Research Article

Study on the Preparation and Application of Lignin-Derived Polycarboxylic Acids

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Lignin was oxidized by NaOCl, and the main product of the reaction was named lignin-derived polycarboxylic acids (LPCAs). The effect of the reaction conditions was studied. With the mix ratio [n(NaOCl)/m(lignin)] increasing, the content of carboxyl of LPCAs increased. When the reaction temperature or the reaction time increased, the content of carboxyl decreased in different degrees. After the oxidation by NaOCl, the content of hydroxyl and methoxyl of lignin decreased, and the molecular weight of lignin decreased as well. The FT-IR and ^{1}H-NMR spectrum of lignin suggested that the benzene rings of lignin were disrupted after the oxidation. A possible mechanism of the oxidation of lignin by sodium hypochlorite is supposed to briefly demonstrate the reason that the benzene rings were disrupted and the content of carboxyl increased. Finally, an application example shows that LPCAs can strengthen the mechanical properties of waterborne polyurethane elastomers.

1. Introduction

Lignin is the second most abundant natural polymer after cellulose [1]. It plays an important role in plants, providing rigidity to strengthen the structures of cell walls and resistance to microbial attack [2]. Through different isolation processes, the original lignin can be converted to other types such as kraft lignin, lignosulfonate, organosolv lignin, and steam explosion lignin [3]. The chemical structure of lignin consists of three kinds of phenylpropane units: *p*-hydroxyphenyl unit (H unit, from *p*-coumaryl alcohol), guaiacyl unit (G unit, from coniferyl alcohol), and syringyl unit (S unit, from sinapyl alcohol) [4]. These three alcohol monomers are also called monolignols. The content of each monolignol in lignin depends on the plant species [5]. Via radical coupling reactions, the monolignols are linked together to form lignin, which gives lignin a complex three-dimensional structure [6].

Generally, lignin exhibits a certain color due to its chromophores [7]. In some cases, the color of lignin is unnecessary and needs to be reduced. For example, in papermaking industry, after the bleaching process, the color of lignin is reduced remarkably so as to obtain white paper [8].

NaOCl, a common bleaching reagent, has been used in the bleaching process for a long time. By the oxidization effect, NaOCl disrupts the chromophores of lignin to reduce its color. The reactions during NaOCl bleaching on lignin have been demonstrated roughly in previous studies [9], but there are still some aspects which are worth being discussed further, e.g., the variance of the content of functional groups of lignin.

Although the annual production of lignin is very large in the biosphere, lignin is highly underutilized [10]. In pulp mills, many kinds of oxidative reagents, such as NaOCl, ClO$_2$, and H$_2$O$_2$, have been used to oxidize lignin in the bleaching process [8]. However, lignin and its derivative reaction products are usually discarded with waste water, which leads to the waste of resources and the pollution of the environment. To avoid these problems, the utilization of lignin is very necessary. As oxidation is a kind of chemical modification method of lignin, the oxidization products of lignin can be obtained under certain reaction conditions and be utilized in some aspects [11, 12]. For example, kraft lignin could be oxidized by H$_2$O$_2$, and the oxidization products were employed as a dispersant for kaolin suspensions [13]. Besides oxidization, other modification methods of lignin

are useful as well [14]. For instance, lignin can be modified by phenolation, Mannich reaction, and oxypropylation to prepare lignin-based phenol-formaldehyde resins, cationic surfactants, and lignin-based rigid polyurethane foams, respectively [15–17].

In this work, NaOCl was applied to oxidize lignin because the oxidation reaction by NaOCl can be carried out under mild conditions in labs. The main product of the reaction was named lignin-derived polycarboxylic acids (LPCAs). We studied the effect of the reaction conditions of the oxidation. We used several instrumental analysis methods to study the changes of lignin before and after the oxidation. Then, we supposed a possible mechanism of the oxidation of lignin by NaOCl to briefly explain some experimental facts. Finally, we presented an application example of LPCAs in the field of waterborne polyurethane.

2. Materials and Methods

2.1. Materials. Steam explosion lignin was donated by Jilin KAIYU Biomass Development and Utilization Co., Ltd. All the other reagents used in this study were purchased in China and were of analytical grade. The concentration of NaOCl solution was calibrated according to the China National Standard GB 19106–2003.

2.2. Oxidation of Lignin. 5.00 g steam explosion lignin and 150 mL distilled water were placed into a 500 mL three-neck round-bottom flask. The mixture in the flask was heated to 30°C in a water bath and was stirred mechanically. Then, NaOCl solution was added at a mix ratio [n(NaOCl)/m(lignin)] of 12 mmol g^{-1} in 10 min. The total time of stirring was 30 min. Afterwards, 6 mol L^{-1} HCl was added to achieve a pH of 2 (using pH test strips with a range of 1 to 14). The precipitate was centrifuged, washed once with distilled water, dried at 80°C for 24 h, and ground to obtain LPCAs. To compare the effect of oxidative modification, some amount of acid-precipitated lignin was prepared from steam explosion lignin.

2.3. Product Characterization

2.3.1. Determination of Carboxyl Groups. The content of carboxyl was determined by titration analysis [18]. 200 mg LPCAs and 20 mL 0.4 mol L^{-1} calcium acetate solution were mixed in a 100 mL round-bottom flask. The mixture was heated at 85°C for 30 min. Then, it was cooled to room temperature and filtrated. The filtrate was transferred into a 50 mL volumetric flask and was diluted by distilled water to reach the graduation. 20 mL distilled water and 10 mL solution in the volumetric flask were added into a 250 mL conical flask. 0.05 mol L^{-1} NaOH solution was used in titration with phenolphthalein as the indicator. Blank test was performed meanwhile, in which the sample was not used. The content of carboxyl was calculated according to the following equation:

$$w(\text{COOH}) = \frac{(V_1 - V_0) \times c \times 5 \times 45.018}{m} \times 100\%, \quad (1)$$

where V_1 and V_0 are the volume of NaOH solution that the sample and the blank test consumed separately; c is the concentration of the NaOH solution; 5 is the conversion factor, i.e., 50 mL/10 mL; 45.018 is the molar weight of carboxyl; m is the weight of the sample in the round-bottom flask.

2.3.2. Determination of Other Functional Groups. The content of methoxyl and aliphatic hydroxyl was determined according to *Methods in Lignin Chemistry* [19]. The content of phenolic hydroxyl was analyzed using the Folin–Ciocalteu reagent [20].

2.3.3. Instrumental Analysis of Lignin. The infrared spectrum of lignin was obtained from Shimadzu FT-IR 8400S Fourier-transform infrared (FT-IR) spectroscopy. The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum of lignin was analyzed by AVANCE III 500, whose frequency was 500 MHz. The solution of lignin was d_6-DMSO, and the weight of lignin was 10 mg. Elemental analysis of lignin was conducted with a CHNS-O elemental analyzer Elementar Vario Micro Cube to determine the content of carbon, hydrogen, nitrogen, sulfur, and oxygen. The molecular weight of lignin was measured by gel permeation chromatography (GPC) using the Agilent PL-GPC 220. The temperature of the column was 70°C. The type of the column was PLgel. The solvent of lignin was DMF (*N,N*-dimethylformamide, chromatographic pure). PS (polystyrene) was used for calibration. The type of the detector was the differential refractive index detector.

3. Results and Discussion

3.1. Effects of the Reaction Conditions on the Yield and the Content of Carboxyl. The reaction conditions of the oxidation of lignin, including the mix ratio, reaction temperature, and reaction time, were investigated, respectively. The yield and the content of carboxyl of LPCAs were both determined.

3.1.1. Mix Ratio. Figure 1 shows the effect of the mix ratio on the yield and the content of carboxyl of LPCAs. The reaction temperature was set as 30°C, and the reaction time was set as 30 min. The mix ratio of 0 mmol/g stands for acid-precipitated lignin. When the mix ratio was 4 mmol/g, the amount of NaOCl was relatively small. The effect of the oxidation was not evident, so that the content of carboxyl did not increase and other reactions might increase the weight of lignin. With the mix ratio increasing from 4 mmol/g to 20 mmol/g, the yield decreased while the content of carboxyl increased. It is supposed that lignin was oxidized by NaOCl to the products with smaller molecular weight. Some of the products were the final products of the oxidation (CO_2 and H_2O). Some were still organic compounds but could not be precipitated by HCl because their molecular weight was too
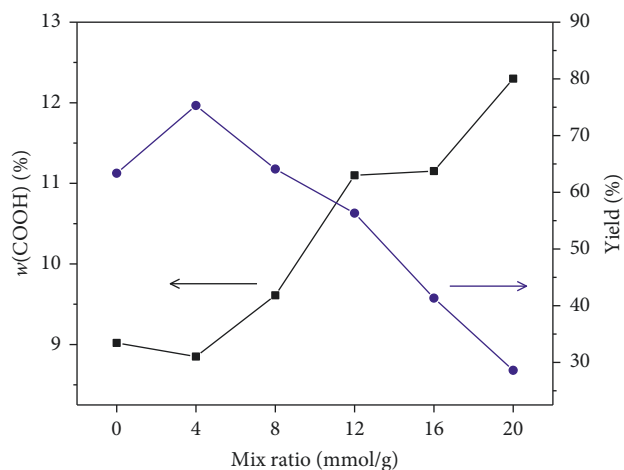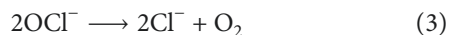
FIGURE 1: Effect of the mix ratio on the yield and the content of carboxyl of LPCAs.

FIGURE 2: Effect of the reaction temperature on the yield and the content of carboxyl of LPCAs.

small, and hence, the yield of the main product of the reaction (i.e., LPCAs) decreased. Under the oxidation by NaOCl, some functional groups might be transformed into carboxyl groups, causing the increase of the content of carboxyl.

3.1.2. Reaction Temperature. Figure 2 shows the effect of the reaction temperature on the yield and the content of carboxyl of LPCAs. The mix ratio was set as 12 mmol/g, and the reaction time was set as 30 min. As the temperature increased from 30°C to 80°C, the yield increased slowly in general, but the content of carboxyl decreased evidently. The reason is probably the decomposition of OCl^- ions. When the solution was heated to a high temperature, OCl^- was unstable and would disproportionate into Cl^- and ClO_3^-:

$$3OCl^- \longrightarrow 2Cl^- + ClO_3^- \qquad (2)$$

Cl^- is not oxidative, while the oxidative effect of ClO_3^- is weaker than OCl^- in water solution. Besides, another decomposition reaction of OCl^- ions would occur as well. Both the solution of steam explosion lignin and the solution of NaOCl are basic, so that the mixture of the two was basic at the beginning. OCl^- would decompose in a basic and high temperature environment, forming Cl^- and O_2 [21]:

$$2OCl^- \longrightarrow 2Cl^- + O_2 \qquad (3)$$

In conclusion, these two reactions can both lead to the decomposition of OCl^-. With the reaction temperature increasing, the effective concentration of NaOCl solution decreased, and hence, the oxidative effect of NaOCl decreased. As a result, the content of carboxyl of LPCAs decreased.

3.1.3. Reaction Time. Figure 3 shows the effect of the reaction time on the yield and the content of carboxyl of LPCAs. The mix ratio was set as 12 mmol/g, and the reaction temperature was set as 30°C. The reaction time of 0 min stands for acid-precipitated lignin. With the reaction time
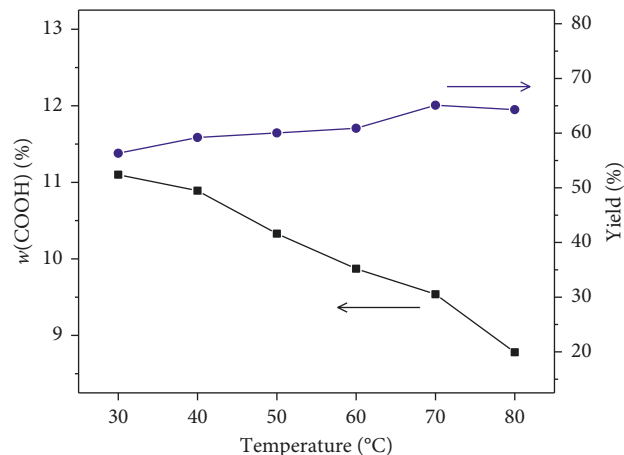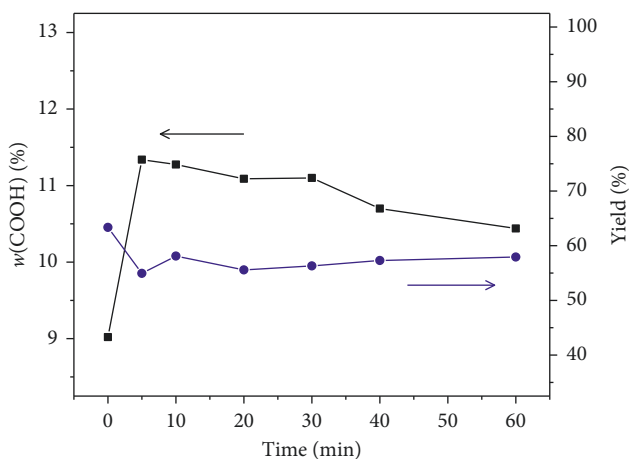

FIGURE 3: Effect of the reaction time on the yield and the content of carboxyl of LPCAs.

increasing, the yield varied in a narrow range while the content of carboxyl decreased slowly. It is suggested that the reaction of lignin and NaOCl was relatively fast. When the reaction time increased, the decarboxylation of LPCAs might occur, causing the decrease of the content of carboxyl.

3.2. Spectral Analysis of Lignin

3.2.1. FT-IR Spectrum of Lignin. Figure 4 shows the FT-IR spectrum of LPCAs which were prepared under different mix ratios. From the top (a) to the bottom (f), the mix ratios are 0, 4, 8, 12, 16, and 20 mmol/g separately. 1506 and 1597 cm^{-1} are the absorption peaks of the skeleton vibration of aromatic rings. 1717 cm^{-1} is the absorption peak of the telescopic vibration of C=O bond. With the amount of NaOCl increasing, the absorption peaks of the skeleton vibration of aromatic rings weakened, suggesting that the benzene rings of lignin were disrupted. Meanwhile, the absorption peak of the telescopic vibration of C=O bond strengthened, which was corresponding with the result in Section 3.1.1.
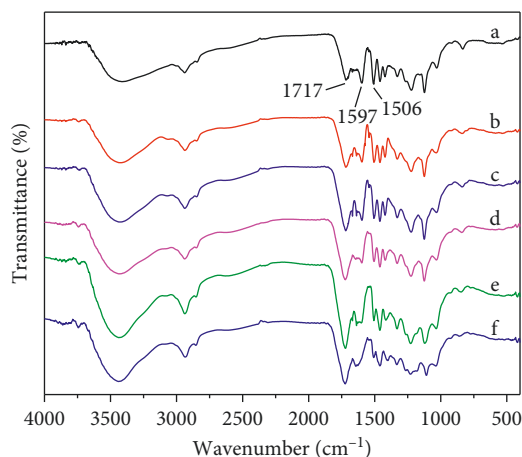
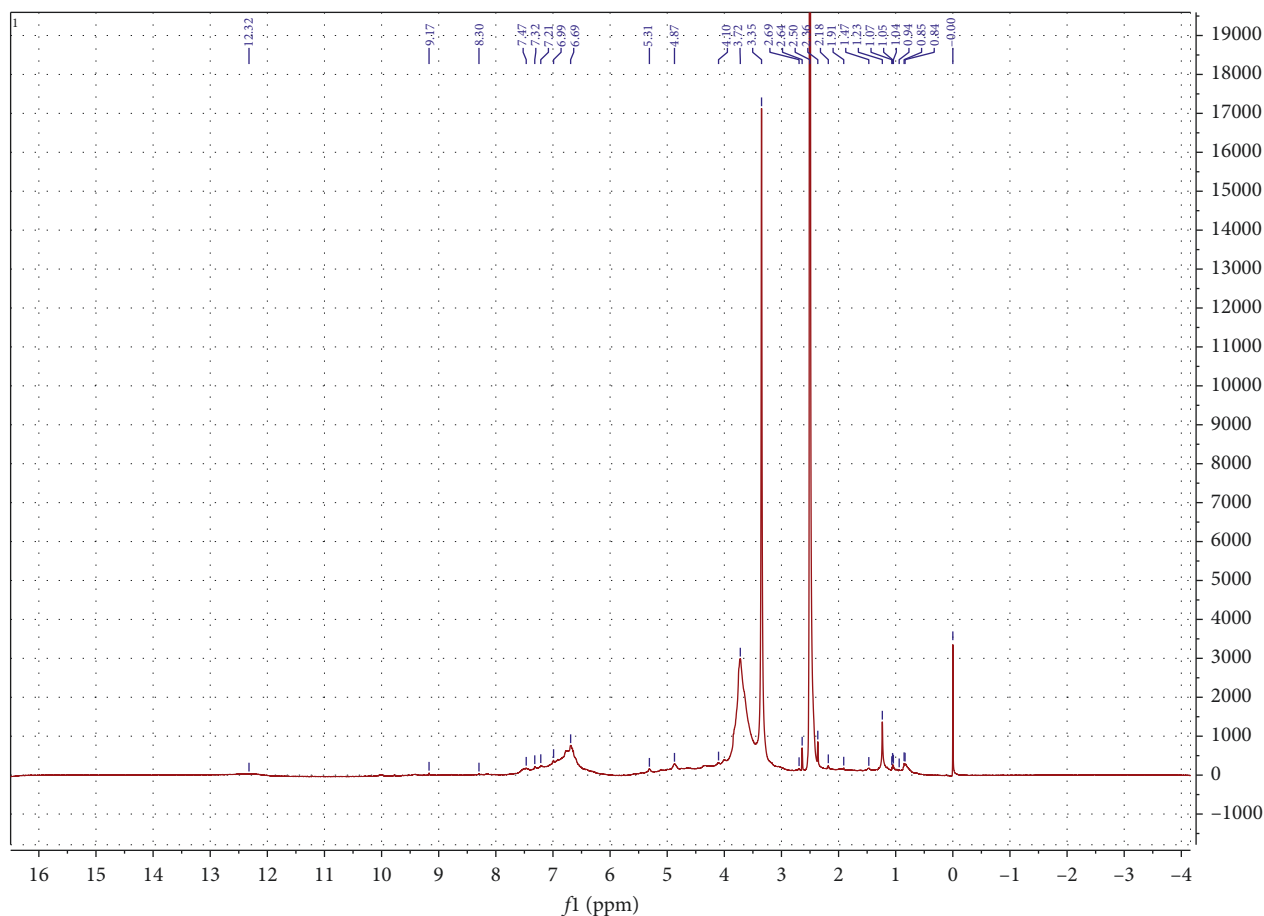Figure 4: The FT-IR spectrum of different kinds of LPCAs.

Figure 5: ^{1}H-NMR spectrum of acid-precipitated lignin.

3.2.2. ^{1}H-NMR Spectrum of Lignin. Figures 5 and 6 are the ^{1}H-NMR spectrum of acid-precipitated lignin and LPCAs (prepared under a condition of 12 mmol/g, 30°C, and 30 min), respectively. The δ_H value of 2.50 is assigned to the ^{1}H atoms of DMSO. The δ_H values of 3.35 and 3.72 are assigned to the ^{1}H atoms of methylene (-CH$_2$-) and methine (=CH-), respectively, which are connected to benzene rings.

The δ_H values between 6.69 and 7.47 are assigned to the ^{1}H atoms of benzene rings. After the oxidation by NaOCl, the signals of ^{1}H atoms of methylene and methine weakened. Besides, some signals of ^{1}H atoms of benzene rings weakened, and some disappeared. Since the amount of acid-precipitated lignin and the amount of LPCAs were the same (i.e., 10 mg), the weaker the signal intensity of ^{1}H
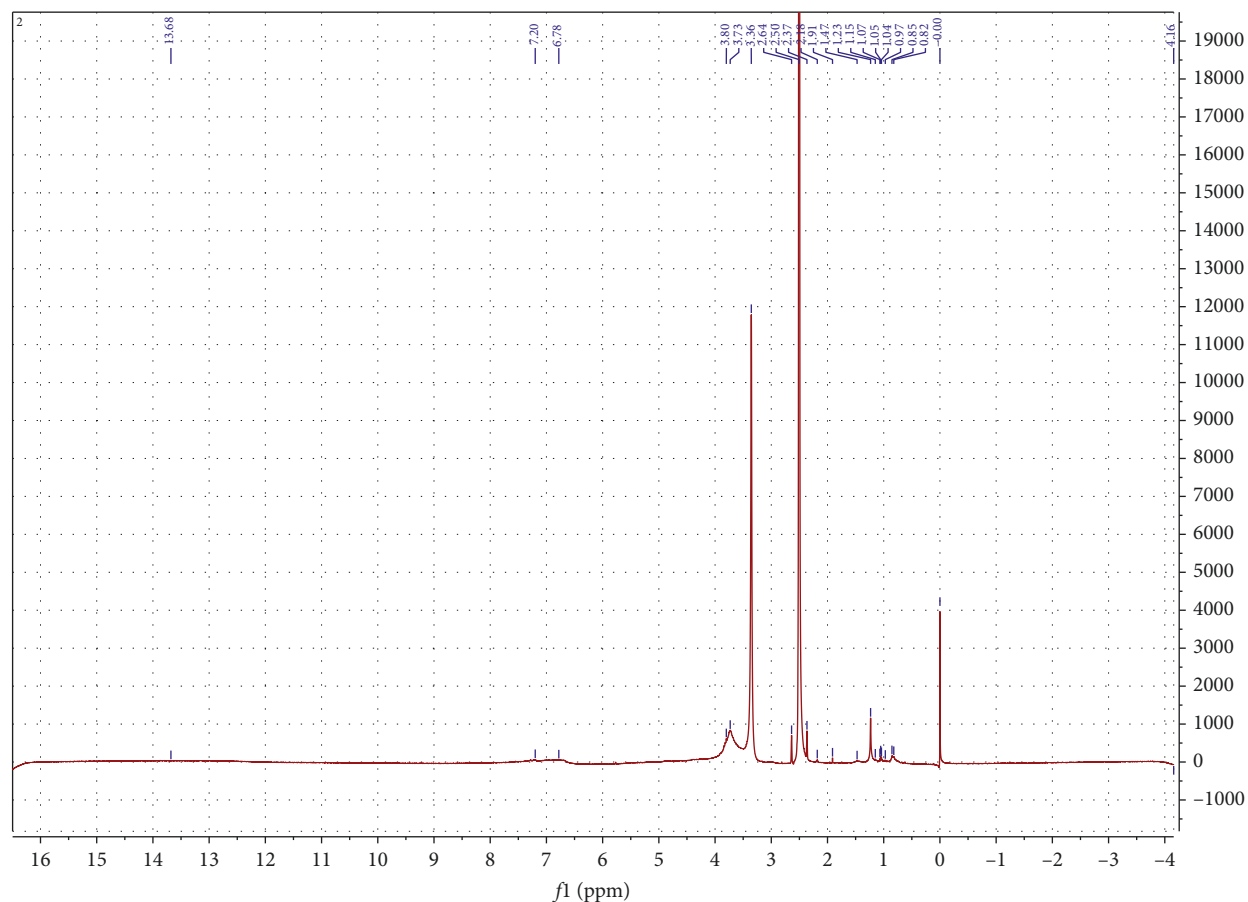
FIGURE 6: ^{1}H-NMR spectrum of LPCAs.

atoms of benzene rings, the less the amount of benzene rings. Therefore, it is suggested that the benzene rings of lignin might be disrupted by NaOCl.

3.3. Other Characterization Results of Lignin.
In order to further study the changes of lignin after oxidation by NaOCl, acid-precipitated lignin and LPCAs, which were prepared under a condition of 12 mmol/g, 30°C, and 30 min, were used to perform other characterizations.

3.3.1. The Content of Functional Groups of Lignin.
Table 1 shows the change of the content of some functional groups of lignin before and after the oxidation by NaOCl. After the oxidation, the content of methoxyl, aliphatic hydroxyl, and phenolic hydroxyl decreased, while the content of carboxyl increased. The decrease of the content of phenolic hydroxyl suggests that the benzene rings of lignin might be disrupted by NaOCl. Meanwhile, NaOCl has a certain degree of demethylation effect on lignin, and NaOCl can fully oxidize aliphatic hydroxyl of lignin.

3.3.2. The Content of 5 Elements of Lignin.
Table 2 shows the analysis result of the content of 5 elements of lignin, which are C, H, N, S, and O. The content of oxygen was calculated based on the content of the rest 4 elements. After the oxidation by

TABLE 1: The determination result of the content of functional groups of lignin.

	Acid-precipitated lignin (%)	LPCAs (%)
-COOH	9.02 ± 0.03	11.10 ± 0.03
-OH (aliphatic)	0.19 ± 0.03	N/A
-OH (phenolic)	4.23	1.50
-OCH$_3$	8.32 ± 0.03	4.90 ± 0.03

NaOCl, the content of oxygen increased while the content of the rest 4 elements decreased, which was corresponding with the fact that the content of carboxyl increased.

3.3.3. The Molecular Weight of Lignin.
Table 3 shows the GPC characterization result of lignin. M_n and M_w are number-average molecular weight and weight-average molecular weight, respectively. After the oxidation by NaOCl, the molecular weight of lignin decreased obviously, and the dispersion index M_w/M_n also decreased, indicating that the chain structure of lignin was affected greatly by NaOCl. Some phenylpropane units were disrupted or separated from the main chain structure of lignin. Thus, the molecular weight of lignin decreased.

3.4. A Possible Mechanism of the Oxidation of Lignin by NaOCl.
In order to demonstrate the reason that the benzene

TABLE 2: The analysis result of the content of 5 elements of lignin.

	Acid-precipitated lignin (%)	LPCAs (%)
C	60.90	47.93
H	5.70	4.28
N	1.07	0.74
S	0.24	0.27
O	32.09	46.78

TABLE 3: The GPC characterization result of lignin.

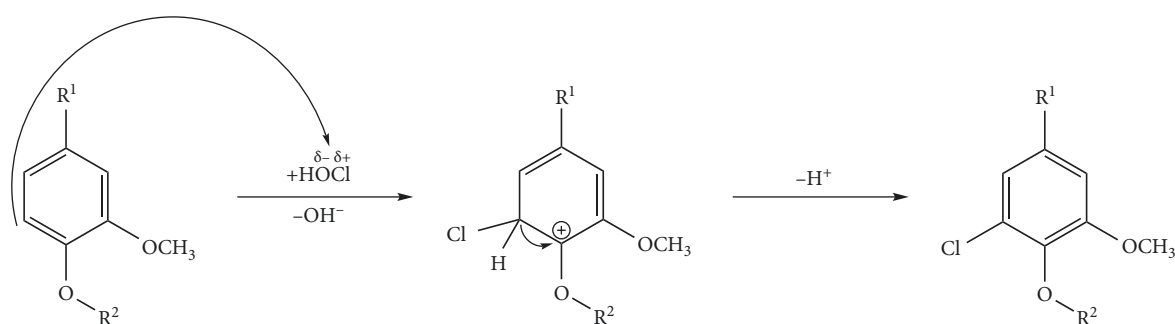|	Acid-precipitated lignin	LPCAs
M_n	2.91×10^4	1.23×10^4
M_w	3.48×10^4	1.25×10^4
M_w/M_n	1.12	1.01

FIGURE 7: A possible mechanism of the oxidation of lignin by NaOCl.

rings were disrupted and the content of carboxyl increased, a possible mechanism of the oxidation of lignin by NaOCl is briefly supposed as follows, and the relevant reactions are shown in Figure 7–9. For convenience, the guaiacyl unit of lignin is taken as the example for explanation. As HOCl is a weak acid, OCl⁻ ions will be hydrolyzed into HOCl in water. The electronegativity of O is 3.44 while Cl is 3.16 [22]. Because the electronegativity of O is larger than Cl, in the HOCl molecule, the O atom is negatively charged and the Cl atom is positively charged. HOCl can act as an electrophile reagent to attack the ortho positions of the -OR groups of lignin. Then, H⁺ ions are eliminated from the intermediate, and the chlorination products of lignin are formed. It is well known that the relative atom weight of Cl is larger than H. When Cl atoms substitute H atoms, the molecular weight of lignin will increase while the content of other functional groups will decrease. Therefore, when the mix ratio is relatively small (e.g., 4 mmol/g), the yield of LPCAs increases and the content of carboxyl decreases compared with acid-precipitated lignin.

As the reaction continues, the ether bonds of lignin will be affected. The Ph-O-CH₃ bonds will break down into phenolic hydroxyl and methanol [23]. Considering that the molecular weight of lignin can decrease by more than half, the cleavage of the chain structure of lignin can occur within the chain. Thus, the Ph-O-R bonds (e.g., the β-O-4 linkages) may break up, forming new phenolic hydroxyl groups [24, 25]. The other fragments of lignin are denoted by ROH, which can also react with NaOCl and undergo a similar reaction process described above. As a result, the intermediate products with an o-benzenediol structure are formed, and the molecular weight of lignin decreases greatly.

When the amount of NaOCl increases, the oxidation reaction will continue with various processes. The main intermediate products with an o-benzenediol structure might be oxidized to the intermediate products with a 1,2,3-triketone structure. The 1,2,3-triketone structure can be oxidized into carboxyl and CO₂ by NaOCl. Finally, more carboxyl groups are formed, and the benzene rings are totally disrupted.

3.5. An Application Example of LPCAs. LPCAs can be introduced into waterborne polyurethane (WPU) elastomers to strengthen the mechanical properties of WPU elastomers [26]. In this application example, LPCAs were prepared under a condition of 12 mmol/g, 30°C, and 30 min. When the loading of LPCAs (based on polypropylene glycol-1000) was 2.5 wt.%, the mechanical properties of the LPCA-WPU elastomer were the best. The enhancement mechanism was supposed as the interactions between LPCAs and the soft segments of WPU. The data of the mechanical properties of the blank WPU elastomer and the LPCA-WPU elastomer are shown in Table 4.

4. Conclusion

Lignin was oxidized by NaOCl, and the effect of the reaction conditions was studied. With the mix ratio increasing, the
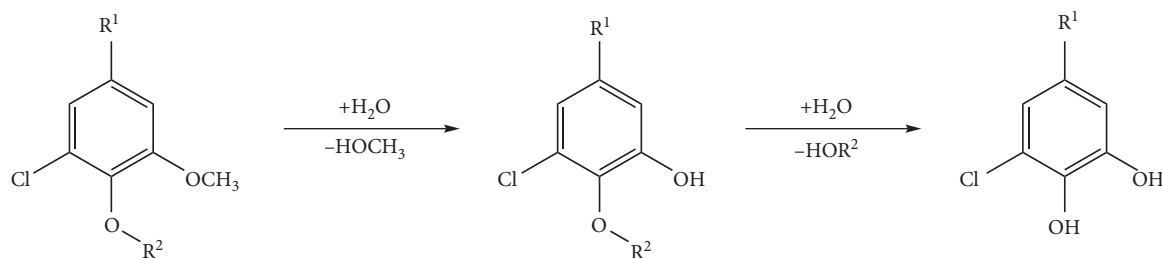
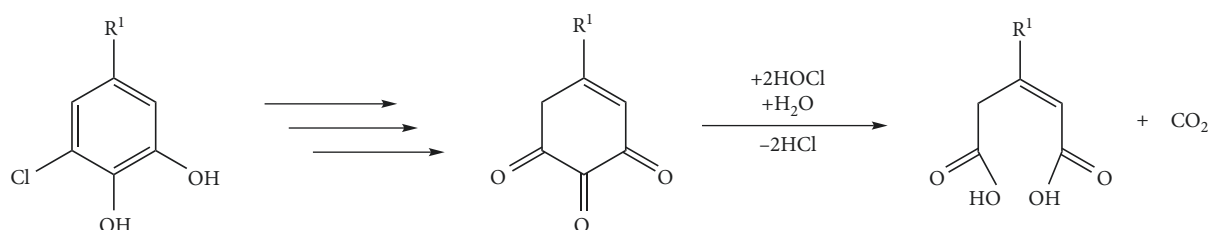FIGURE 8: A possible mechanism of the oxidation of lignin by NaOCl.

FIGURE 9: A possible mechanism of the oxidation of lignin by NaOCl.

TABLE 4: The mechanical properties of WPU elastomers.

	Blank WPU elastomer	LPCA-WPU elastomer
LPCAs loading	0 wt.%	2.5 wt.%
Tensile stress at 100% strain (MPa)	2.96 ± 0.12	6.97 ± 0.37
Tensile stress at 300% strain (MPa)	5.16 ± 0.07	9.83 ± 0.49
Modulus of elasticity in tension (MPa)	22.2 ± 1.6	107.1 ± 6.1
Tensile strength (MPa)	13.48 ± 1.73	18.60 ± 1.37
Tensile strain at break (%)	736 ± 108	707 ± 31

yield of LPCAs decreased and the content of carboxyl increased. When the reaction temperature increased, the content of carboxyl decreased evidently for the decomposition of OCl^- ions. When the reaction time increased, the content of carboxyl decreased slightly. The FT-IR and ^{1}H-NMR spectrum of lignin suggests that the benzene rings of lignin were disrupted after the oxidation. The determination result of the content of functional groups of lignin shows that after the oxidation by NaOCl, the content of hydroxyl and methoxyl decreased. The GPC characterization result indicates that the molecular weight of lignin decreased obviously. A possible mechanism of the oxidation of lignin by NaOCl is supposed to briefly demonstrate these experiment results. The cleavage of the Ph-O-R bonds (e.g., the β-O-4 linkages) leads to the decrease of the molecular weight mostly. The disruption of the benzene rings contributes to form new carboxyl groups. Therefore, lignin was oxidized by NaOCl accompanied by its degradation. Finally, an application example shows that LPCAs can strengthen the mechanical properties of WPU elastomers.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

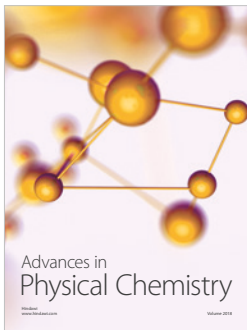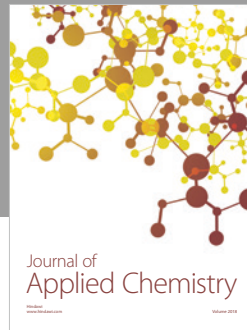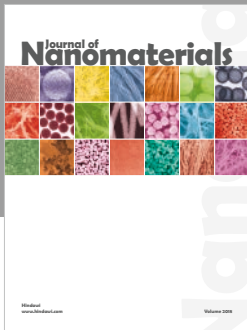The authors declare that they have no conflicts of interest.

Acknowledgments

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