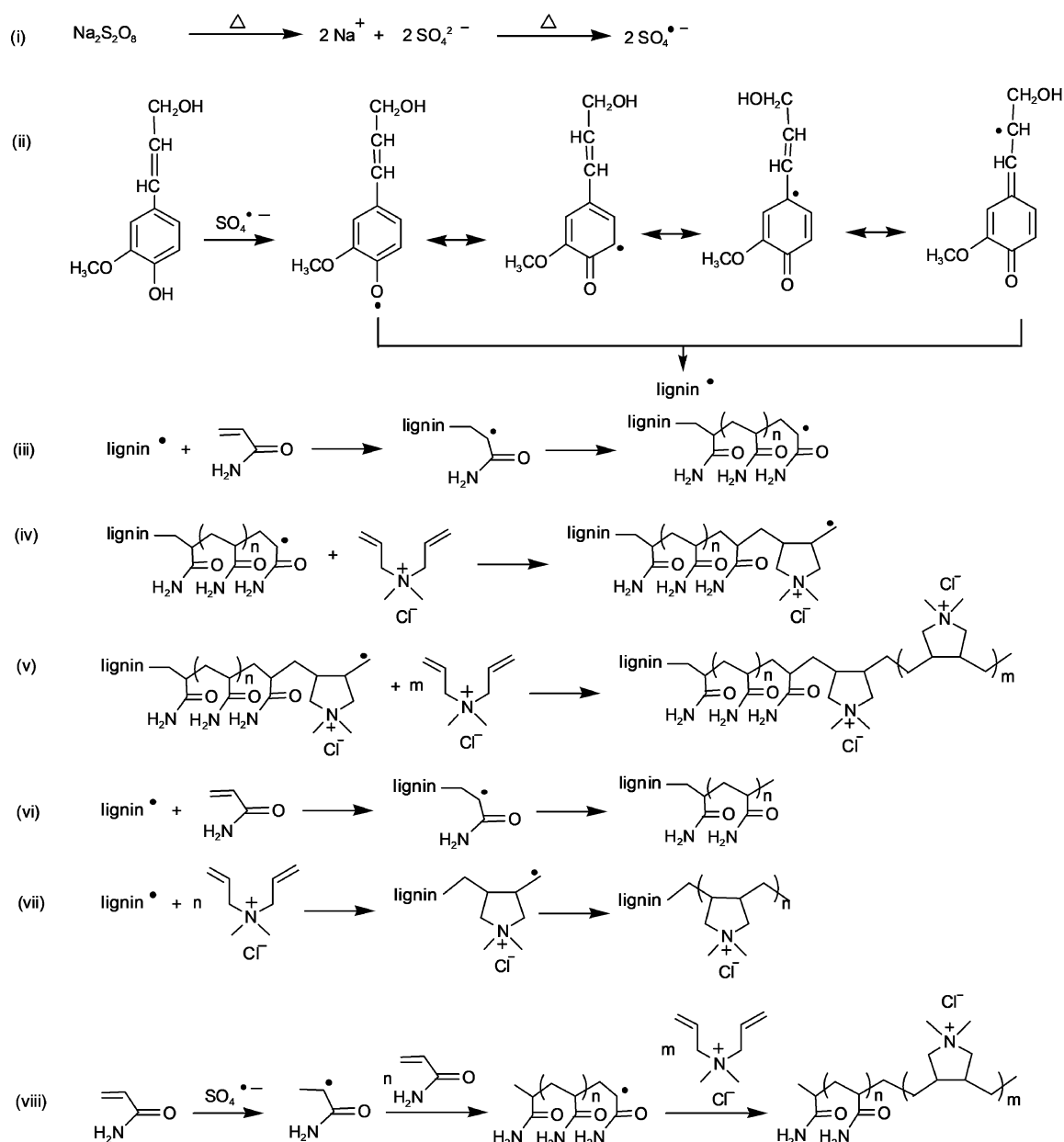
The free radical copolymerization of lignin, acrylamide, and DADMAC using sodium persulfate as the free-radical initiator was performed under an N_2 atmosphere. The copolymerization mechanism of lignin is shown in Scheme 1. Softwood kraft lignin consists of mostly coniferyl alcohol groups, and this was chosen as the site of propagation for lignin, as this is the dominant repeating unit present in softwood lignin.^[30] The thermal decomposition of sodium persulfate into two sulfate radical anions ($\text{SO}_4^{\cdot -}$) consists of the initiation step in the polymerization (Scheme 1 i).^[31] The free radical generated from the thermal decomposition of sodium persulfate can then be transferred to either lignin, DADMAC, or AM present in the reaction mixture. When the free radical is transferred to lignin, it will attack the hydroxyl group on the phenyl ring generating a phenoxy radical (Scheme 1 ii) along with the corresponding resonance structures.^[32] The phenoxy radicals present will then react with the acrylamide monomers to form the initial propagating lignin-PAM' chain, which can then continue further to react with the DADMAC monomers present in the reaction mixture (Scheme 1 iii–iv). In addition to forming the triblock lignin-PAM-PDADMAC copolymer, the diblock copolymers P(AM)-g-P(DADMAC), lignin-g-P(AM), and lignin-g-P(DADMAC) propagate during the reaction mixture, as shown in Scheme 1 vi to viii. Finally, the propagating lignin-g-P(AM), lignin-g-P(DADMAC), lignin-g-P(AM)-g-P(DADMAC), and P(AM)-g-P(DADMAC) can react with each other to produce either lignin-g-P(AM)-g-P(DADMAC) or P(AM)-g-P(DADMAC), terminating the polymerization. Additional polymer termination during the reaction also includes disproportionation and chain transfer.^[19]

2.2. Effects of Reaction Conditions on Lignin-g-P(AM)-g-P(DADMAC) Copolymer

A 5×4 factorial experiment was designed to determine the optimal reaction parameters for the copolymerization of lignin with DADMAC and AM. The reaction conditions and resulting copolymer properties can be found in Table 1, the analysis of variance can be found in Table 2, and the elemental analysis of lignin, P(AM)-g-P(DADMAC), and lignin-g-P(AM)-g-P(DADMAC) can be found in Table 3.

2.2.1. Orthogonal Design Analysis

An orthogonal experimental design was used to determine the optimal process parameters, which would have a significant effect on the charge density and solubility of the lignin copolymer. The sum of squared deviation (SS), mean squared (MS), F value, and probability can be found in Table 2. When the F value is large and the model probability $> F$ is less than 0.05, the process parameters will have a significant effect on the yield, charge density, solubility, and grafting ratio of the resulting lignin copolymer. As seen from the F test in Table 2, the in-



Scheme 1. Copolymerization mechanism of lignin with acrylamide and diallyldimethyl ammonium chloride.

fluence of the reaction conditions on the charge density was in the order of temperature > pH > DADMAC, but time and the AM concentration did not have a significant effect on the charge density. The reaction temperature was the most important determinant of charge density, whereas time was not an important factor indicating that the reaction was most likely completed in 2 h. Examining the F values and probability > F for solubility results, the influence of the reaction conditions on solubility was in the order of AM > temperature > DADMAC > pH > time. The dosage of AM was found to be the most important determinants for the solubility of the lignin-g-PAM-g-PDADMAC copolymer. The optimal conditions for the lignin copolymer production were 0.26 mol L^{-1} of lignin, 1.4 mol L^{-1} of AM, 0.6 mol L^{-1} of DADMAC at $90\text{ }^\circ\text{C}$, pH 2 for 2 h. The model

analysis predicted a lignin copolymer with 80 wt% solubility and 1.5 meq g^{-1} charge density. However, the experimental results led to a copolymer with a maximum charge density of 1.27 meq g^{-1} and solubility of 83 wt% under these conditions.

Figure 1 shows $\ln k$ versus $1/T$ for various reactions for the copolymerization of lignin-g-P(AM)-g-P(DADMAC), lignin-g-P(AM), and lignin-g-P(DADMAC). From the slope of the curves, the activation energy of lignin copolymer was found to be 212 kJ mol^{-1} . This activation energy was significantly higher than those for the homopolymerization of DADMAC (100.5 kJ mol^{-1}),^[33] the homopolymerization of AM (45 kJ mol^{-1}),^[34] the copolymerization of DADMAC and lignin (116 kJ mol^{-1}), and the copolymerization of lignin and AM (83 kJ mol^{-1}). In addition, the reactivity ratios of AM is 7.14,

Table 1. The 5×4 factorial experiments.^[a]

Run	Time [h]	pH	Temp [°C]	DADMAC	AM	Charge density [meq g ⁻¹]	Nitrogen [wt %]	Solubility [%]	Yield [%]
1	2	2	60	1	1	0.00	2.06	57	18
2	3	2	70	2	2	1.02	9.90	73	46
3	4	2	80	3	3	1.16	11.00	82	55
4	5	2	90	4	4	1.30	12.35	81	58
5	2	3	70	3	4	0.68	8.31	83	35
6	3	3	60	4	3	-0.15	1.28	33	32
7	4	3	90	1	2	0.54	10.24	74	59
8	5	3	80	2	1	-0.15	2.07	32	23
9	2	4	80	4	2	0.81	6.65	68	19
10	3	4	90	3	1	1.21	5.94	55	8
11	4	4	60	2	4	-0.13	2.92	50	10
12	5	4	70	1	3	0.33	11.03	78	46
13	2	5	90	2	3	0.57	11.26	78	44
14	3	5	80	1	4	0.19	11.11	75	26
15	4	5	70	4	1	-0.50	1.69	44	13
16	5	5	60	3	2	-0.45	1.72	53	15
optimal	2	2	90	4	4	1.27	11.91	83	63

[a] Based on a 1 wt % aqueous solution.

Table 2. Analysis of variance for the impact of charge density, yield, solubility, and grafting ratio for the copolymerization of lignin with AM and DADMAC.

Source of variation	SS	DF	MS	F value	prob > F	R ² [%]
Charge density [meq g⁻¹]						
model	4.86	9	0.54	5.85	0.0217	89.77
pH	1.13	3	0.38	4.09	0.0672	
temperature	3.15	3	1.05	11.36	0.0069	
DADMAC	0.58	3	0.19	2.10	0.2018	
Yield [%]						
model	4321.56	9	480.17	8.28	0.0091	92.55
pH	1440.19	3	480.16	8.28	0.0149	
temperature	1163.19	3	387.73	6.69	0.0243	
AM	1718.19	3	572.73	9.88	0.0098	
Solubility [wt %]						
model	3952.50	3	1317.50	3.66	0.0440	47.80
AM	3952.50	3	1317.50	3.66	0.0440	
Nitrogen content [wt %]						
model	270.56	12	22.55	69.06	0.0025	99.64
pH	24.05	3	8.02	24.55	0.0130	
temperature	138.72	3	46.24	141.64	0.0010	
DADMAC	20.20	3	6.73	20.62	0.0166	
AM	87.60	3	29.20	89.22	0.0020	

Table 3. Elemental analysis of lignin, P(AM)-g-P(DADMAC), and lignin-g-P(AM)-P(DADMAC).

Sample	N [wt %]	C [wt %]	H [wt %]	S [wt %]	AM [mmol (%)]	DADMAC [mmol (%)]	MW [g mol ⁻¹]	Charge density [meq g ⁻¹]
lignin	–	49.48	5.20	1.50	n/a	n/a	(7.9 ± 2.1) × 10 ⁴	
P(AM)-g-P(DADMAC)	13.34	50.27	9.22	–	7.37 (65.22)	2.16 (34.78)	(3.15 ± 0.36) × 10 ⁷	2.16
lignin-g-P(AM)-g-P(DADMAC)	11.91	48.90	7.66	2.05	7.24 (51.38)	1.27 (20.45)	(1.33 ± 0.08) × 10 ⁶	1.27

whereas that of DADMAC is 0.22.^[33] Thus, the incorporation of AM into the copolymer enables DADMAC to be incorporated more readily into the lignin copolymer.^[33]

2.3. Effect of Reaction Conditions on Charge Density

Figure 2 shows the effect of reaction conditions on the charge density, yield, and solubility of copolymer. The factors that had a significant effect on the charge density of the copolymer

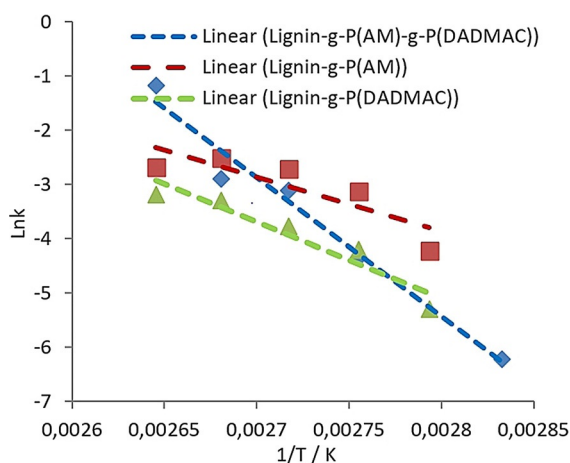


Figure 1. Activation energy of lignin-g-P(AM)-g-P(DADMAC), lignin-g-P(AM), and lignin-g-P(DADMAC).

were pH, temperature, and the dosage of DADMAC. Time and dosage of acrylamide did not affect the overall charge density of the lignin copolymer. By increasing the reaction temperature from 60 to 90 °C, the resulting charge density increased from -0.18 to 0.92 . It was stated that DADMAC monomer had a slow reactivity and high activation energy.^[33] Increasing the temperature of the reaction mixture allows for an increase in the amount of DADMAC monomer incorporated into the resulting copolymer. By conducting the reaction at a low pH, a copolymer with a high positive charge density (0.88 meq g^{-1}) was produced. When the reaction was conducted at pH 5, the lignin copolymer had an average charge density of -0.04 meq g^{-1} . When the reaction was conducted at higher pH values, the hydrolysis of the acrylamide and degradation of the quaternary ammonium ring group of DADMAC would occur.^[35,36] In other words, the decrease in positive charge density is attributed to 1) the hydrolysis of the acrylamide monomer as the amide groups could be converted to carboxylic acids groups and 2) the loss of the quaternary ammonium groups in the DADMAC monomer. The amount of acrylamide added to the reaction mixture had an insignificant effect on the overall charge density of the resulting copolymer, as the

dosage of acrylamide was increased from 0.35 to 1.4 mol L^{-1} , but the charge density of the lignin copolymer increased slightly from 0.39 to 0.52 meq g^{-1} , respectively.^[33] Although acrylamide is a neutral monomer and does not contribute to the overall charge density of the lignin copolymer, this slight increase in charge density is associated with the fact that acrylamide most probably helped cross-linked DADMAC to lignin.^[33] The high reactivity ratio of acrylamide suggests that acrylamide reacts with other acrylamide monomers, whereas DADMAC monomers with a relatively low reactivity ratio have higher tendency to react with acrylamide than with DADMAC monomers.^[33,37] Thus, the higher concentration of acrylamide present in the reaction mixture, the more DADMAC monomer can be incorporated into the copolymer, increasing the overall charge density of the copolymer.^[33] Extending the reaction time for the copolymerization had a slightly negative effect on the overall positive charge density of the resulting copolymer. When the reaction time was extended from 2 to 5 h, there was a decrease in the charge density from 0.51 to 0.27 meq g^{-1} , respectively. This decrease in charge density is most likely caused by the hydrolysis of acrylamide after an extended period of time and the hydrolysis of the ether linkage between lignin and P(AM)-g-P(DADMAC) portion of the copolymer. This phenomenon was observed in the copolymerization of liginosulfonate-acrylonitrile-methyl methacrylate copolymers (i.e. isolated polyacrylic chains from the copolymer).^[38,39]

2.4. Effect of Reaction Conditions on Yield

The reaction conditions that more significantly affected the overall yield of the lignin copolymer were the pH, reaction temperature, and reaction time. Decreasing the pH from 5 to 2 tended to increase the yield of the copolymer from 24 to 44%. By decreasing the pH of the reaction mixture, the amount of acrylamide and DADMAC incorporated into the lignin copolymer increased. At a low pH (e.g. pH 2), lignin has a low solubility with limited affinity to act as a free radical scavenger, thus increasing the half-life of radical initiator and the propagating radical chain.^[40] Increasing the reaction temperature from 60 to 90 °C significantly increased the yield of the lignin copolymer

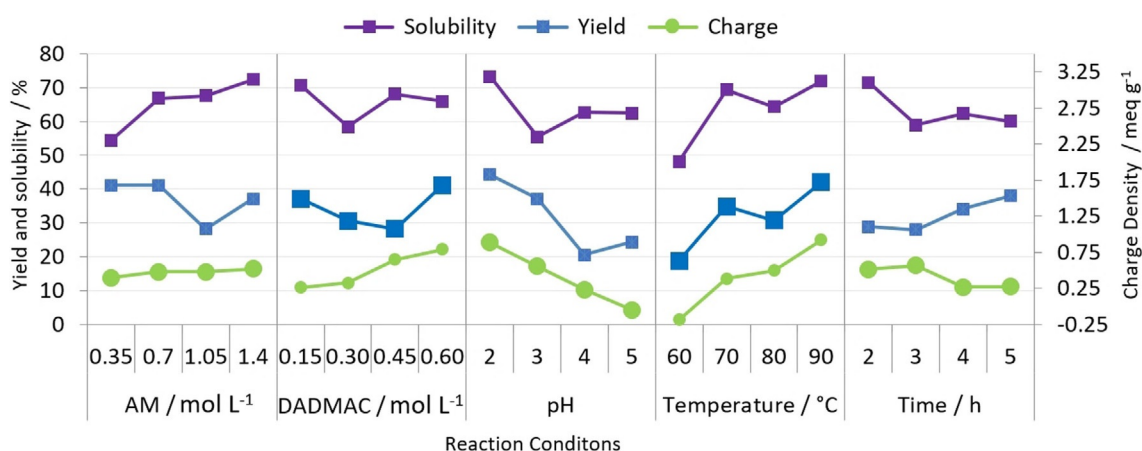


Figure 2. Effect of reaction conditions on the yield, solubility, and charge density of the lignin-g-P(AM)-g-P(DADMAC) copolymer.

from 18 to 42%. The increase in yield is attributed to the fact that this reaction had a high activation energy and elevated temperatures are required to overcome this energy barrier. In addition, the reactivity of DADMAC is very low and higher temperatures are required for initiating its copolymerization.^[33] Extending the reaction time from 2 to 5 h increased the yield of lignin copolymer from 28 to 38%. Owing to the sluggish nature of this copolymerization, a time extension would allow for an increase in the grafting of acrylamide and DADMAC onto lignin.

2.5. Effects of Reaction Conditions on the Grafting Ratio

Figure 3 shows the effect of reaction conditions on the grafting ratio of lignin copolymer. It is seen that the dosage of AM in the reaction mixture had a significant effect on the grafting ratio of both AM and DADMAC onto lignin. As the concentration of AM in the reaction mixture increased from 0.35 to 1.41 mol L⁻¹, the amount of AM grafted onto the lignin increased from 36 to 92%. In addition, the increased concentration of AM enabled a slightly higher grafting ratio of DADMAC onto the lignin backbone. The slight increase in the grafting ratio of DADMAC is also reflected in the charge density increase from 0.39 to 0.52 meq g⁻¹.

As the concentration of DADMAC increased in the reaction mixture from 0.15 to 0.62 mol L⁻¹, the grafting ratio of DADMAC onto lignin increased from 4.5 to 16.5%, and the charge density of lignin copolymer was increased from 0.26 to 0.79 meq g⁻¹. In addition, as the grafting ratio of DADMAC increased, the grafting ratio of AM decreased from 85 to 55%. The decrease in AM is most likely caused by a decrease in AM amount relative to lignin and DADMAC in the copolymer.

As the pH of the reaction mixture decreased from 5 to 2, the grafting ratio of both DADMAC and AM increased significantly. At pH 5, the grafting ratio of AM was 50% and it increased to 72% when the pH dropped to 2. In the same vein, the grafting ratio of DADMAC increased from 3 to 17% when pH dropped from 5 to 2. The increase in grafting ratio for both AM and DADMAC at a low pH was attributed to the fact that,

at higher pH values, the hydrolysis of both the amide and quaternary ammonium groups may occur, thus decreasing the nitrogen content of the lignin copolymer.^[35,36] Also, at higher pH values, the grafted polymer can be cleaved from the lignin backbone, and hence decreasing the grafting ratio of both AM and DADMAC.^[38]

The effects of reaction temperature on the grafting ratio of DADMAC and AM can also be observed in Figure 3. As the temperature of the reaction mixture increased from 60 to 90 °C, the grafting ratio of AM increased significantly from 13 to 86% and the grafting of DADMAC increased from 0 to 17%. The increase in grafting ratio of both AM and DADMAC upon increasing the reaction temperature was attributed to the high activation energy for this lignin copolymerization. High temperatures were required for initiating and propagating the copolymerization of both DADMAC and AM onto lignin.^[33]

Time had only a slight effect on the grafting ratio of both AM and DADMAC. As time extended from 2 to 5 h, the grafting ratio of DADMAC did not change significantly, but the grafting ratio of AM decreased from 70 to 50%. The decrease in the grafting of AM could be the result of hydrolysis of the amide bond. Once the amide bond has undergone hydrolysis, the nitrogen content of the lignin copolymer and hence the grafting ratio will decrease.

Table 3 lists the properties of unmodified lignin, lignin-g-P(AM)-g-P(DADMAC), and P(AM)-g-P(DADMAC). The lignin copolymer was produced under the optimal conditions of an AM/DADMAC/lignin molar ratio of 5.5:2.4:1 at 90 °C, 0.26 mol L⁻¹ of lignin at pH 2. It can be seen that unmodified lignin did not have nitrogen, but the lignin copolymer contained about 12 wt% nitrogen originating from AM and DADMAC. The hydrogen content of the copolymer was slightly higher than that of unmodified lignin. Compared with lignin copolymer, P(AM)-g-P(DADMAC) had slightly higher carbon, hydrogen, and nitrogen, which led to slightly higher charge density. The results also indicate that the lignin-based polymer had a smaller molecular weight than synthetic polymer implying that the participation of lignin in the reaction hampered the progress in polymerization of AM and DADMAC. As can be

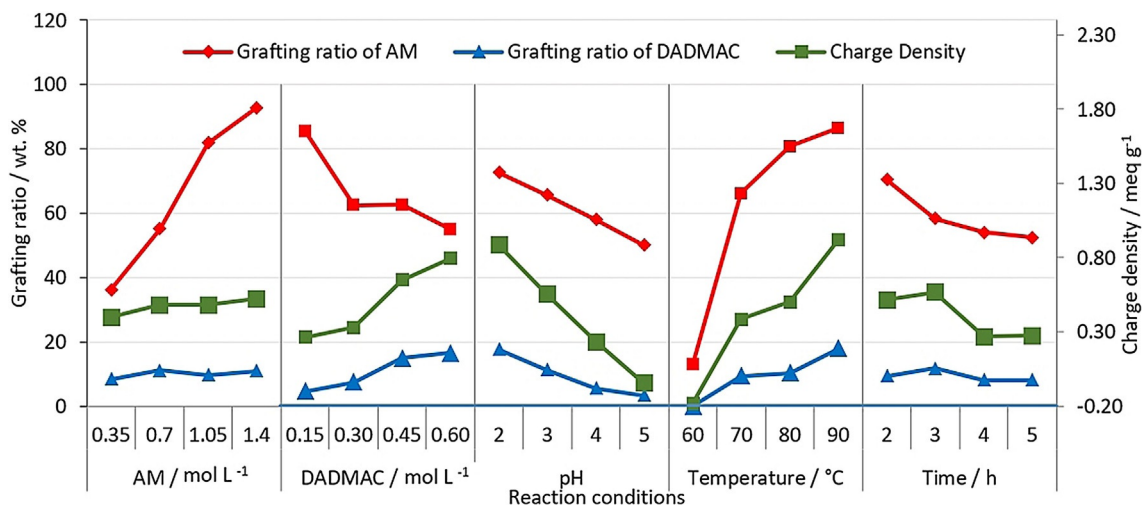


Figure 3. Effect of reaction conditions on the grafting ratio and charge density.

seen, the incorporation of lignin in P(AM)-g-P(DADMAC) polymer also reduced the overall charge density of the polymer, which might be associated with reduction in progress during polymerization between AM and DADMAC and the presence of lignin as uncharged materials, which would reduce the overall charge of the polymer.

2.6. Structural Analysis

2.6.1. ^1H NMR Spectroscopy

The ^1H NMR spectra of unmodified lignin, P(AM)-g-P(DADMAC), and lignin-g-P(AM)-g-P(DADMAC) are depicted in Figure 4. Examining the ^1H NMR spectrum of lignin shows that the peak at 9.4 ppm can be attributed to the aldehyde groups.^[36] The peak at 8.5 ppm is attributed to the unsubstituted phenolic protons and the broad resonance between 6 and 7.5 ppm is associated with the substituted phenolic protons,^[38] which confirmed the generation of a phenoxy radical (Scheme 1 ii) and, subsequently, the reaction of the radical with AM and DADMAC monomers. The peak at 6–7 ppm is attributed to aromatic protons including the vinyl protons on the carbon adjacent to the aromatic ring.^[38] The broad resonance of 3.25–3.81 ppm is assigned to the methyl protons and the resonance at 3.36 ppm is attributed to the methylene protons in the β - β structure.^[41] Examining the ^1H NMR spectrum of P(AM)-g-P(DADMAC) shows that the resonance from the P(DADMAC) portion of the copolymer occurs at 3.61 ppm, which is assigned to the $-\text{CH}_2-$ group in the five-membered ring. The peaks in the range of

2.84 and 3.06 ppm are attributed to the $N\text{-CH}_3$ protons and the resonance at 2.5 ppm is attributed to the $-\text{CH}-$ proton.^[42–44] The protons found in the main polymer backbone from both P(AM) and P(DADMAC) occurred at 1.6 and 2.2 ppm.^[42–44] The ^1H NMR spectrum of lignin-g-P(AM)-g-P(DADMAC) depicts peaks that exist in the spectra of lignin and P(AM)-g-P(DADMAC). Thus, it was concluded that the lignin-g-P(AM)-g-P(DADMAC) copolymer contained lignin, AM, and DADMAC, as described in Scheme 1 iii and 1 iv.

2.6.2. FTIR Spectroscopy

The FTIR spectra of unmodified lignin, P(AM)-g-P(DADMAC), and lignin-g-P(AM)-g-P(DADMAC) copolymer prepared under optimal conditions is shown in Figure 5. Both lignin and lignin-g-P(AM)-g-P(DADMAC) have absorption bands at 1266 and 1140 cm^{-1} , attributed to the C–O and C–H stretching frequency of the guaiacyl unit, respectively.^[35] The characteristic aromatic stretching bands of the lignin skeleton are also observed at 1591, 1510, and 1425 cm^{-1} .^[38] Several new absorption bands appear in the spectrum of the lignin-g-P(AM)-g-P(DADMAC) copolymer, including a strong absorption at 3315 cm^{-1} attributed to O–H unsymmetrical stretch, 3015 cm^{-1} attributed to the C–H symmetrical stretch in $N\text{-CH}_2$, and 2940 cm^{-1} attributed to C–H unsymmetrical stretch of CH_3 from the DADMAC portion of the copolymer,^[40] indicating the grafting of DADMAC onto lignin (Scheme 1 iv and 1 v). The stretching frequencies for the acrylamide portion in the lignin copolymer can be found at 3179 cm^{-1} associated with the NH_2 stretching vibrations,

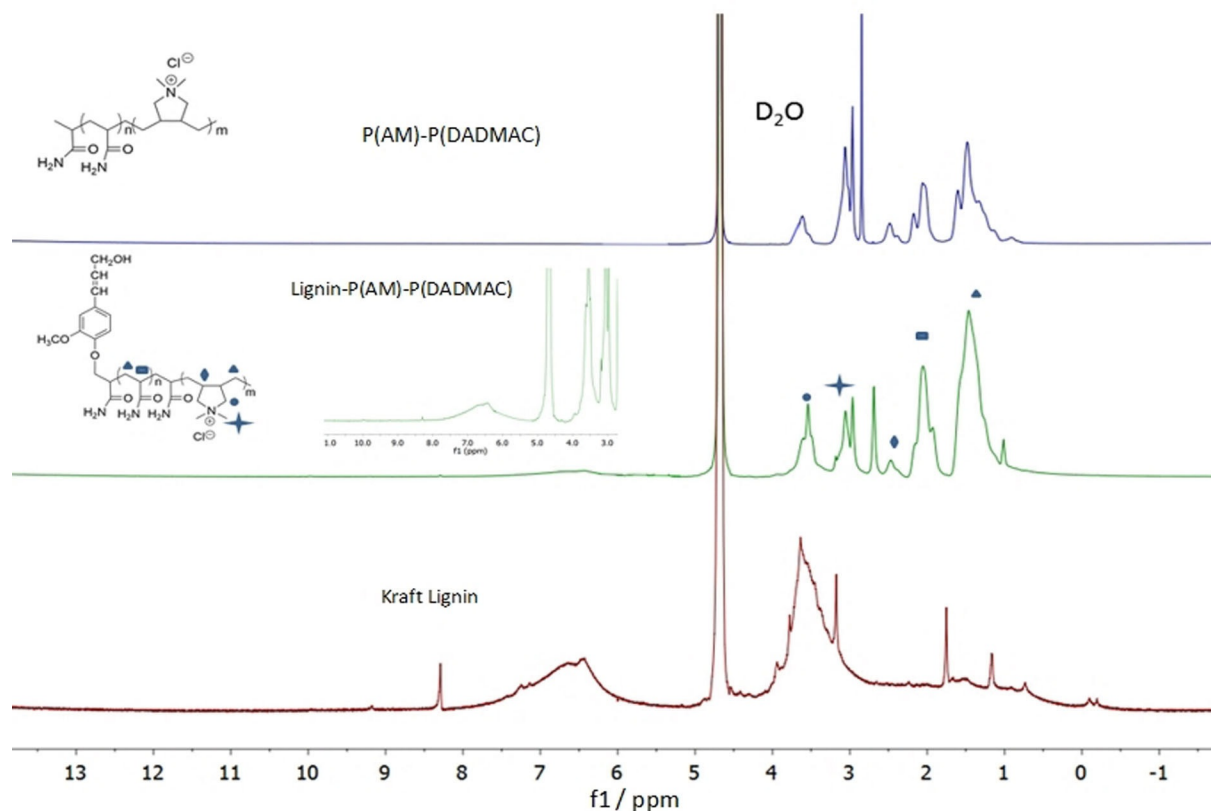


Figure 4. ^1H NMR spectra of P(AM)-g-P(DADMAC) (top), lignin-g-P(AM)-g-P(DADMAC) (middle), and kraft lignin (bottom).

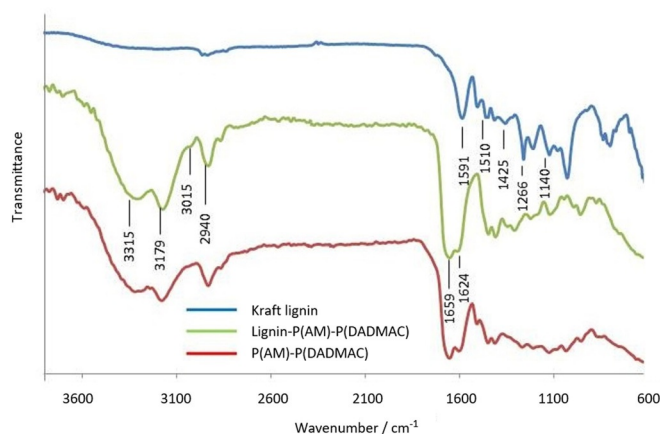


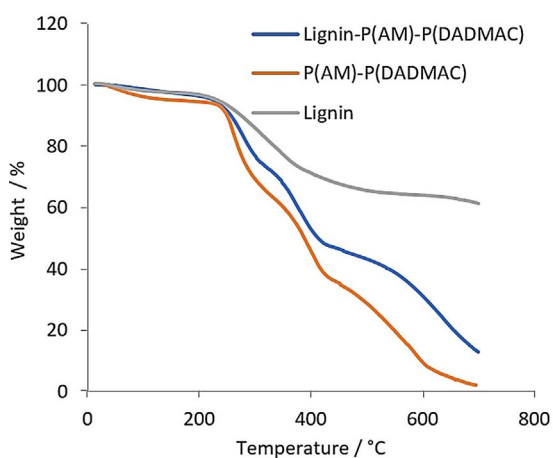
Figure 5. FTIR spectra of kraft lignin (top), lignin-g-P(AM)-g-P(DADMAC) (middle), and P(AM)-P(DADMAC) (bottom).

1659 cm^{-1} associated with C=O of the amide stretch, and 1624 cm^{-1} [41] associated with NH_2 bending; suggesting the incorporation of lignin and AM (Scheme 1 iii).

2.6.3. Thermal Properties

The weight loss and weight loss rate of lignin, lignin-g-P(AM)-g-P(DADMAC), and P(AM)-g-P(DADMAC) can be found in Figure 6.

All three samples were stable under 200 °C. Lignin was significantly more stable than both copolymers; however, the lignin copolymer had a slightly higher thermal stability than the synthetic AM-g-DADMAC. This increase in thermal stability would be an advantage for its end-use applications. The increase in thermal stability is attributed to the presence of kraft lignin in the copolymer. The unmodified lignin decomposed continuously above 200 °C with a 40% weight loss by 700 °C. The lignin copolymer and synthetic polymer had three weight loss events in the temperature range of 200–330 °C, 340–440 °C, and 445–600 °C. At a temperature higher than 600 °C, only 2% of synthetic copolymer and 14% of lignin copolymer



remained. The first weight loss range 200–330 °C is from the release of water, ammonia, and small quantities of CO ; however, the polymer chain remains intact and most of the decomposition occurred at the pendant amide groups on the acrylamide portion of the polymer.[45] The second decomposition occurred between 330 and 440 °C, in which the main chain started to breakdown releasing carbon dioxide, water, nitrile compounds, and imides.[46] In addition, the DADMAC portion of the polymer chain begins to decompose and the quaternary ammonium salts release ammonia and an alkyl halide over 400 °C.[47]

The glass transition (T_g) of lignin, lignin-g-P(AM)-g-P(DADMAC), and P(AM)-g-P(DADMAC) were also determined and the results can be found in Figure 7. The results showed

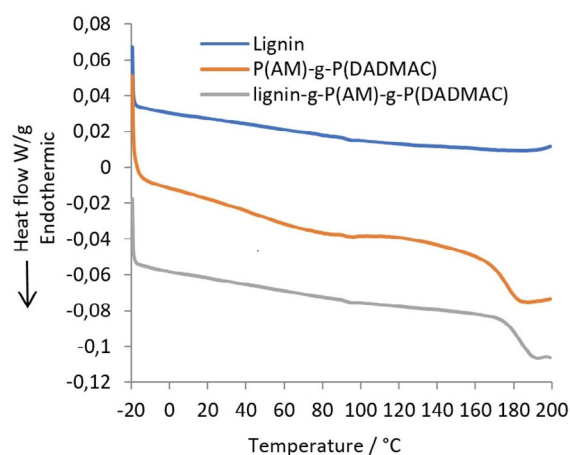


Figure 7. Glass transition (T_g) of lignin-P(AM)-P(DADMAC), P(AM)-P(DADMAC), and lignin.

no T_g for unmodified lignin; this could be attributed to the fact that the T_g of lignin may occur beyond the decomposition temperature of 200 °C.[48] However, the lignin copolymer and synthetic copolymer had T_g at 184 and 175 °C, respectively. The T_g of lignin-g-P(AM)-g-P(DADMAC) was 9 °C higher than that of the synthetic copolymer, which is attributed to the presence of

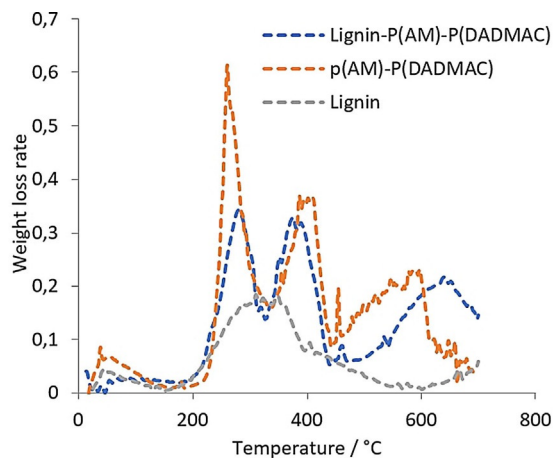


Figure 6. Weight loss (solid line) and weight loss rate (dashed line) of lignin, lignin-g-P(AM)-g-P(DADMAC), and P(AM)-g-P(DADMAC) synthesized under the optimal conditions of pH 2, 0.26 mol L^{-1} lignin, 0.6 mol L^{-1} DADMAC and 1.05 mol L^{-1} AM at 90 °C for 2 h under nitrogen.

lignin that hardened the structure of the copolymer. To understand the properties of this newly developed copolymer, thermal analysis was conducted, and the results confirmed that the copolymer was indeed more thermally stable than its synthetic analogue. These results would be advantageous for use of the lignin copolymer in composite productions. Moreover, the wastewater system of some chemical processes, for example mining, involves oxidation as well as acid and alkaline treatments at a high temperature. The thermal analysis confirmed that the advantage of the copolymer over its synthetic analogue as the copolymer may maintain its functionality and integrity more greatly in these processes. However, more studies are needed to better understand the stability of the copolymer under different conditions, for example pressure and acidity, which is out of the scope of this study.^[49–51]

2.6.4. Solubility and Rheological Properties

The pH of the solution has a significant impact on the solubility of lignin-based products and their potential end-use applications. The effect of pH on the solubility of unmodified lignin and the lignin copolymer was investigated and is shown in Figure 8. The solubility of both unmodified lignin and lignin

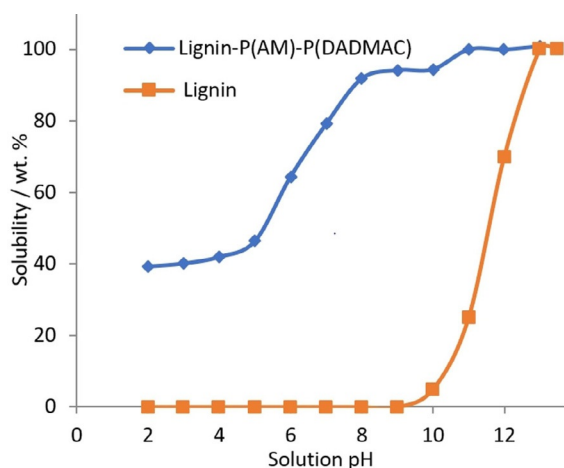


Figure 8. Effect of pH on the solubility of unmodified lignin and lignin-g-P(AM)-g-P(DADMAC) copolymer at a concentration of 10 g L^{-1} , 25°C , and stirred for 12 h.

copolymer was carried out in a 1 wt% solution. This concentration was chosen because of a low dosage requirement for flocculant use in wastewater treatment systems. Both unmodified lignin and the lignin copolymer are soluble at pH values higher than 12; however, unmodified lignin became insoluble at a pH lower than 11.^[52] The solubility of lignin copolymer dropped to 60% at pH 6 and to 40% at a lower pH. The improvement in the solubility of the lignin copolymer was attributed to the presence of water soluble component on the lignin copolymer backbone, that is, AM and DADMAC. However, the results show that the copolymerization was not sufficiently efficient to make the lignin copolymer 100% water soluble.^[37,53]

The dynamic viscosity of the lignin copolymer produced under optimal conditions was evaluated at different concentrations and pH values, and the results are shown in Figure 9. The rheological properties of the copolymer are important for de-

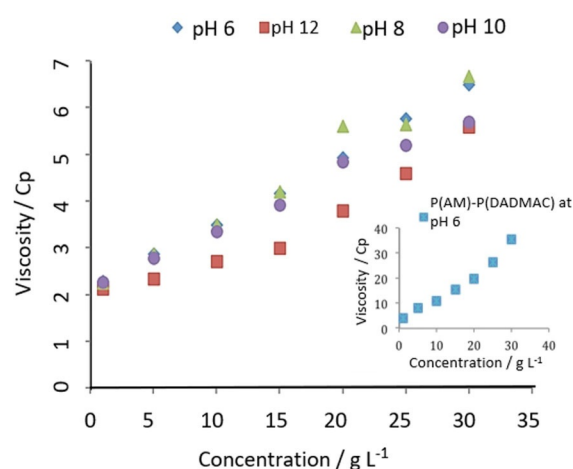


Figure 9. The viscosity of lignin-g-P(AM)-g-P(DADMAC) prepared under the optimal conditions at varying pH values and concentrations and the synthetic analogue P(AM)-g-P(DADMAC) at pH 6 at 25°C .

termining the flow of the polymer in solution. Generally, flocculants must be pumped into wastewater treatment plants, and a less viscous polymer would be preferred for this application. The viscosity of the lignin copolymer at pH 12 and 30 g L^{-1} was 5.69 Cp, which was higher than that of unmodified kraft lignin (2.30 Cp). However, P(AM)-g-P(DADMAC) prepared under the same optimal conditions had a much higher viscosity of 35.5 Cp. This difference in viscosity is caused by the difference in the molecular weight of the lignin-g-P(AM)-g-P(DADMAC) and P(AM)-g-P(DADMAC), as discussed earlier. Furthermore, pH did not have a significant effect on the viscosity of the lignin-g-P(AM)-g-P(DADMAC) copolymer, suggesting there was no reconfirmation or self-aggregation of the copolymer at different pH values under the conditions studied.

In another attempt, the viscosity of the copolymer at various shear rates were analyzed, as shown in Figure 10. The results showed that the viscosity decreased with an increase in shear rates, demonstrating that the lignin copolymer exhibited shear thinning behavior. This is consistent with the rheological properties of kraft lignin and P(AM)-g-P(DADMAC), both of which exhibited shear thinning behavior.^[45,46]

2.6.5. Flocculation

The flocculation efficiency of lignin, lignin-g-P(AM)-g-P(DADMAC), and P(AM)-g-P(DADMAC) were investigated by using a 0.25% kaolin suspension, and the results are shown in Figure 11.

The optimal dosage of P(AM)-g-P(DADMAC) to kaolin suspension was found to be 0.2 mg g^{-1} , which reduced the relative turbidity of the kaolin solution by 93%. However, the lignin copolymer reduced the relative turbidity by 95% at a

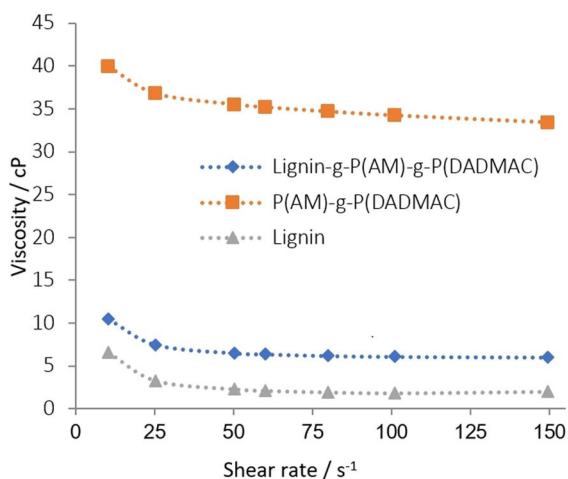


Figure 10. Viscosity of lignin-g-P(AM)-g-P(DADMAC) copolymer, lignin, and P(AM)-g-P(DADMAC) solution at 30 g L^{-1} as a function of shear rate at $25 \text{ }^\circ\text{C}$.

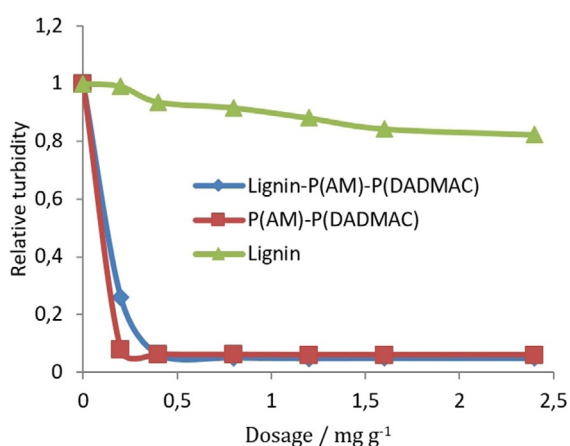


Figure 11. Relative turbidity of a 0.25 % Kaolin solution in the presence of lignin, P(AM)-g-P(DADMAC), and lignin-g-P(AM)-g-P(DADMAC) as a flocculant at pH 6.

slightly higher dosage of 0.4 mg g^{-1} . The lignin copolymer had almost 40 wt% lignin and 60% synthetic monomers, but the synthetic copolymer was produced from AM and DADMAC (100% synthetic monomer).

At a dosage of 0.4 mg g^{-1} , the efficiency of the lignin copolymer and synthetic copolymer was similar, implying that the use of lignin copolymer will be beneficial, as it reduces the use of synthetic monomers by 40%. The flocculation of kaolin can occur through several different mechanisms, including bridging, charge neutralization, hydrophobic/hydrophobic interactions, and patch mechanisms.^[53–55] Owing to the high molecular weight of the polymer, both bridging and patch mechanisms are responsible for the flocculation of kaolin.^[56] Kraft lignin had a poor flocculation performance, which is attributed to the overall negative charge density of lignin originating from the carboxylate groups and its poor solubility at neutral pH.^[14] Lignin-g-P(AM)-g-P(DADMAC) has shown to be an efficient flocculant for kaolin suspensions and compared to its

synthetic copolymer, it is a less expensive and environmentally friendly alternative.

It is also seen that lignin-g-P(AM)-g-P(DADMAC) was less soluble under acidic conditions at a concentration of 1 g L^{-1} . Therefore, its functionality as a flocculant may be hampered if used at this concentration and acidic pH. However, flocculants including lignin-g-P(AM)-g-P(DADMAC) would be used at a very low dosage in wastewater treatment systems. This lower concentration would have a minimal effect on the solubility and, thus, use of the copolymer as a flocculant at acidic pH. However, further investigation is needed to determine the correlation between the functionality and concentration of this copolymer at different pH, which is out of the scope of this study.

Table 4 lists the status of cationic flocculants used in wastewater treatment systems. With a relatively high molecular weight and a comparable charge density, the flocculant synthesized in this study required a much lower dosage than other flocculants in other studies to achieve an acceptable removal. In addition, in opposition to other systems, lignin-g-P(AM)-g-P(DADMAC) does not need a dual polymer system to achieve an acceptable performance. Therefore, the generated copolymer may be a promising flocculant for various wastewater systems.

3. Discussion

Owing to the increased thermal stability and higher T_g temperature of the lignin copolymer (compared to that of the synthetic copolymer), the lignin copolymer could have potential applications in composites and thermoplastics, as these polymers could be used at higher temperatures with less risk of decomposition.^[49] Additionally, lignin-g-P(AM)-g-P(DADMAC) could have potential as a flocculant for industrial wastes, for example tailing pond or wastewater effluents. As mentioned above, the lignin copolymer performed very similarly to the synthetic copolymer in terms of flocculating kaolin particles in a suspension under dynamic conditions. The advantages of using the lignin copolymer over the synthetic copolymer is that the lignin copolymer is more biodegradable and environmentally friendly, and probably less expensive to produce.

4. Conclusions

The synthesis of lignin-g-P(AM)-g-P(DADMAC) copolymer was successful. The FTIR, ^1H NMR, and elemental analyses provided further evidence that lignin was copolymerized with both AM and DADMAC. The activation energy for the copolymerization of lignin-g-P(AM)-g-P(DADMAC) under the optimal conditions was determined to be 212 kJ mol^{-1} , which is significantly higher than that of lignin-g-P(AM) and lignin-g-P(DADMAC). The optimal copolymerization conditions were found to be AM/DADMAC/lignin ratio of 5.5:2.4:1 molar ratio at $90 \text{ }^\circ\text{C}$, 0.26 mol L^{-1} of lignin at pH 2. The lignin copolymer produced under the optimal conditions was 83% soluble in an aqueous solution at 10 g L^{-1} and neutral pH, had a charge of 1.27 meq g^{-1} , and an AM grafting ratio of 112% and DADMAC

Table 4. Status of cationic flocculants in different wastewater systems.

Flocculant	MW [g mol ⁻¹]	Charge density [meq g ⁻¹]	Type of wastewater	Dosage [mg L ⁻¹]	Flocculation performance
lignin-g-P(AM)-g-P(DADMAC)	1.33 × 10 ⁶	1.27	kaolin suspension	1	turbidity removal: 95 %
lignin-base dimethylamine-acetone-formaldehyde copolymer ^[6]	2669–6143	1.79–2.55	simulated azo-dyes	35–75	dye removal: 89–96 %
polyDADMAC ^[57]	8.5 × 10 ⁵ –1.57 × 10 ⁵	–	pulp and paper mill	0.4–2.0	chemical oxygen demand (COD) removal: > 90 %
cationic polyAM ^[58]	3 × 10 ⁶ –7 × 10 ⁶	10–35 %	kaolinite suspensions	12	reduction in turbidity of > 98 %
chitosan-g-polyDMC ^[59]	–	–	blending black liquor	17.8 (with 1017 mg L ⁻¹ aluminum chloride as the coagulant)	turbidity removal: 99.4 % lignin removal: 81.3 % COD removal: 90.7 %

grafting ratio of 26 % by mass. The rheological analysis confirmed that lignin-copolymer increased the viscosity of water less significantly than synthetic copolymer, and lignin copolymer had shear thinning behavior. Thermogravimetric analysis showed that the incorporation of AM and DADMAC reduced the thermal stability of lignin; however, the thermal stability of lignin copolymer was greater than that of the synthetic copolymer. T_g was observed at 184 °C for the lignin copolymer, which was slightly lower than that of the synthetic copolymer (175 °C). In addition, the lignin copolymer was proven to be an effective flocculant for a kaolin suspension, but its efficiency was inferior to synthetic copolymer (Table 4).

Experimental Section

Materials and Methods

Softwood kraft lignin was produced by the LignoForce™ technology of FPInnovations in Thunder Bay, ON, and was used as received.^[47] Diallyldimethylammonium chloride (65 wt % in water), acrylamide, acetic anhydride, sodium persulfate, pyridine, dimethyl sulfate, 2-chloro-4,4'-5,5'-tetramethyl-1,2,3-dioxaphospholane, chromium(III) acetylacetonate, CDCl₃, polydiallyldimethylammonium chloride (PDADMAC, 100 000–200 000 g mol⁻¹), internal standard trimethylsilyl propionic acid-d, sodium hydroxide, all analytical grades, were obtained from Sigma Aldrich and were used without any further purification.

Copolymerization of Kraft Lignin with AM and DADMAC

A 2.0 g sample of lignin was added to 40 mL of deionized water in 250 mL three-neck round bottom glass flasks.^[60] A specified amount of AM and DADMAC was then added to the same glass flasks and the pH was adjusted accordingly with a 25 wt % solution of H₂SO₄(aq) with continuous stirring at 500 rpm. The reaction mixture was purged for 20 min with nitrogen, and then 30 mg of Na₂S₂O₈ was dissolved in 5 mL of H₂O, which was then added to the reaction mixture. The reaction was then purged with nitrogen for an additional 10 min, stirring at 500 rpm.^[60] The reaction mixture was then submerged into a heated water bath. The copolymerization was repeated under varying reaction conditions including temperature (60, 70, 80, and 90 °C), time (2, 3, 4, 5 h), pH (2, 3, 4, and 5), AM to lignin molar ratio (2.6, 5.2, 7.8, 10.4 mol/mol) and DADMAC to lignin molar ratio (1.16, 2.32, 3.48, 4.64 mol/mol), and 500 rpm. The mole number of lignin was determined based on the molar mass of C9 monomeric unit of lignin (i.e. 180 g mol⁻¹). Upon completion, the reaction mixture was cooled to room temperature

and mixed with 400 mL of 95 % ethanol, resulting in the precipitation of kraft lignin-based copolymers.^[53,60–62] The precipitates were washed with 50 mL of 95 vol % ethanol, and then dried in a 105 °C oven overnight. The yield of the copolymerization reaction was determined based on the mass of collected lignin-g-P(AM)-g-P(DADMAC) and initial masses of lignin, AM, and DADMAC used in the copolymerization reaction.^[53,60–62]

Synthesis of P(AM)-g-P(DADMAC) Copolymer

The copolymer of P(AM)-g-P(DADMAC) was synthesized under the optimized conditions determined for lignin-g-P(AM)-g-P(DADMAC). A 4.0 g sample of acrylamide and 6.15 g of DADMAC (65 % wt solution) were added to a 250 mL three-neck glass flask containing 40 mL of water. The pH of the reaction mixture was adjusted to 2 by using 30 wt % H₂SO₄, which was then purged with nitrogen for 20 min. A 30 mg sample of Na₂S₂O₈ was then dissolved in 5 mL of H₂O, and subsequently added to the reaction mixture. The reaction mixture was purged with nitrogen for 10 min while stirring at 500 rpm. The reaction mixture was next submerged into a 90 °C water bath for 2 h. Upon completion, the reaction mixture was precipitated into 300 mL of acetone. The precipitated product was isolated and dried in an oven overnight at 105 °C. This product was used as the synthetic analogue of the lignin-g-P(AM)-g-P(DADMAC) copolymer.

Experimental Design

A Taguchi orthogonal array was used to determine the maximum charge density, solubility, yield, and grafting ratio for the lignin copolymer under the optimized conditions. An L₁₆ orthogonal experimental design was generated with five factors and four levels (5 × 4) to determine the optimal conditions. The analysis of the variance model (ANOVA) using the *F* test was used to determine which parameters significantly affected the copolymerization and which effect produced the highest charge, solubility, yield, and grafting ratio. The sample variance is defined in Equation (1):^[63]

$$S^2 = \frac{1}{n-1} \sum (y_i - \bar{y})^2 \quad (1)$$

where $\sum (y_i - \bar{y})^2$ refers to the SS deviation from the mean, $\frac{1}{(n-1)}$ is the degrees of freedom (df), and S^2 refers to the mean square.

The *F* test measures the significance of variance for a factor which is determined by Equation (2):^[63]

$$F = \frac{MS_F}{MS_E} \quad (2)$$

where MS_F is the mean square of the factor and MS_E is the mean square of the error. If the variance due to the factor (MS_F) is higher than the variance due to the error (MS_E), the factor will have a greater effect on the response. The larger the number generated from the F test, the greater the effect that factor has on the reaction conditions and the lignin copolymer product. The probability factor (probability $> F$) is an indication of the chance for the F values to occur due to noise. When the probability factor for the model was less than 0.05, the model terms were significant. The R^2 value is a measure of how close the experimental observations fit the theoretical results.

Solubility

The solubility of the lignin-g-P(AM)-g-P(DADMAC) copolymer was determined by adding 0.2 g of lignin copolymer to 20 mL of distilled water. The suspension was stirred at 300 rpm for 2 h. Upon completion, the solution was centrifuged at 1000 rpm for 5 min. The supernatant was then dried in an oven overnight at 105 °C. The solubility of the lignin copolymer was reported as a weight percentage (wt%), as this represents the amount of original lignin that was solubilized.^[53,60–62]

Charge Density

Approximately 0.2 g of the lignin-g-P(AM)-g-P(DADMAC) copolymer was dissolved in 20 g of water, and the solution was stirred for 2 h at 300 rpm. The suspension was then centrifuged at 1000 rpm for 5 min. The supernatant was collected and used for a charge density analysis.^[53,60–62] The charge density of the copolymer was measured using a particle charge detector, Müttek PCD 04 titrator (Arzbergerstrae, Herrsching, Germany) with PVS_K (0.005 mol L⁻¹) as the titrant. The reported data in this paper are the averages of three runs.

Elemental Analysis

Kraft lignin used in the study had a negligible nitrogen content. The nitrogen content found in the lignin-g-P(AM)-g-P(DADMAC) copolymer was attributed to the nitrogen present in the AM and DADMAC grafted onto the lignin backbone. Therefore, the nitrogen content of the copolymer corresponds to the grafting ratio of AM and DADMAC onto kraft lignin. The higher nitrogen content, the higher grafting ratio of the monomers on the lignin copolymer would be obtained. The elemental analysis was conducted on all samples to determine the overall nitrogen content of the copolymers and used to determine the optimal reaction conditions. The elemental analysis of the copolymer was performed using a Vario Micro Select elemental analyzer. The grafting ratio of AM and DADMAC to lignin was calculated using Equation (3) to obtain the total grafting ratio. The DADMAC content of the copolymer was determined from the charge density measurement, as DADMAC is the only part of the copolymer that contributes to the cationic charge density of the copolymer (a charge density of +1 meqg⁻¹ equals to 1 mmolg⁻¹ of DADMAC). By subtracting the nitrogen content of the copolymer associated with DADMAC from the overall nitrogen content of the copolymer, the nitrogen content of AM portion of the copolymer was determined [Eq. (4)]. The grafting ratio of acrylamide was then calculated using Equation (5):^[22,60]

$$\text{Overall nitrogen (mmol g}^{-1}\text{)} = \frac{\left(\frac{\%N}{14}\right) \times 1000}{100} \quad (3)$$

$$\text{Nitrogen content of AM (mmol g}^{-1}\text{)} = \quad (4)$$

$$\text{overall nitrogen (mmol g}^{-1}\text{)} - \text{nitrogen of DADMAC (mmol g}^{-1}\text{)}$$

$$\text{Grafting ratio} = \frac{M \times m}{1 - (M \times m)} \times 100 \quad (5)$$

where M is the nitrogen content of DADMAC or AM (mmolg⁻¹) in the copolymer and m is the molar weight of either acrylamide (0.071 mmolg⁻¹) or DADMAC (0.161 mmolg⁻¹).

Structural Analysis

Fourier Transform Infrared (FTIR)

The FTIR spectra of lignin, lignin-g-P(AM)-g-P(DADMAC), and P(AM)-g-P(DADMAC) were recorded using a Bruker Tensor 37 FT-IR spectrophotometer. Each spectrum was recorded in a transmittance mode with 32 scans in the frequency range of 600 and 4000 cm⁻¹ with a 4 cm⁻¹ resolution.

NMR Analysis

The structure of lignin, lignin-g-P(AM)-g-P(DADMAC), and P(AM)-g-P(DADMAC) were analyzed using ¹H NMR spectroscopy. The samples were dissolved in D₂O at pH 11. ¹H NMR spectra of these samples were recorded using an INOVA-500 MHz machine (Varian, USA) with a 45° pulse and a relaxation delay time of 1.0 s.

Activation Energy Analysis

The activation energy was determined by using the Arrhenius Equation [Eq. (6)]:

$$k = Ae^{-\Delta E/RT} \quad (6)$$

where k is the rate constant of the chemical equation, A is the collision frequency factor, ΔE is the activation energy of the copolymer, T is the absolute temperature, and R is the universal gas constant (8.314 J mol⁻¹). In one set of experiments, the copolymerization was performed under the optimal conditions in water with a constant monomer concentration of [lignin] = 0.26 × 10⁻³ M, [AM] = 1.05 × 10⁻³ M, [DADMAC] = 0.6 × 10⁻³ M and [Na₂S₂O₈] = 3.1 × 10⁻⁶ M at 85 °C, 80 °C, 75 °C, 70 °C and 60 °C for various time intervals. The reactions were monitored by ¹H NMR and the integrated area under the resonances originating from the allyl groups in both acrylamide and DADMAC monomers between 5–6 ppm were considered for copolymerization analysis. These values were then compared with the integrated area of an internal standard trimethylsilyl propionic acid-*d*.^[4] The consumption of monomer was then plotted against time and the slope was taken as the rate of copolymerization (k). Plotting $\ln k$ versus $1/T$ (K), a straight line was achieved with the slope representing the apparent activation energy of the copolymers.

Thermal Analysis

Thermogravimetric Analysis (TGA)

The TGA of lignin, lignin-g-P(AM)-g-P(DADMAC), and P(AM)-g-P(DADMAC) was performed by using a thermogravimetric analyzer, Instrument Specialist, i1000, in order to characterize the decomposition temperature of these samples. The samples were heated from room temperature to 700 °C at the heating flow rate of 10 °C min⁻¹ under nitrogen at the flow rate of 100 mL min⁻¹.^[61]

Differential Scanning Calorimetry (DSC)

The thermal properties of the unmodified lignin, lignin copolymer and synthetic copolymer were investigated using a differential scanning calorimeter, TA instrument, Q2000, and the standard cell RC mode of DSC was used for analysis. The samples were treated at 60 °C in an oven for removing moisture, and then 8–10 mg of the dried samples were loaded into Tzero aluminum pan and analyzed by using a heat/cool/heat method in a temperature range of –20 to 200 °C at 50 mL min⁻¹ in nitrogen: the heating and cooling rate were both controlled at 10 °C min⁻¹, and the second heating cycle (showed as exotherm up) was chosen for glass transition and melting point analyses. Glass transition temperatures (T_g) were obtained from the second heating cycle of DSC analysis.

Viscosity Analysis

The viscosity of lignin, lignin-g-P(AM)-g-P(DADMAC), and P(AM)-g-P(DADMAC) were measured at different concentrations and 25 °C using a Discovery hybrid DHR-2 rheometer with a concentric cylinder. The measurements were conducted in an aqueous solution at varying pH values and 25 °C. Varying concentrations of the lignin-g-P(AM)-g-P(DADMAC) copolymer were used at different pH values, and the shear rate was adjusted from 1 to 150 s⁻¹ every 2 min.

Flocculation of Kaolin Suspension

A photometric dispersion analyzer (PDA, PDA 3000, Rank Brothers, UK) connected to a dynamic drainage jar (DDJ) was used to examine the flocculation performance of lignin-g-P(AM)-g-P(DADMAC) copolymer for kaolin suspension. Firstly, 450 mL of deionized water was poured into the DDJ without any mesh. The system circulated water through PDA and DDJ for 10 min to reach a steady flow. Then, 50 mL of 2.5 wt% kaolin suspension was added whilst stirring at 200 rpm. The kaolin suspension was circulated in the system continuously at a flow rate of 50 mL min⁻¹. After reaching steady state, the lignin-g-P(AM)-g-P(DADMAC) copolymer, P(AM)-g-P(DADMAC), or lignin solution with 1 g L⁻¹ concentration was added into the DDJ at different dosages of 0.2–2.4 mg g⁻¹ to induce the flocculation process. The degree of flocculation was presented as a relative turbidity with respect to the turbidity of kaolin suspension.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: composite materials • copolymerization • flocculants • green chemistry • kraft lignin

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