

# Lignin — a promising biomass resource

YONG QIAN, HONGMING LOU, WEIFENG LIU, DONGJIE YANG,  
XINPING OUYANG, YUAN LI, AND XUEQING QIU

**ABSTRACT:** Lignin, the second most abundant component in plants, is a class of complex aromatic polymer. Industrial lignin is a major byproduct of pulp and paper production and biorefineries, with more than 50 megatons generated annually. However, more than 98% of industrial lignin is either burned as fuel or discharged as wastewater, causing serious environmental pollution. From a sustainable feedstock perspective, finding additional high-volume and high-value applications for lignin is an extremely important and long-term pursued objective. Thus, lignin resources deserve to be further exploited as biorenewable raw materials for energy-saving and low-carbon polymer production. Inspired by the natural three-dimensional structure, excellent ultraviolet-blocking and antioxidant properties of lignins, the authors have focused their research on lignin-based biorenewable resources. This review summarizes research achievements of the recent decade. Progress has been made in several aspects, such as nonionic and amphoteric lignin-based surfactants, lignin-based functional materials, lignin-based photoelectric materials, lignin-based resins and polymer composites, and catalytic depolymerization of lignin.

**Application:** This review summarizes recent research and provides some novel strategies for the application and understanding of lignin.

In response to environmental problems and energy concerns, the development and use of biomass energy has aroused wide attention [1]. Lignin, a biopolymer derived from trees and crops, is the second-most abundant component in the plants [2]. Historically, the majority of lignin was burned as fuel or used in low-value applications such as activated carbons, [3-5] dispersants [6-10], and adhesive agents [11-13]. In the past few years, lignin has risen to stardom because of its remarkable properties. Scientists have noticed that high-value use of lignin, based on its inherent features, is the most effective and green strategy [14,15].

Qiu and coworkers have dedicated more than 20 years researching value-added uses of industrial lignin. After chemical modifications of industrial lignin by sulfonation, sulfomethylation, carboxylation, amination, and so on, they developed a series of lignin-based macromolecular amphiphilic surfactants successfully used in areas such as construction, agriculture, and energy [6-10]. To counter the competition of surfactants derived from oil in the last 10 years, they developed a new lignin adjuvant to enhance the enzymatic hydrolysis of cellulose. They also developed methods to depolymerize lignin into aromatic chemicals and explored new applications in cosmetics, photoelectric, and polymer areas.

## LIGNIN FOR ENHANCING ENZYMATIC HYDROLYSIS

In the production of cellulosic ethanol, lignin in lignocellulosic substrates has significant effects on the enzymatic hydrolysis of cellulose [16-18]. Previous studies have suggested that lignin would affect the activity of cellulase and then inhibit the enzymatic hydrolysis of cellulose [19,20]. Several methods have been developed to improve the enzymatic hydrolysis of

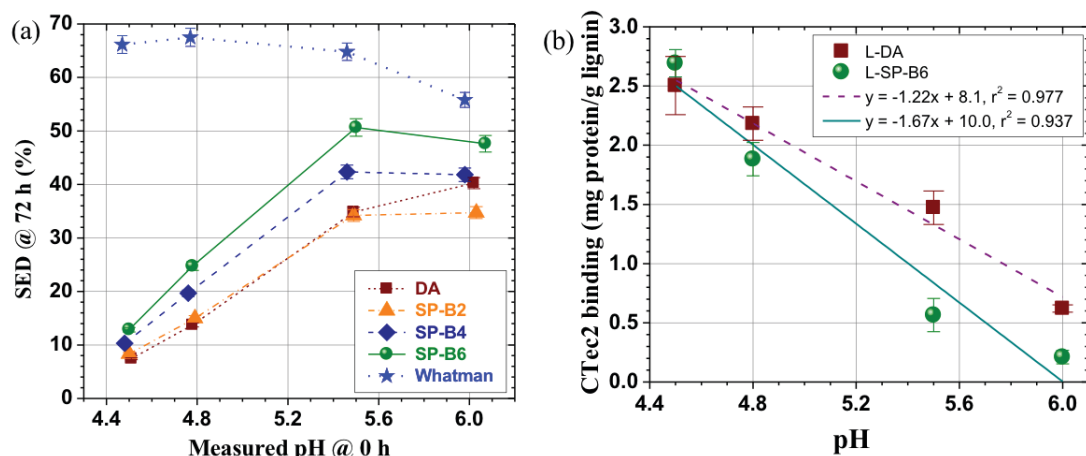
cellulose. Those include reducing the non-productive adsorption of cellulase on lignin and covalent or noncovalent modification of lignin [16,21]. Meanwhile, enzymatic hydrolysis has generated a large amount of enzymatic hydrolysis lignin (EHL). Recycling and improving the efficiency of using EHL is an urgent problem to be solved [22]. In that regard, some new methods and technologies to enhance the enzymatic hydrolysis and to increase the use of EHL are introduced.

### Enhancing the enzymatic hydrolysis of lignocelluloses by adjusting pH

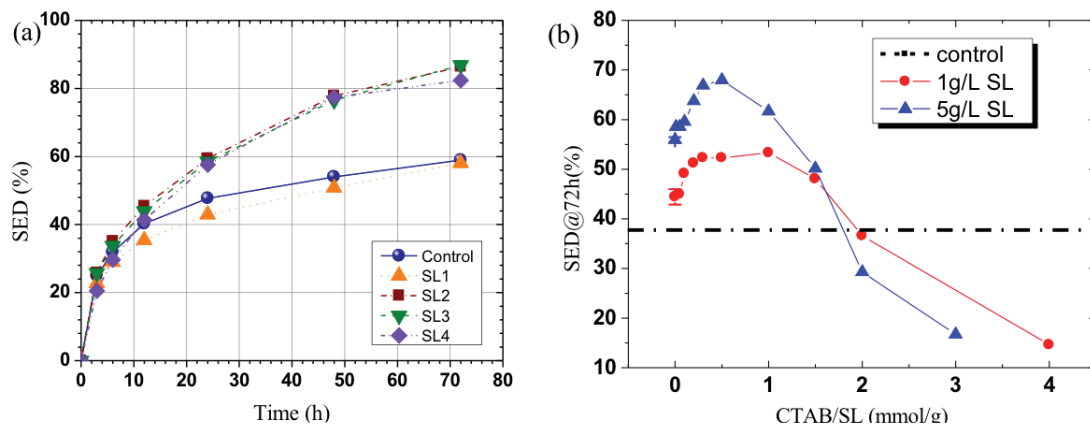
Cellic CTec2 (Novozymes; Bagsvaerd, Denmark) cellulase exhibited best activity at the pH value of about 4.8 [23], but lignocellulosic substrates had higher substrate enzymatic digestibility (SED) at pH 5.5~6.0 (**Fig. 1a**). Especially when softwood substrates were pretreated by sulfuric acid, the SED value at pH = 5.5 was one time higher than that at pH = 4.8 [24]. By comparison, it was found that higher pH could increase the hydrophilicity and negativity of lignin in lignocellulosic substrates, thereby weakening the affinity of lignin to cellulase and reducing the non-productive adsorption of cellulase on lignin [25]. Simultaneously, the higher pH increased the negative charge of cellulase and the electrostatic repulsion between lignin and cellulase (**Fig. 1b**). Because the higher pH helps reduce the cost of enzymatic hydrolysis and fermentation, it is of great value to improve the enzymatic efficiency by simply changing the pH.

### Sodium lignosulfonate in the enzymatic hydrolysis of lignocelluloses

Sulfite pretreatment to overcome recalcitrance of lignocelluloses (SPORL) is a recently developed method for pretreat-



1. (a) Effects of pH on enzymatic saccharification of four lignocelluloses and Whatman paper, and (b) effects of pH on CTec2 binding to enzymatic hydrolysis lignin residues (SED = substrate enzymatic digestibility).

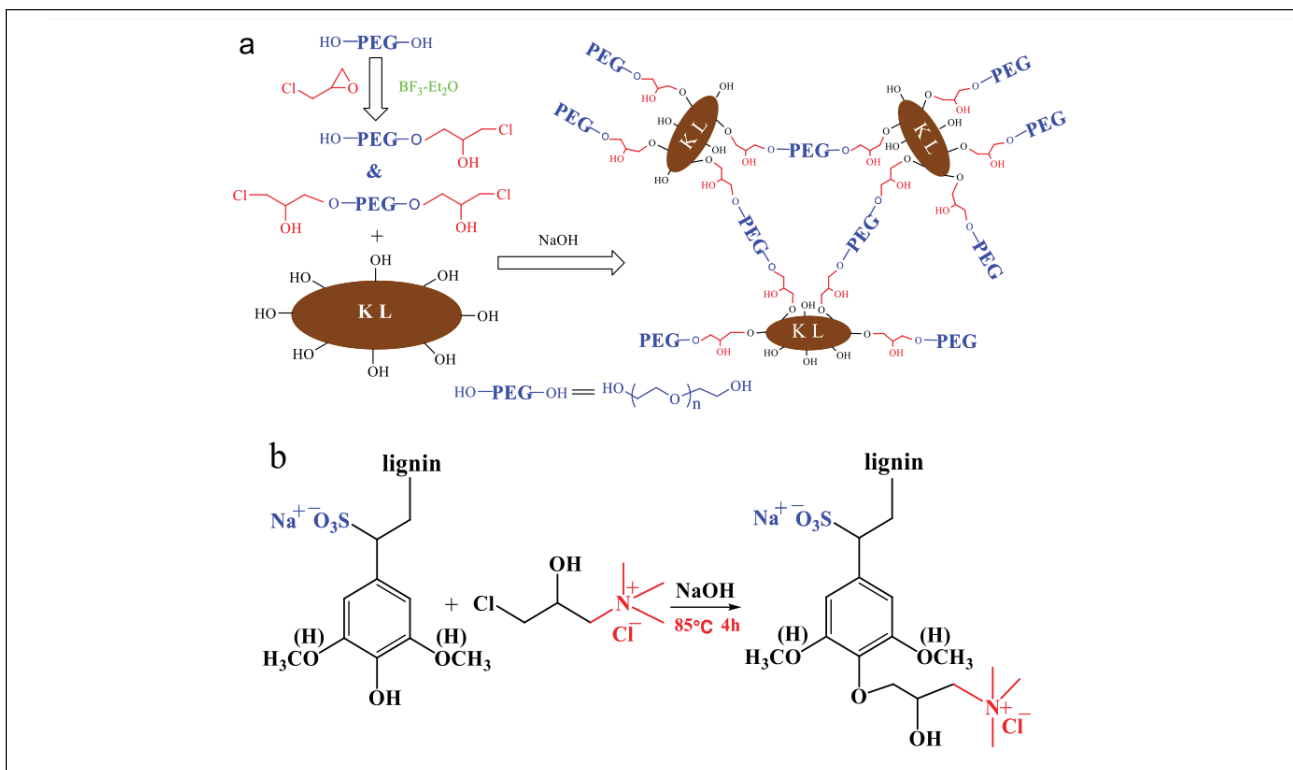


2. (a) Effects of different sodium lignosulfonate (SL) fractions on the SED of Whatman paper at CTec2 enzyme loading of 10 FPU/g glucan, and (b) effect of SL-cetyltrimethyl ammonium bromide (CTAB) on the SED of lignocelluloses.

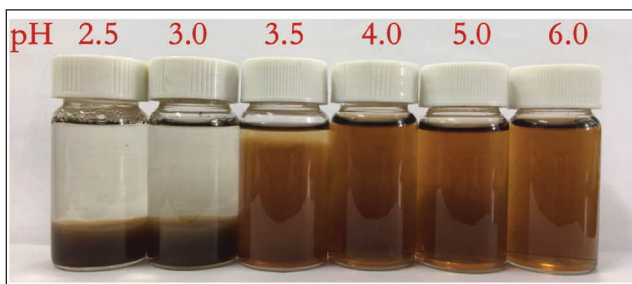
ment of lignocelluloses, which facilitated the biotransformation of softwoods. Lignocelluloses can release water-soluble sodium lignosulfonate (SL) when pretreated by SPORL. SLs with small molecular weight and high sulfonation have very good effects on the enzymatic hydrolysis of different lignocellulosic substrates [4]. **Figure 2a** shows the effects of different SL fractions on the SED of Whatman paper. Adding 5 g/L of SL2 or SL3 increases the SED of filter paper from 59% to 85% [26]. Further study found that SL compounded with cationic cetyltrimethyl ammonium bromide (CTAB) could further improve the SED of lignocelluloses (Fig. 2b) [27]. CTAB was thought to increase the adsorption of SL on lignin to form more effective steric hindrance and reduce the non-productive adsorption of cellulase on lignin by neutralizing the negative charge of SL.

## Modification of EHL and its use in enzymatic hydrolysis

To improve the value of using insoluble lignin, lignin-based polyoxyethylene ether (enzymatic hydrolysis lignin and polyethylene glycol; EHL-PEG) and pH-responsive lignin amphoteric surfactant (TCSL-N25) were synthesized by modifying the EHL (**Fig. 3**), and their application in enzymatic hydrolysis was studied. The results showed that EHL-PEG could effectively reduce the particle size of cellulase while reducing the non-productive adsorption of cellulase on lignin compared with PEG [28]. TCSL-N25 had a sensitive pH response (**Fig. 4**); it was dissolved at pH 4.5~6.0, which was for normal enzymatic hydrolysis and precipitated when pH was less than 3.5. When it precipitated, it could recover the cellulase in solution through electrostatic forces. The addition of 2 g/L of



**3. Synthesis mechanisms of (a) enzymatic hydrolysis lignin-PEG copolymer and (b) pH-responsive lignin amphoteric surfactant (TCSL-N25).**



**4. The solubility of TCSL-N25 changes with pH. The concentration of TCSL-N25 is 2 g/L.**

TCSL-N25 could increase the SED of eucalyptus pretreated by dilute acid from 33.4% to 83.2% at a cellulase loading of 5 FPU/glucan. After enzymatic hydrolysis, more than 85% of TCSL-N25 and 30% of cellulase activity could be recovered by adjusting the pH of enzymatic hydrolysate to 3.0.

Generally, pretreatments of lignocelluloses are operated under high temperature and low pH conditions [29]. Furfural and 5-hydroxymethyl furfural are formed from hexose degradation [30], and lignin is degraded into cinnamic acid, vanillin, and other kinds of phenols [31]. These degradation products will aggregate in pre-hydrolysates and inhibit the enzymatic hydrolysis and fermentation of lignocelluloses. Therefore, the pre-hydrolysates usually must be separated before enzymatic hydrolysis and fermentation [32].

Effects of EHL on the adsorption and removal of the in-

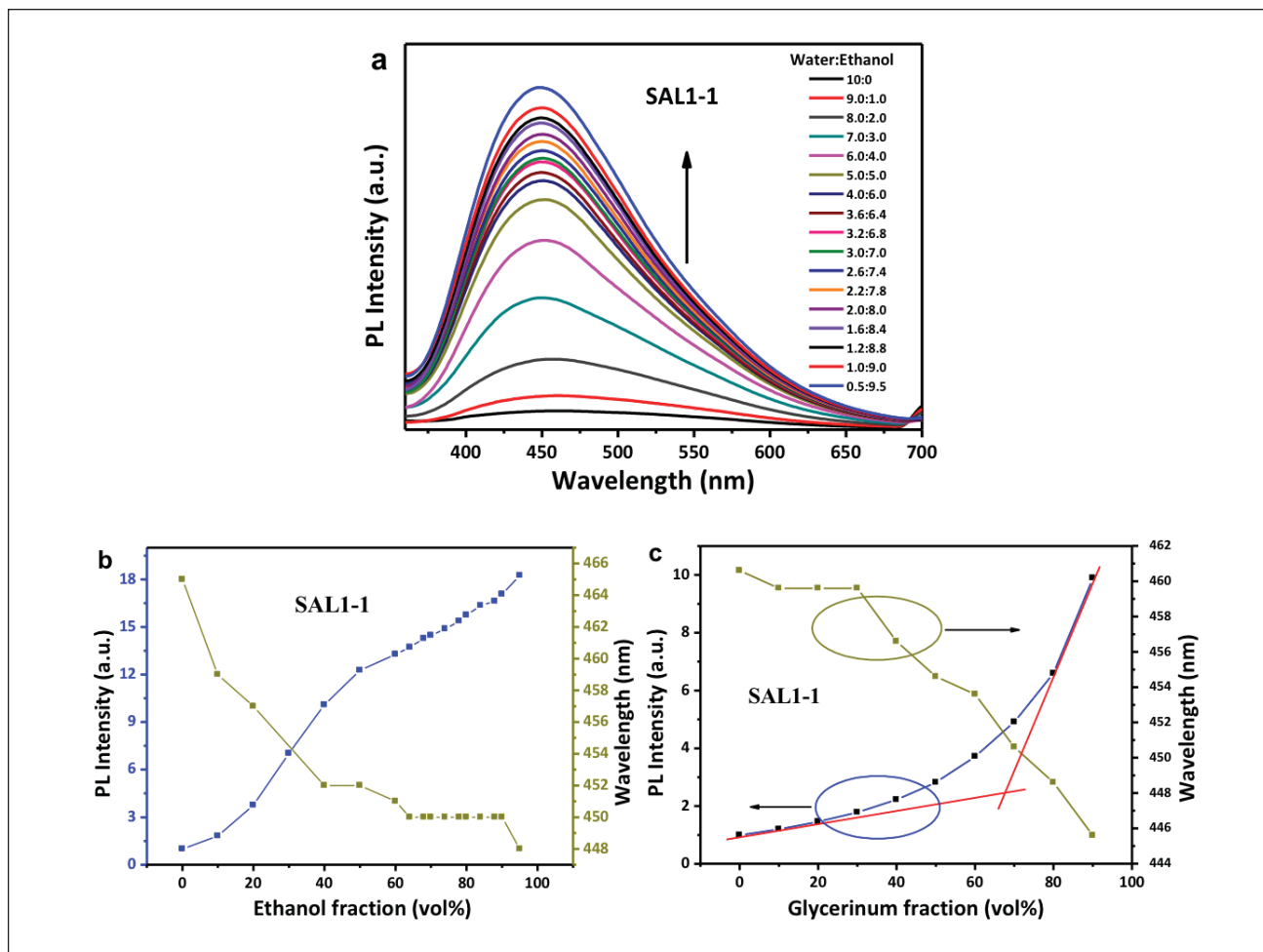
hibitor in the pre-hydrolysate have been studied experimentally [33]. EHL had good adsorption and removal ability to furfural and 5-hydroxymethylfurfural. The adsorption process was in agreement with the Freundlich model and was exothermic. The adsorption capacity of EHL for furfural was stronger than that for 5-hydroxymethylfurfural. It is feasible for EHL to remove furfural and 5-hydroxymethylfurfural in the pre-hydrolysate.

## LIGNIN FOR PHOTOELECTRIC APPLICATION

### The origin of lignin fluorescence

Plant cell walls containing lignin exhibit fluorescence when exposure to ultraviolet (UV) or visible light excitation of the aromatic rings in lignin. The fluorescent feature enables the lignin to be used as a sensitive probe for lignin constituent analysis. The fluorescence of lignin was discovered many years ago, but the UV/visible-excited lignin fluorophore remains elusive. Still, the origin of its fluorescence has been periodically proposed: an anion of coniferyl alcohol, stilbene structures, and phenylcoumarone structures [34-37]. However, the real origin of lignin fluorescence is still unclear.

Inspired by the fluorescence of wood cell walls, which might come from the presence of lignin, we are interested in the mechanism of the emission of lignin, because it is almost non-conjugated. In the wood cell walls, the molecular structure of raw lignin is fixed by cross-linking with hemicelluloses, which is similar to the aggregation in the solid state. Lignin becomes relatively highly luminescent in poor solvents



**5. (a)** Photoluminescent (PL) spectra of sulfonated alkali lignin fraction (SAL1-1) in water and water-ethanol mixtures (100 mg/L,  $\lambda_{ex} = 350$  nm); **(b)** the fluorescent image of SAL1-1 in water and water-ethanol (1:9) mixtures and the change curves of PL intensity (yellow line) and emission peak (blue line) in water and water-ethanol mixtures; and **(c)** the change curves of PL intensity (yellow line) and emission peak (blue line) in water and water-glycerinum mixtures.

or in the solid state as aggregates. The fluorescent behaviors of sulfonated alkali lignin (SAL) were studied and evaluated in mixed solvent systems (**Fig. 5**) [38]. SAL fraction (SAL1-1) showed a weak blue light emission at 450 nm under the excitation of 350 nm in distilled water. With the increase of ethanol fraction, the fluorescence intensity showed a sustained increase until the ethanol fraction reached 95%, accompanied by a blue shift of 17 nm. We proposed that the fluorescence of lignin might come from its aggregation. A similar phenomenon was observed in a water-glycerin system.

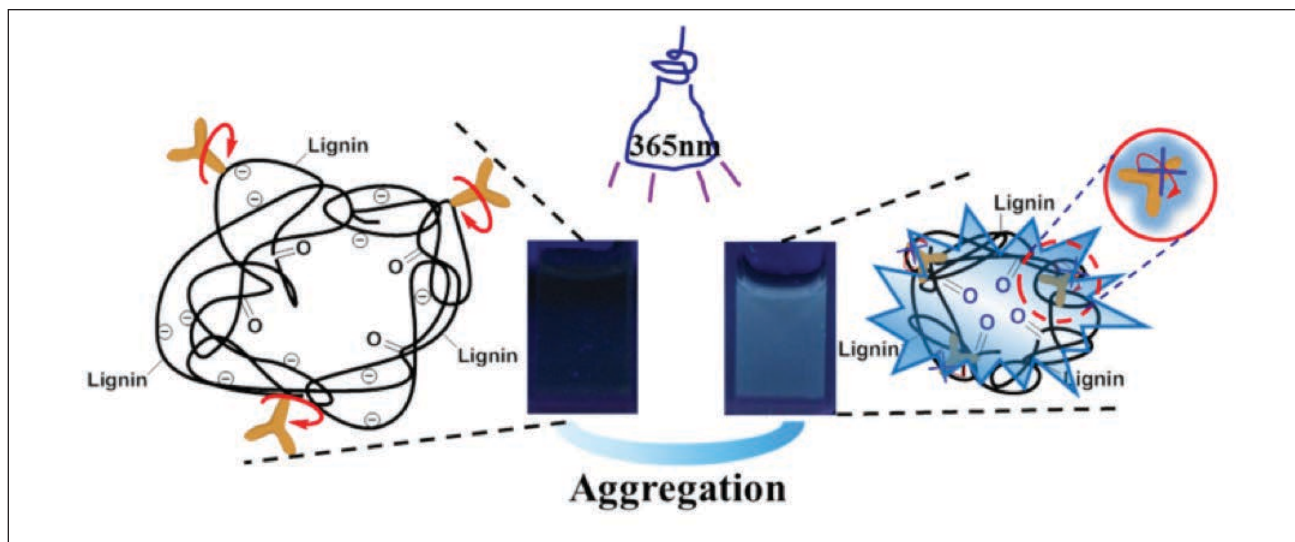
The aggregation-induced emission (AIE) property of SAL was also observed after adding CTAB, which promoted the aggregation of SAL [38]. We proposed that AIE played a role in the origin of blue lignin fluorescence because of clustering of the carbonyl groups and restriction of intramolecular rotation (**Fig. 6**). Large conjugated  $\pi$  electron systems of SAL were well established by the aggregation of nonconventional luminogens, which contained electron-rich atoms, such as oxygen and sulfur. These results provided a new perspective

to understand the fluorescence in lignin and explore novel potential application for the AIE activity of lignin.

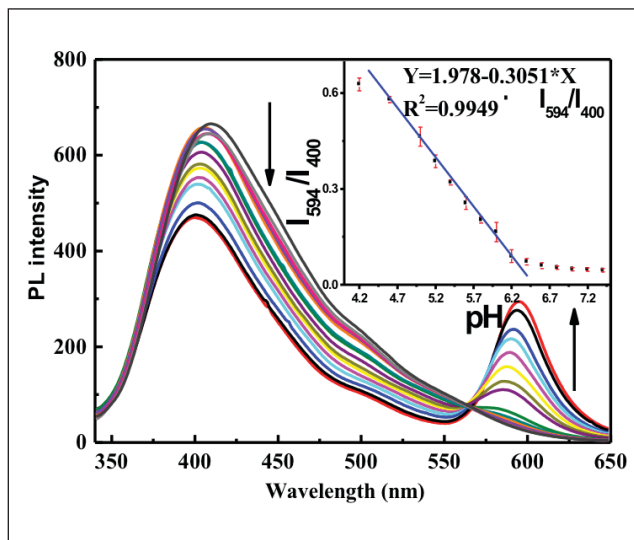
As an inexpensive and environmentally friendly fluorescent chromophore, the application based on the fluorescent property of lignin is rarely reported. Lignin has a broad fluorescence emission range and can be excited with UV and visible light. This indicates that lignin has potential as a donor in fluorescence resonance energy transfer (FRET)-based probes.

A water-soluble, ratiometric fluorescent pH probe was synthesized by grafting spirolactam rhodamine B (SRhB) to SL (L-SRhB) [39]. SL serves as the donor, whereas the SRhB works as a recognition element for hydrogen ions ( $H^+$ ) and acts as the energy acceptor when the long-wavelength fluorophore, Rhodamine B, is generated. L-SRhB showed a rapid response to pH changes from 4.60 to 6.20, with a  $pK_a$  of 5.35 (**Fig. 7**), which indicated that L-SRhB has the potential for pH detection of acidic organelle.

Encouraged by the pH-responsive property of L-SRhB, the biological application of the probe was also studied [39]. The



6. Mechanism model diagram of lignin fluorescence.



7. Fluorescence spectra of spirolactam rhodamine B (L-SRhB) in phosphate-buffered saline (PBS) (0.2 mg/mL) at various pH values. Inset is the linear plots of fluorescence intensity to pH (4.60-6.20).  $\lambda_{ex} = 330$  nm.

L-SRhB was successfully internalized by living cells through the endocytosis pathway. This is good for acidic organelle detection by the fusion of cytomembrane. Rhodamine B is known as a mitochondrion localization agent. However, the pH of mitochondrion is alkaline. The alkaline environment would have a negative effect on the cell staining experiment because the  $pK_a$  of the reversible ring-opening reaction of L-SRhB is 5.35. The ring-opening product of L-SRhB with red fluorescence might be stabilized by the interaction between sulfur trioxide ( $-SO_3^-$ ) and quaternary ammonium salt, which came from SL and the ring-opening product of L-SRhB, respectively, in alkaline condition. In addition, L-SRhB could distinguish normal cells from cancer cells by the different staining times. There was almost no red fluorescence in the normal

cells after incubation for 8 h with L-SRhB and fuchsia L-SRhB (FL-SRhB), respectively, whereas an obvious red fluorescence from the probes was observed in the cancer cells in the same condition (**Fig. 8**). Our results provide an interesting design strategy for bioimaging dyes based on lignin.

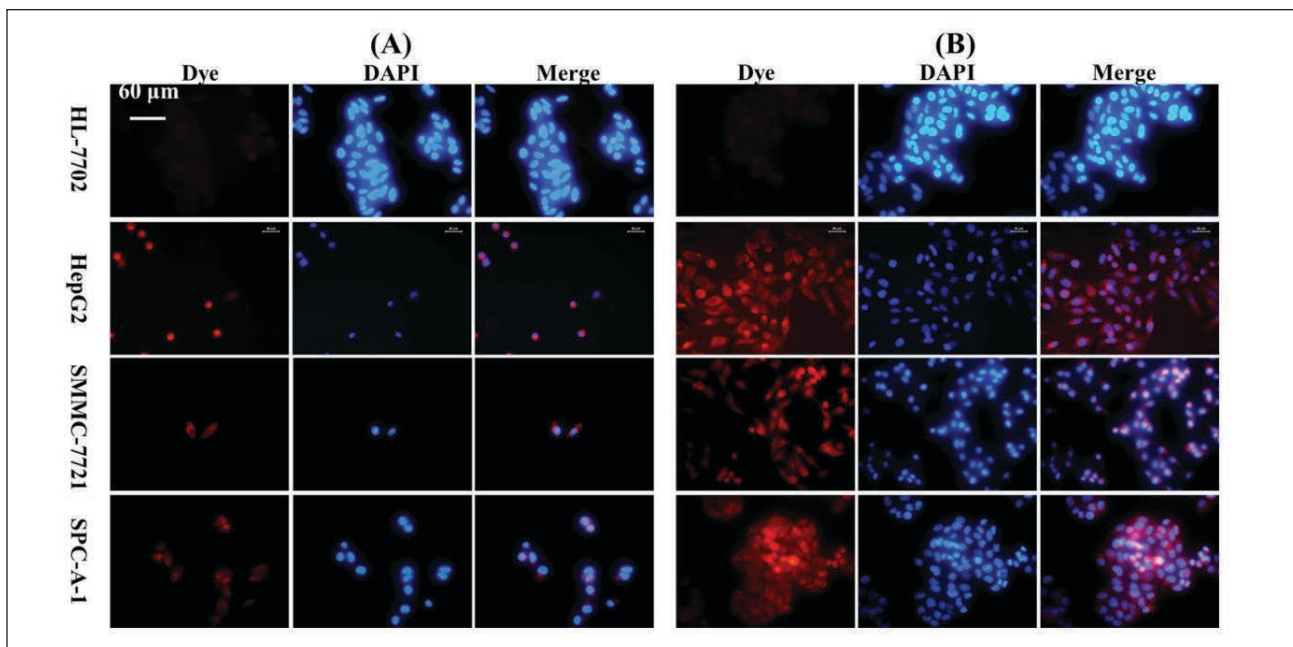
Even though the fluorescence quantum yield of lignin is relatively low, such AIE mechanisms should have strong implications for understanding the structure of lignin. Meanwhile, high value-added use of lignin on the basis of its auto-fluorescence also shows enormous potential.

### Sulfobutylated SL with ultra-high molecular weight and high sulfonation

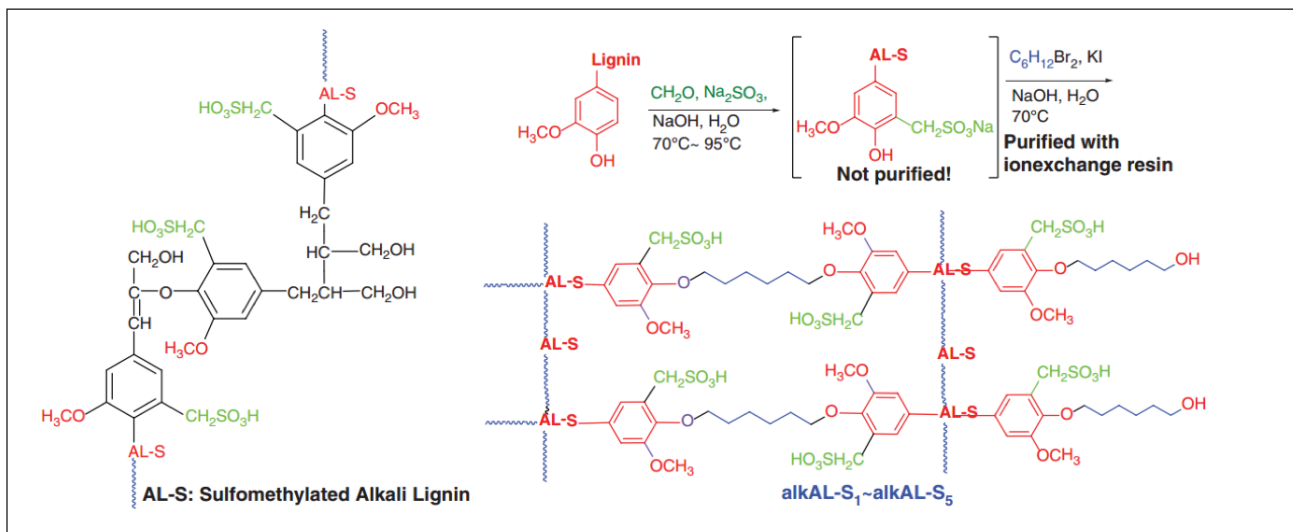
Increasing the molecular weight of SL is highly desirable to improve its dispersion ability [40]. Graft copolymerization, graft sulfonation, and enzyme catalysis reaction are suitable for increasing the molecular weight of SL. Graft sulfonation is an effective way to improve the sulfonation degree and molecular weight of SL [41-43]. However, these methods still could not obtain SL with a molecular weight over 50 kDa, which is required in many industrial applications.

To address this problem, Qiu et al. developed a one-pot modification method that includes two steps: sulfomethylation of alkali lignin (AL) as raw material leading to AL-S and alkylation with different proportions of 1,6-dibromohexane ( $C_6H_{12}Br_2$ ) in sodium hydroxide aqueous solutions leading to alkAL-S samples [44]. Sulfomethylation of AL rendered products with water solubility, and the subsequent alkyl chain reaction led to the increment in molecular weight via polymerization. They hypothesized that sulfomethylation occurs in ortho-position to the phenolic hydroxyl groups and the alkylation proceeds better via the phenolic hydroxyl groups (**Fig. 9**). As a result, a significant increase of molecular weight from 5200 Da of AL-S to 201000 Da of alkAL-S with high degree of alkylation was obtained. The relatively high molecular weight of alkAL-S yielded unexpected viscosity

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8. Images of human hepatocyte cell (HL-7702), human hepatocellular liver carcinoma cell (SMMC-7721, HepG2) and human lung adenocarcinoma cancer cells (SPC-A-1) treated with (a) spirolactam rhodamine B (L-SRhB) and (b) FL-SRhB for 8 h.



9. Synthetic approach of ultrahigh molecular weight alkAL-S polymers via sulfomethylation and reaction with 1,6-dibromohexane ( $\text{C}_6\text{H}_{12}\text{Br}_2$ ).

reducing effect, stability and good rheological properties on a low-rank coal-water slurry.

## Application of lignin in organic optoelectronic devices

During the past decades of development of organic electronic devices, including organic light-emitting diodes (OLEDs), organic solar cells (OSCs), perovskite solar cells and polymer solar cells, interface engineering has been of critical importance to improve the performance of these optoelectronic devices. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) is the most widely used commercial

water-soluble conductive polymer, which is used as an anode interlayer for high performance organic electronic devices. The PSS dopes PEDOT through protonic acid doping and PSS acts as a polyanion to stabilize the p-doped PEDOT [45-47]. However, it is known that PEDOT:PSS could corrode indium tin oxides (ITO) at elevated temperatures because of its high acidity. New solution-processable hole transporting materials (HTMs) are still in demand and chemistry scientists have made great effort.

There were very few studies aiming to produce better conducting PEDOT by replacing PSS with new dopants. Inspired by the electron transfer process during the oxidation of the phenol

| Sample | Thickness (L), nm | Slope ( $\rho$ ) | Hole-mobility, $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ |
|--------|-------------------|------------------|--------------------------------------------------------|
| SL     | 110               | 2.90             | $3.75 \times 10^{-6}$                                  |
| SL     | 100               | 2.95             | $2.91 \times 10^{-6}$                                  |
| SL     | 35                | 14.96            | $3.21 \times 10^{-6}$                                  |
| ASL    | 30                | 6.46             | $4.57 \times 10^{-6}$                                  |

## I. The hole mobilities of the samples of sodium lignosulfonate (SL) and alkyl chain cross-linked SL (ASL).

derivatives of lignin, in which radicals are produced, we explore a series of lignin derivatives as dopants to replace PSS as conducting PEDOT materials. SL and alkyl chain cross-linked SL polymer (ASL) exhibited unexpected hole mobility because of phenolic oxidation and J-aggregation behavior [48,49]. This unexpected hole mobility provides a novel perspective for the application of SL and ASL as potential polymeric p-type semiconductors. A novel water solution-processable hole transport material, which was prepared from the oxidation of EDOT dispersed in SL or ALS. For comparison, commercial PEDOT:PSS 4083 was studied as a control for the hole transport performance test. **Table I** shows SL with a higher phenolic group content having higher hole mobility than ASL with a lower phenolic group content, which further suggests that phenolic groups are conducive to the hole transporting property.

As a hole-transport material in organic photovoltaic (OPV) with a power conversion efficiency (PCE) of 5.79%, PEDOT:SL showed comparable performance to that of the conventional PEDOT:PSS with a device structure of ITO/HTM/PTB7:PC71BM/Al. We found that the performance of PEDOT:SL is not very dependent on the mass ratio of PEDOT in PEDOT:SL.

Furthermore, we explored grafted sulfonated-acetone-formaldehyde lignin (GSL) as a dopant to replace PSS. An unexpected hole mobility of  $2.27 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was achieved. GSL is a potential water soluble polymeric p-type semiconductor. Taking advantage of the hole transporting property of GSL, PEDOT:GSLs with controllable work functions were developed and applied as a hole transport layer (HTL) in organic electronic devices, including OLEDs, OPVs, and perovskite solar cells [50,51].

Based on the previously mentioned works [48-51], alkyl chain sulfobutylated SL (ASLS) with phenol derivative was expected to have an intrinsic hole transport property [52]. Water processable PEDOT:ASLS was applied as a hole injection layer (HIL) to modify ITO in Firpic-based phosphorescent OLEDs. This new HIL material showed improved device performance compared to that of PEDOT:PSS under the same device structure (**Table II**). Comparing with PSS with regular structure, strong aggregation and oxidation behavior of ASLS contribute to the hole injection capability of PEDOT:ASLS.

In this section, we explored a series of lignin derivatives as a dopant to replace PSS as dispersant and template for water soluble polymeric semiconductor PEDOT. Our results provide

| Anode Modifier  | $V_{on}$ , V* | $CE_{max}$ , $\text{cd/A}^\dagger$ | $PE_{max}$ , $\text{lm/W}^\ddagger$ |
|-----------------|---------------|------------------------------------|-------------------------------------|
| None            | 4.6           | 14.5                               | 5.82                                |
| PEDOT: PSS      | 4.5           | 25.09                              | 8.25                                |
| PEDOT: ASLS-1:1 | 4.2           | 37.65                              | 12.84                               |

\* turn-on voltages,  $^\dagger$  maximum current,  $^\ddagger$  power efficiency.

## II. Performances of organic light-emitting diodes with no anode modifier, with oly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS), and with PEDOT: alkyl chain sulfobutylated sodium lignosulfonate (ASLS) as anode modifier, respectively.

a novel concept for the application of bi-radicals containing polyaromatic hydrocarbons and provide a promising scaffold for the design and feasible synthesis of HTMs based on the interconversion between phenol and benzoquinone for organic electronics in the future.

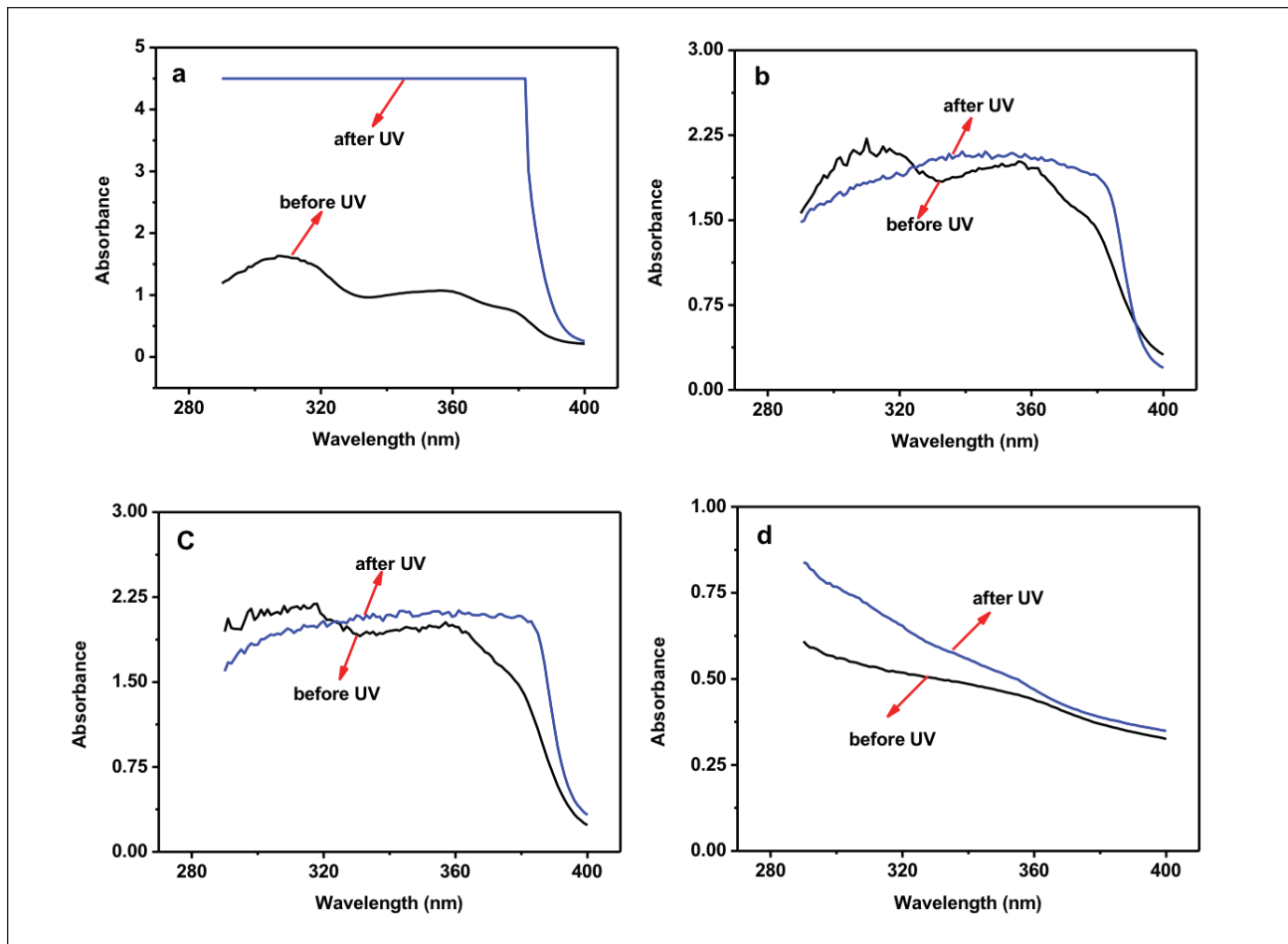
## LIGNIN FOR NATURE-INSPIRED SUN BLOCKER

Lignin is a unique aromatic polymer in plants. It exhibits excellent ultraviolet (UV)-blocking and antioxidant properties because of its functional groups such as phenols, ketones and other chromophores. Recently, Qiu and co-workers demonstrated lignin could be used as a highly efficient nature-inspired sun blocker [53].

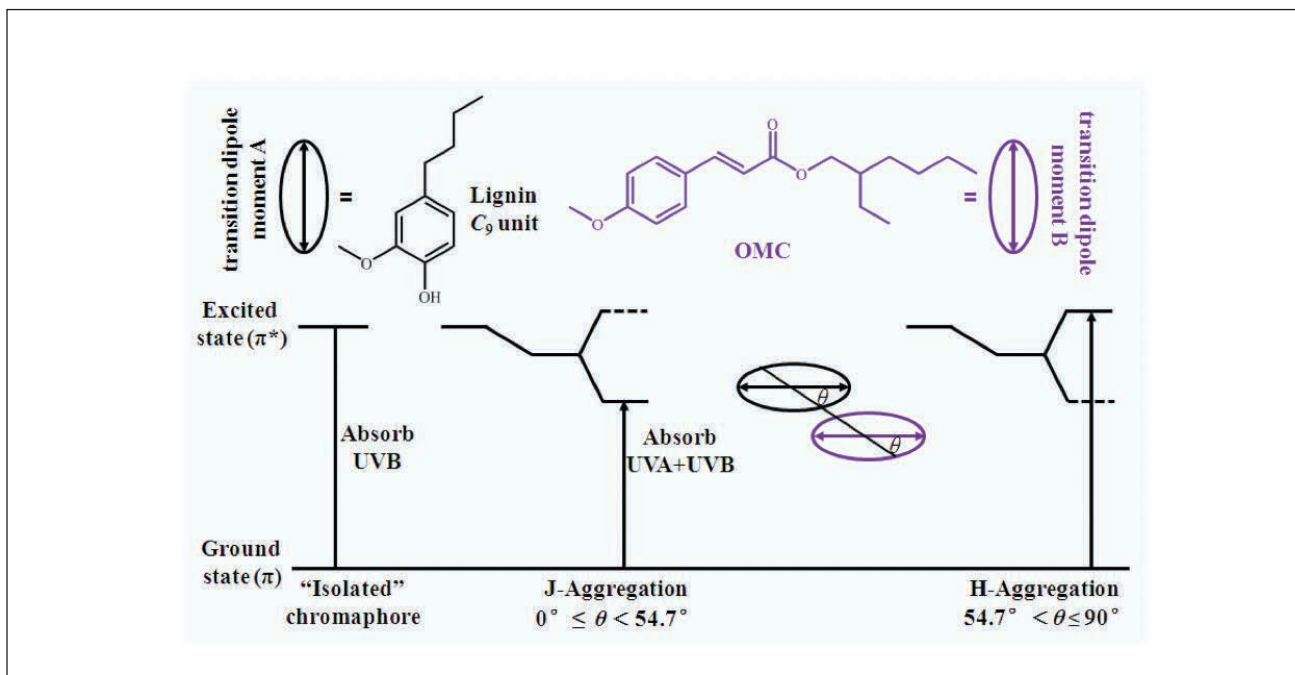
When lignin was added into commercial sunscreen products, significant enhancements in UV absorbance were observed. The sunscreen performance of the cream with sun protection factor (SPF) 15 could reach that of the cream with SPF 30 when 2 wt% lignin was added. Adding 10 wt% lignin made SPF 15 cream outperform SPF 50 cream. The synergistic effect between lignin and chemical sunscreen was found first and was more obvious after UV irradiation (**Fig. 10**). This means lignin-based sunscreens could improve the duration of protection from sunshine. Further, Qian et al. demonstrated lignin from different technical resources has a general synergistic effect with sunscreen actives in the commercial lotion and tried to elucidate radical mechanisms of the synergy [54]. Their exploration suggested that the synergistic effect in the lignin-modified sunscreen lotions could be attributed to the  $\pi-\pi^*$  stacking between lignin and chemical sunscreen actives (**Fig. 11**) and the formation of UV radiation-induced conjugated chromophores. However, they also found that the sunscreen performance of pure lignin could not meet the daily requirement and the color should be whitened.

The dark color of industrial lignin is the main obstacle for its high value-added uses in areas such as sunscreen products or dyestuff dispersants. By acetylating modification and self-assembling in selective solvents, Qian et al. first fabricated uniform lignin colloidal spheres and the formation mechanism was evaluated (**Fig. 12**) [55]. Because of the blocking of phenolic hydroxyl chromophores and effect of the Mie

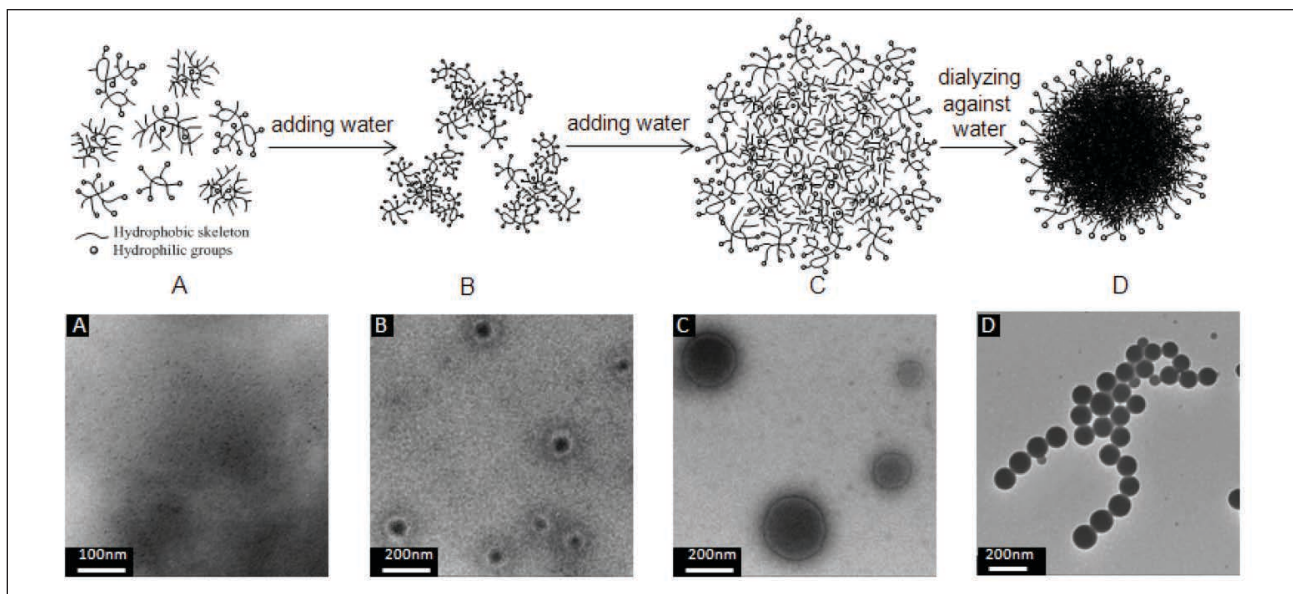
# LIGNIN PRODUCTS



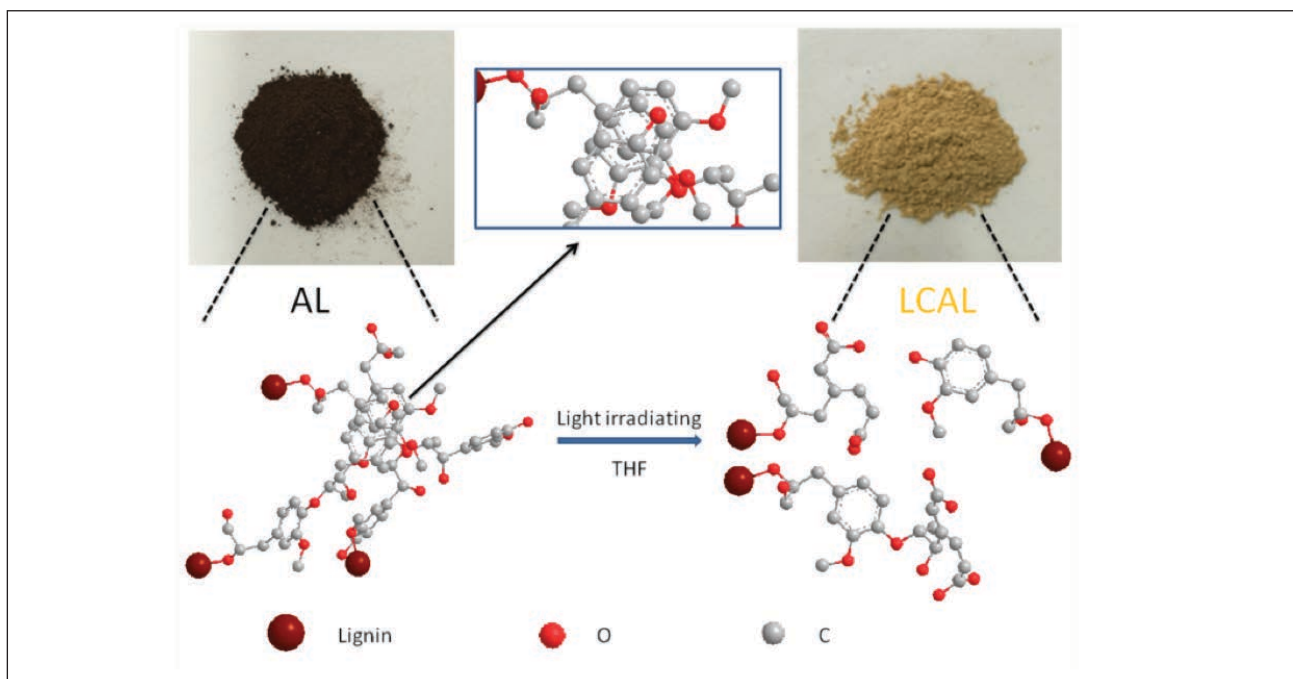
10. Ultraviolet (UV) absorbance of the sunscreens before and after 2 h UV radiation: (a) sun protection factor (SPF) 15 cream + 10 wt% lignin, (b) SPF 15 cream, (c) SPF 30 cream, and (d) pure cream +10 wt% lignin.



11. Typical energy diagram of  $\pi$ - $\pi^*$  stacking between lignin and chemical sunscreen active octyl methoxycinnamate.



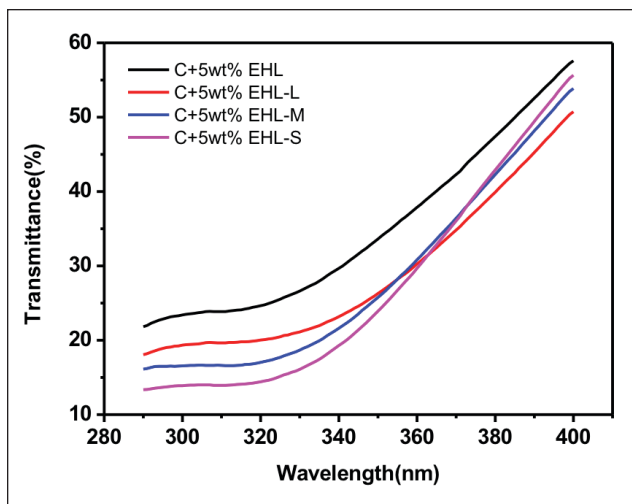
**12. Schematic representation of the colloid formation process of the acetylated lignin in a tetrahydrofuran-water (THF-H<sub>2</sub>O) medium and transmission electron microscopy (TEM) images of the samples obtained from the dispersions with different water contents. Water content: (A) 0–13 vol%, (B) 13–44 vol%, (C) 44–67 vol%, and (D) >67 vol%, removing THF for recycling.**



**13. Schematic representation of whitening lignin via ultraviolet radiation.**

scattering, lignin was obviously whitened [56]. Furthermore, they presented a one-step UV radiation method to reduce the color of lignin and characterized the structural changes of the whitened lignin [57]. When lignin was exposed to UV in solvents producing peroxides, its content of aromatic ring, methoxyl and phenolic hydroxyl groups would decrease, while the content of carboxylic groups increased. Lignin was not only intermolecular and intramolecular disaggregated, but also partially depolymerized (**Fig. 13**).

However, both whitening methods sacrificed the phenolic hydroxyl groups of lignin, which are not only responsible for scavenging free radicals, but also helpful for blocking UV radiation. Thus, Qian et al. prepared lignin colloidal spheres with different sizes and structures by self-assembling without chemical modification, and then blended with pure skin cream to develop lignin-based sunscreens [58]. The sunscreen performance of lignin colloidal spheres was better than that of original lignin (**Fig. 14**). The SPF value of the



**14. Ultraviolet (UV) transmittance of pure cream blended with 5 wt% lignin and lignin colloidal spheres in UVA and UVB.**

sunscreen containing 10 wt% lignin colloidal spheres with the size of about 50 nm reached 15. The SPF value of sunscreen containing 10 wt% middle size lignin colloidal spheres (~200 nm) can be boosted from 11 to 48 by adding 2 wt% UVA and 2 wt% UVB chemical sunscreens.

Further research in this area is being carried out. Whiteness without sacrifice of the UV blocking performance is practically important for many applications, not only for the sunscreen creams but also for its use as functional fillers in polymer applications.

## LIGNIN FOR POLYMER COMPOSITES APPLICATION

### *Lignin-based phenol-formaldehyde resin*

As a natural polyphenol compound rich in phenol hydroxyl groups, lignin has attracted much attention for partial or even complete replacement of phenol in phenol-formaldehyde (PF) resin production. In our early research, we developed lignin-based phenol-formaldehyde (LPF) resin using wheat straw soda lignin (WSSL) as partial substitute of phenol. WSSL was first modified by phenolation in alkaline medium [59,60]. After modification, the content of methoxyl group in lignin decreased from 11.04% to 8.72%, and the content of phenolic hydroxyl increased from 2.64% to 4.20%. The molecular weight of WSSL also decreased, which resulted in improved WSSL reactivity and decreased LPF viscosity. The adhesive strength and storage stability of LPF were also improved compared with non-phenolated LPF adhesive. When 70% of phenol was replaced by the phenolation-modified WSSL, the adhesive strength of LPF (1.9 MPa) was comparable to traditional PF adhesives (2.1 MPa). Therefore, the modification of WSSL by phenolation increased its reactivity and improved the performance of lignin-based phenol-formaldehyde adhesive.

To study the effect of WSSL molecular weight on the performance of LPF, ultrafiltration was conducted to fractionate

WSSL, and three fractions with different molecular weight ranges were obtained [61]. Analysis results showed that WSSL with lower molecular weight contained less methoxy group and more phenolic hydroxyl group, thus exhibiting higher reactivity in the synthesis of LPF. Further experiments showed that as the molecular weight of WSSL decreased, the adhesive strength of LPF increased, but the free formaldehyde content and the viscosity decreased; therefore, better performance of LPF was achieved. When 2%~3% of urea was added into the LPF with the WSSL-to-phenol ratio of 70:30, the adhesive performance could be further improved. The adhesive strength improved from 2.0 MPa to 2.2 MPa, the free formaldehyde content decreased from 0.16% to 0.05%, and the viscosity of LPF reduced from 858 mPa.s to 306 mPa.s [62,63]. The overall performance has reached that of traditional PF resins.

Later research showed that hydroxymethylation modification could also increase the reactivity of WSSL [64,65]. With 50% of phenol substituted by hydroxymethylation modified WSSL, the adhesive strength of LPF could reach 2.0 MPa. Without need of purification, the residual content of formaldehyde and phenol was much lower than the national standard. In comparison with traditional PF adhesives, the prepared LPF had lower curing temperature but faster curing rate.

Recently, researchers developed new demethylation techniques to improve the content of phenolic hydroxyl groups of lignin and enhance their reactivity for preparation of LPF [66-69]. Ma et al. found that the content of phenolic hydroxyl groups of EHL could increase 20% after high-intensity ultrasound processing for 20 min [66]. Sawamura et al. investigated demethylation efficiency of 1-dodecanethiol (DSH), hydroiodic acid (HI), and iodocyclohexane (ICH) on guaiacyl-type synthetic lignin (GDHP) [67]. ICH was the most effective demethylation reagent for increasing the phenolic hydroxyl levels in GDHP. GDHP demethylated with ICH showed higher tannin-like properties. Using rhodium chloride ( $\text{RhCl}_3$ ) in the presence of a promoter as a catalyst, Mei et al. demonstrated that more than 80% of the methoxyl group in lignin could react with carbon monoxide and water to generate acetic acid, and the lignin was modified to be rich in phenolic hydroxyls [68]. Li et al. demethylated AL under different mild conditions using sodium sulfite as a catalyst [69]. The methoxyl group content decreased from 1.93 mmol/g to 1.09 mmol/g, whereas the phenolic hydroxyl group content increased from 0.56 mmol/g to 0.82 mmol/g. Prepared LPF resins exhibited faster curing rate and shorter gel time.

### *Lignin-based polymer composites*

Preparing lignin/polymer composites is another way to efficiently use the abundant renewable lignin on a large scale. Rubber, one of the most important polymer materials widely used in daily life, usually needs large quantities of filler (e.g., carbon black) for reinforcement. Considering the abundance of technical lignin produced annually, blending lignin with rubber as a partial substitute for traditional filler is a good choice for massive application of lignin. However, direct

blending results in poor performance because of weak compatibility and severe aggregation of lignin particles in the rubber matrix.

We have studied the influence of three EHL pretreatment methods — ball milling (EHL-BD), spray drying (EHL-SD), and jet milling (EHL-JM) — on their nitrile rubber (NBR) reinforcement ability [70]. EHL-JM gave the finest particle size, averaging 2–3  $\mu\text{m}$ . The particle size from spray drying was about 23  $\mu\text{m}$ , and ball-milling generated coarse particles with a broad size distribution from 4  $\mu\text{m}$  to 300  $\mu\text{m}$ . When the pretreated EHL was blended with NBR in an open roller mill, the viscosity of rubber composite increased with the lignin content. Extending the mixing time could facilitate the distribution of lignin particles in the rubber matrix and shorten the vulcanizing time. EHL could delay the rubber vulcanization process. As the EHL content increased, the delay/inhibiting effect was more obvious. From the dynamic thermomechanical analysis and differential scanning calorimetry analysis, only one glass transition temperature was observed for all the EHL/NBR composites, showing that lignin has a certain degree of compatibility with NBR. The glass transition temperature of rubber composites increased as the lignin content increased, indicating the obvious constraining effect of lignin particle on the NBR chains. Mechanical performance studies revealed that all the EHL pretreated with different methods could reinforce the rubber. EHL-JM showed the best strengthening effect and had better compatibility and stronger interphase adhesion with the NBR matrix. When 40 parts per 100 rubber (phr) EHL-JM was added, the tensile strength of NBR reinforced by EHL-JM was 24% and 61% higher than that of EHL-BM and EHL-SD, respectively. Thermogravimetry results and the analysis of thermal-oxidative aging mechanical properties revealed that EHL could also enhance the thermal stability and anti-aging properties of NBR/EHL blends.

When the EHL-JM was added together with the carbon black, the mechanical properties could be significantly improved [71]. This is because the specific surface area and the particle size of carbon black is much smaller than that of lignin. The NBR composite with 20 phr EHL-JM and 20 phr carbon black showed the best mechanical properties, with a tensile strength of 21 MPa and an elongation at break of 650%, which reached the mechanical requirement of some special rubber applications. However, increasing the proportion of EHL-JM in the composite filler system decreased the tensile strength, the tear strength, and the break elongation. Adding an interfacial modifier, such as a silane coupler, contributed little to the mechanical properties of the NBR/lignin composite, but could improve the anti-thermal oxidative aging property.

Because polyolefin occupies more than half of the global polymer market, our group has also studied lignin-based polyolefin composites. The pretreated AL by ball milling (AL-BM) and jet milling (AL-JM) methods with different sizes were separately blended with high-density polyethylene (HDPE) [72]. AL-JM had the finest particle size of about 3  $\mu\text{m}$ . The results showed that the tensile strength of composite increased

with the AL content. When containing the same addition, the composite prepared by finer AL particles had higher tensile strength. The tensile strength of composite produced by 40 wt% AL-JM reached 26 MPa, higher than the blank HDPE sample (about 22 MPa). However, the elongation at break of composites decreased sharply compared with the blank HDPE sample. The more AL added, the smaller the elongation at break. The rheological properties showed that the addition of AL increased the apparent viscosity ( $\eta$ ) and complex viscosity ( $\eta^*$ ) of the composites, the linear viscoelastic region turned narrow, and the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) also gradually declined with the increasing AL content. The thermogravimetric analysis showed that AL lowered the thermostability of composites.

The effect of plasticizer on the properties of AL/HDPE composites was also systematically studied [73]. With AL content fixed at 20 wt%, the AL/HDPE composites were prepared separately with dioctyl phthalate (DOP), dibutyl phthalate (DBP), and epoxidised soybean oil (ESO). The results showed that these plasticizers could increase the elongation at break of composites, and DOP had the best effect. When we added 7.5 g DOP, the elongation at break of composites reached about 150%. Increasing the DOP dosage helped increase elongation at break and toughness. The fracture surfaces of composites became coarser with the addition of DOP, as verified by scanning electron microscopy. The apparent viscosity ( $\eta$ ) and complex viscosity ( $\eta^*$ ) of the composites were lowered after the addition of DOP, compared with the composites with only AL added. DOP was shown to adsorb on the surface of AL particles and suppress the agglomeration of AL particles in HDPE, which improved the dispersion of AL particles in HDPE, thus the mechanical properties and rheological performance of the composites were improved.

Similarly, the addition of maleic anhydride grafted polypropylene (PP-g-MAH) significantly improved the tensile strength of lignin/PP composites [74]. We also correlated the lignin content to the water absorption of lignin-plastic composite. With the increase of lignin content, the water absorption of the composite indicated a increasing trend. At a lignin content less than 30 wt%, the water absorption of the composites was lower than 1.0%, except for spray-dried AL. We also found that the water absorption of the AL composites was lower than that of the EHL composites [74].

## *The antioxidant performance of lignin in plastics*

Because of its rich functional groups, including phenolic, ketone, and other chromophores, lignin also can be used as an excellent antioxidant for polyolefin plastics. We have systematically studied the effect of lignins on the antioxidant properties of polyolefin [75]. As a result of lignin addition, the thermal aging resistance and UV resistance abilities of polyolefin improved. Pine wood alkali lignin (PAL) had the best protective effect performance in terms of thermal oxidative aging and UV aging. The efficiency of UV absorption of lignin had a positive correlation with its anti-UV effect. In the high tem-

# LIGNIN PRODUCTS

perature environment, the oxidation induction time (OIT) of polyolefins could be significantly increased. For HDPE, adding 1% lignin could increase the OIT up to 22 min. However, 3% lignin was needed for low-density polyethylene (LDPE) and PP to increase their oxidation induction period up to 15 min or more.

In the UV aging environment, an improvement in toughness of HDPE composite with 2% lignin was achieved, and the conservation rate of fracture tensile rate reached 168%, which was comparable to industrial light stabilizer. In the thermal oxidative aging environment, the conservation rate of fracture tensile rate of HDPE, LDPE, and PP with 2% lignin reached about 90%, 54%, and 68%, respectively. Rheological tests showed that lignin could reduce the aging rate of polyolefin in the high temperature condition.

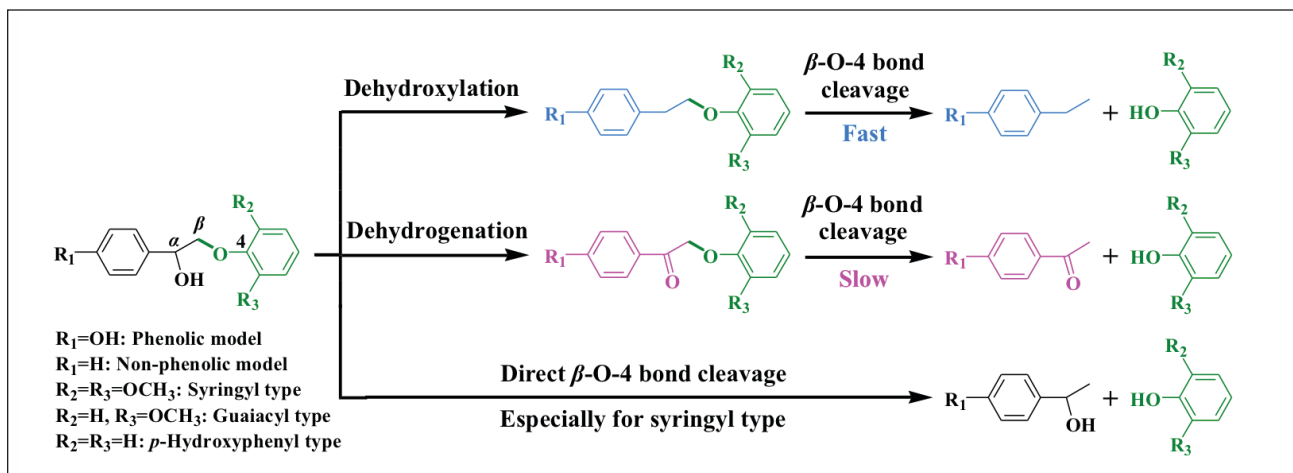
The mechanism for the antioxidant property of lignin was attributed to that the phenolic compounds in lignin that could capture free radicals and prevent the automatic oxidation cycle in polyolefin under the action of thermal oxygen [75]. The conjugated structure in lignin could absorb UV light, and played the role of UV shielding under the action of UV irradiation. Therefore, high purity and high content of phenolic hydroxyl in the lignin from pine wood resulted in low transmission of UV light, which was more suitable for polyolefin antioxidant. Unfortunately, the anti-aging performance of lignin was still poor compared with that of industrial antioxidant Irganox 1010 ( $C_{73}H_{108}O_{12}$ ). To conquer the insufficient protection ability of lignin under the thermal aging condition of polyolefin, additives such as aluminum stearate, stearic acid, and maleic anhydride grafted polyethylene (PE-MA) could be used to improve the dispersion effect of lignin in polyolefin and the anti-aging effect of polyolefin. Commercial Irganox1010 also could be compounded with lignin to realize the synergistic effect. The results showed that the OIT of LDPE compounded with 1% lignin and 0.05% Irganox1010 reached 36.5 min, which could meet the basic requirements of industrial production. Our work has shown that lignin could be used as a co-antioxidant in polyolefin plastics [75].

## LIGNIN-DERIVED CHEMICALS

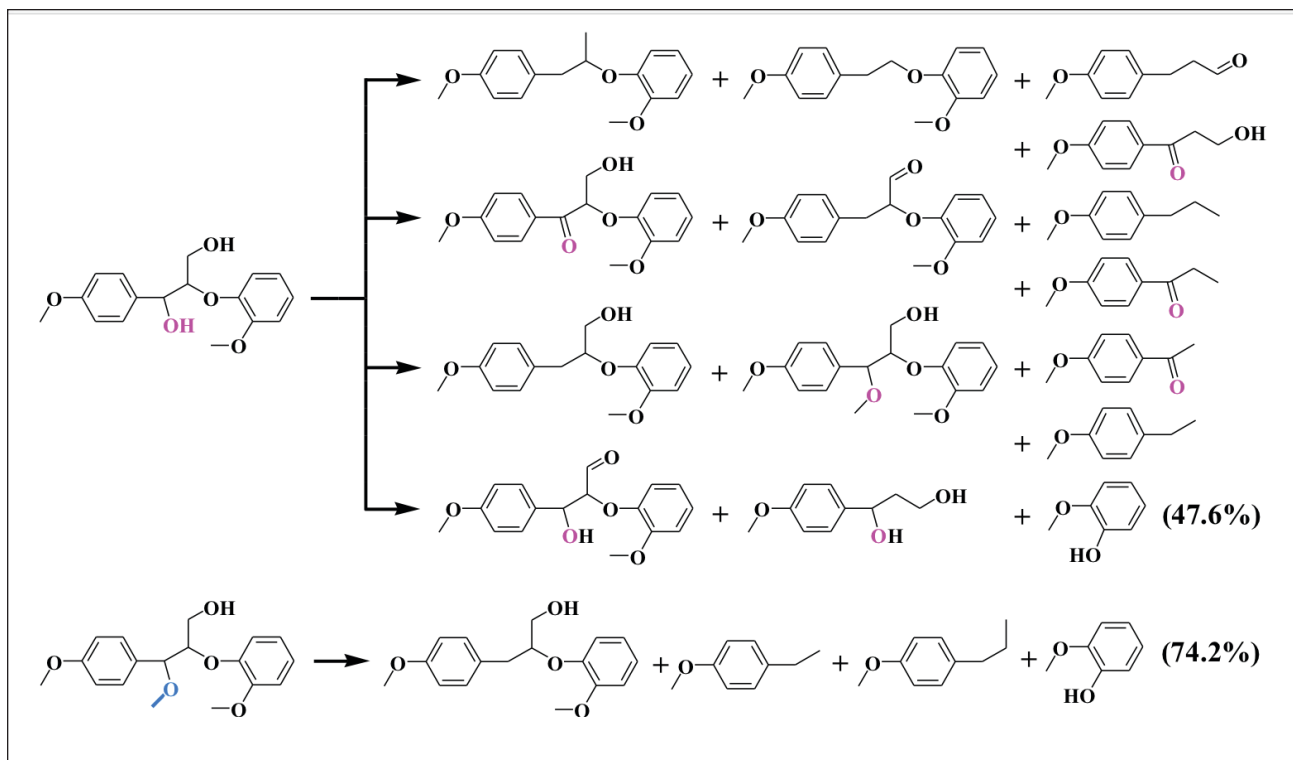
Because lignin is an abundant natural compound rich in aromatic rings, full use of lignin as a raw material for platform chemicals is one promising path for saving petrochemical resources. Therefore, we have also conducted research in the hydrogenolysis of lignin for producing aromatic monomers.

Hydrogenolysis is considered the most promising depolymerized technology for the production of aromatic monomers from lignin [76].  $\beta$ -O-4 linkage is the predominant linkage in lignin. It is important to understand how three major functional groups of lignin — benzylic alcohol group ( $C_a$ —OH), aromatic methoxyl group ( $C_{aryl}$ —OCH<sub>3</sub>), and phenolic hydroxyl group ( $C_{aryl}$ —OH) — affect the behavior of lignin hydrogenolysis [77]. In hydrogenolysis systems, the  $\beta$ -O-4 bond cleavage of lignin with the  $C_a$ —OH followed three reaction routes (**Fig. 15**). First, dehydroxylation of the  $C_a$ —OH led to  $C_a$ —H, followed by a fast cleavage of the  $\beta$ -O-4 bond. Second, dehydrogenation of the  $C_a$ —OH easily led to  $C_a$ =O, followed by a slow  $\beta$ -O-4 bond cleavage. Third, the  $\beta$ -O-4 bond was cleaved directly, and the cleavage route tended to occur on the  $\beta$ -O-4 bond linked with a syringyl unit. The occurrence of the three reaction routes resulted in a complex product distribution from lignin with the  $C_a$ —OH. Both  $C_{aryl}$ —OH and  $C_{aryl}$ —OCH<sub>3</sub> were stable under the hydrogenolysis condition below 180°C and less than 10 min, so they had no effect on the cleavage route of the  $\beta$ -O-4 bond and product distribution.

To avoid the primary dehydrogenation of  $C_a$ —OH during hydrogenolysis, a new two-step lignin depolymerization strategy was developed in which the  $C_a$ —OH of lignin was methylated to  $C_a$ —OCH<sub>3</sub>, followed by hydrogenolysis of methylated lignin [78]. Iron (III) sulfate,  $Fe_2(SO_4)_3$ , and aluminum sulfate  $Al_2(SO_4)_3$ , were excellent catalysts in  $C_a$ —OH methylation under microwave irradiation. An efficient methylation was achieved with various lignin models under a mild reaction condition. A protonation between  $C_a$ —OH and methanol solvent was induced under an acidic environment [79], which resulted in methylation of the  $C_a$ —OH. The protonation preferred the  $C_a$ —OH to  $C_y$ —OH or  $C_{aryl}$ —OH under the acidic



15. The cleavage routes of the  $\beta$ -O-4 bond in hydrogenolysis system.



**16. Evaluation of hydrogenolysis reactivity; 0.10 mmol of lignin model, 10 mL of methanol, 1.0 mmol of formic acid, 0.0165 g of 10% palladium on carbon (Pd/C), 160°C, 30 min, and microwave heating.**

condition, so the methylation selectively occurred only at  $C_a$ —OH rather than  $C_y$ —OH or  $C_{aryl}$ —OH.

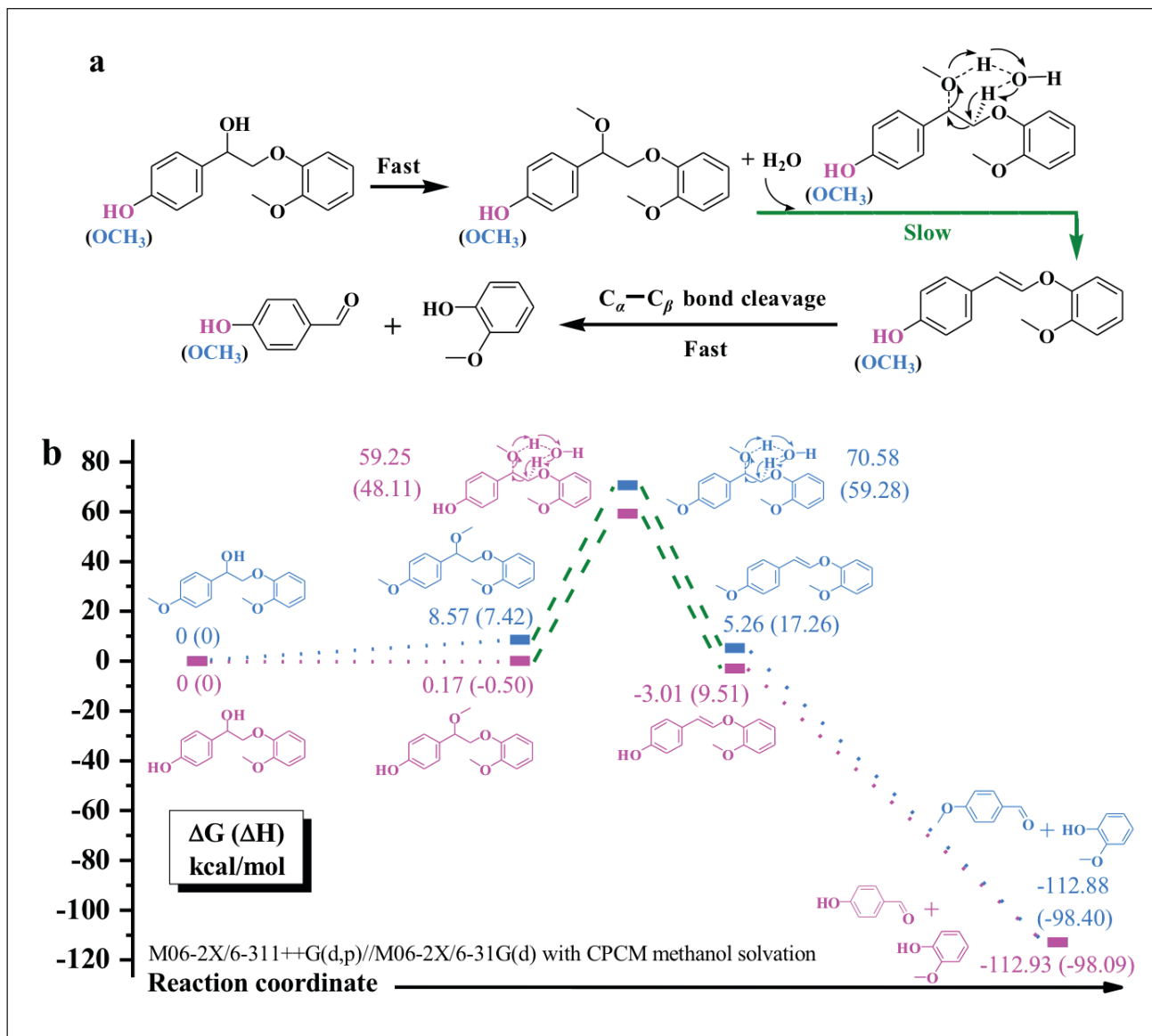
$C_a$ —OH was methylated to improve the hydrogenolysis reactivity of the  $\beta$ -O-4 bond. Methylation of  $C_a$ —OH improved product selectivity in decomposition, yielding only four products instead of 15 products from unmethylated compound (**Fig. 16**). The formation of  $C_a$ =O from the dehydrogenation of  $C_a$ —OH was inhibited through replacement of  $C_a$ —OCH<sub>3</sub>, resulting in the  $\beta$ -O-4 bond cleavage reactivity increasing by 55.9%. These results provided an important foundation for the hydrogenolysis of lignin into aromatic monomers. A methylation pretreatment of lignin allowed for increasing the degree of lignin depolymerization by 24.7% to about 28.7%, and the yield of aromatic monomers by 43.1% to about 54.1%.

The oxygen atom in the  $C_a$  position of aromatic monomers was generally retained when the  $\beta$ -O-4 bond was cleaved [80,81], resulting in a higher oxygen content of alkyl side chain. However, none of the oxygen atoms in the  $C_a$  position were found in aromatic monomers from methylated compounds (Fig. 16). Aromatic monomers with low oxygen content were conducive to further preparation of advanced bio-alkane fuels. The results highlighted the prospect of a reduction of oxygen content of aromatic monomers. Whether or not the  $C_a$ —OH was methylated to  $C_a$ OCH<sub>3</sub>, lignin yielded 18 major aromatic monomers, which included low and high oxygen content of alkyl side chain of aromatic monomers. However, methylation pretreatment contributed to a reduc-

tion of the oxygen content of aromatic monomers, whose ratio of low and high oxygen content of alkyl side chain of aromatic monomers increased to about 6.5–7.4:1 from the ratio of about 1.6–1.8:1 generally obtained on unmethylated lignin.

In addition to the relatively low yield of aromatic monomers from lignin depolymerization, a complicated distribution of aromatic monomers also hinders the large-scale conversion of lignin into aromatic monomers. Hence, we must narrow the distribution of aromatic monomers to achieve the selective production of aromatic monomers from lignin. A complicated distribution of aromatic monomers is derived from an irregular phenyl C3 side-chain, so it is important to unify the side-chain of aromatic monomers. The  $C_a$ — $C_\beta$  bond was the most vulnerable among C—C bonds on the phenyl C3 side-chain [82]. Therefore, we also targeted selective  $C_a$ — $C_\beta$  bond cleavage of the phenyl C3 side-chain [83]. The cleavage of the  $C_a$ — $C_\beta$  bond was achieved with Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as a catalyst under microwave irradiation, and a conversion process with the free energy and enthalpy profile was shown for microwave-assisted cleavage of the  $C_a$ — $C_\beta$  bond (**Fig. 17**).

An acidic environment promoted rapid methylation of the  $C_a$ —OH with methanol into methylated product. A further elimination of  $C_a$ —OCH<sub>3</sub> with  $C_\beta$ —H in the methylated product occurred to form alkenyl product, and the formation of alkenyl product was a decomposition-determining step. Density functional theory calculations indicated that a phenolic lignin model was more thermodynamically favorable to form alkenyl product than a non-phenolic lignin model, so the pres-



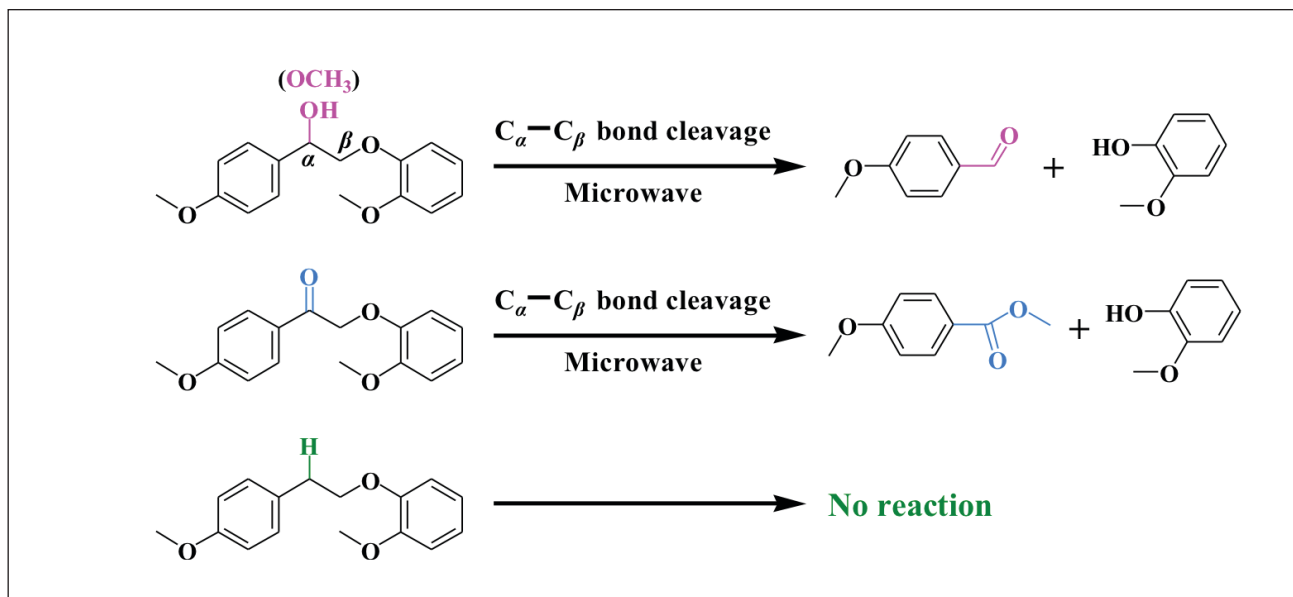
17. (a) Decomposition process and (b) reaction energy diagrams for microwave-assisted selective cleavage of the C<sub>α</sub>-C<sub>β</sub> bond.

ence of C<sub>aryl</sub>-OH enhanced the C<sub>α</sub>-C<sub>β</sub> bond cleavage reactivity in nature.

The result highlighted the prospect of selective C<sub>α</sub>-C<sub>β</sub> bond cleavage of lignin. Compared with conventional heating, microwave heating promoted lignin depolymerization and allowed for increasing the degree of lignin depolymerization by 17.3% to about 28.4%. Meanwhile, microwave heating markedly facilitated C<sub>α</sub>-C<sub>β</sub> bond cleavage of lignin, and the cleavage percentage of the C<sub>α</sub>-C<sub>β</sub> bond in lignin increased to about 65.2% to 96.3% from about 19.3% to 34.0% generally obtained using conventional heating. An excellent microwave-assisted selective cleavage of the C<sub>α</sub>-C<sub>β</sub> bond allowed for a narrowing of aromatic monomers, which only contained four main aromatic monomers (vanillin, syringaldehyde, methyl vanillate, and methyl syringate).

Inspired by the process of the C<sub>α</sub>-C<sub>β</sub> bond cleavage

(Fig. 17), a fundamental understanding of how the benzyl functionality of C<sub>α</sub>-OH to C<sub>α</sub>=O, C<sub>α</sub>-H, or C<sub>α</sub>-OCH<sub>3</sub> controlled the microwave-assisted selective cleavage of the C<sub>α</sub>-C<sub>β</sub> bond was further investigated [84]. The oxidation, reduction, and etherification of C<sub>α</sub>-OH to C<sub>α</sub>=O, C<sub>α</sub>-H, and C<sub>α</sub>-OCH<sub>3</sub> had little influence on the bond length and bond dissociation enthalpies of the C<sub>α</sub>-C<sub>β</sub> bond. Hence, it was still difficult to cleave the C<sub>α</sub>-C<sub>β</sub> bond under mild thermal condition [85]. However, dynamic analysis showed that the oxidation of C<sub>α</sub>-OH to C<sub>α</sub>=O increased the decomposition rate constant by 16.3%. The decomposition determining step was enolate isomerization when C<sub>α</sub>-OH was oxidized to C<sub>α</sub>=O. The density functional theory calculations indicated that ΔG and ΔH of the decomposition determining step decreased by 35.8% and 44.9%, respectively. An increase of the decomposition rate constant and a decreased barrier of the decomposi-



18. Effect of benzyl functionality on the formation of aromatic monomers.

tion determining step improved the  $C_\alpha-C_\beta$  bond cleavage. Methylation of  $C_\alpha-OH$  to  $C_\alpha-OCH_3$  had no effect on the cleavage reactivity of the  $C_\alpha-C_\beta$  bond. Meanwhile, the microwave-assisted selective cleavage of the  $C_\alpha-C_\beta$  bond followed first-order kinetic and radical reaction mechanisms. No reaction occurred between the compound whose  $C_\alpha-OH$  was reduced to  $C_\alpha-H$  with hydroxyl free radical, which resulted in the  $C_\alpha-C_\beta$  bond cleavage being hindered. Additionally, benzyl functionality had an obvious effect on the formation of aromatic monomers (**Fig. 18**). The presence of  $C_\alpha-OH$  or  $C_\alpha-OCH_3$  allowed for the production of aromatic aldehyde, whereas aromatic ester would be produced when  $C_\alpha-OH$  was oxidized to  $C_\alpha=O$ .

## OUTLOOK

Value-added usage of lignin is booming. However, how to improve the technologies, simplify the experimental procedures, and realize industrialization are still obstacles. Our work is developing in several directions. Fabrication of lignin-based adjuvant that can enhance the enzyme hydrolysis of cellulose and make it easy to recycle the cellulase could be more popular. Improving the stability of aggregation-induced fluorescence and efficiency of the transfer free electron is the key for the application of lignin in photoelectrics. To realize the application of lignin in skin-care products, the dark color of lignin should be whitened. The sunscreen performance of lignin itself cannot meet the daily requirement. Physical or chemical modification should be tested, but should not sacrifice the phenolic hydroxyl groups, which are very important for UV-blocking and antioxidant performance. To break through the original depolymerization of lignin to platform chemicals, key technical issues include making clear the dynamic relation of activating mechanisms of lignin mole-

cules, catalytic active center, and catalyst supporter. Several technologies are expected to result after several years' exploration. **TJ**

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## ABOUT THE AUTHORS

We chose to research this topic because lignin is one of the world's most promising biomass resources. This research differs from previous research in that we take an application-oriented basic approach.

The most difficult aspect of this research was developing lignin as a natural UV blocker for the very first time. It was surprising to discover that lignin is a natural macromolecular sunscreen and that it can be used in high-end cosmetic applications. Also, it was interesting to find that lignin can be used at large scale in polymeric materials.

Mills should consider that their lignin byproduct may become more appealing for a range of applications in the future. Our next step is developing lignin-based products and pushing their use in cosmetic and materials areas.

*Qian is professor, Lou is professor, Liu is associate professor, Yang is professor, Ouyang is professor, Li is associate professor, and Qiu is professor and vice president, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, China. Qian, Lou, and Qiu are also associated with the State Key Laboratory of Pulp and Paper Engineering, South China University of Technology. Email Qiu at xueqingqiu66@163.com.*



**Qian**



**Lou**



**Liu**



**Yang**



**Ouyang**



**Li**



**Qiu**