

# Polyacrylate-based Water-absorbent Hydrogels Prepared with Lignin-related Compounds: Process Conditions and Performance

Shuang Qian, Fang Zhang, Bo Liu, Hao Ren,\* and Guolin Tong

Utilizing biomass resources to synthesize water-absorbent resin has attracted global interest as a new research direction. Lignin, as the second most abundant renewable biopolymer in nature, is a strong candidate for use in renewable materials. In this study, water-absorbent resins were synthesized from lignosulfonate (LS) and acrylic acid (AA) by grafting copolymerization with an aqueous solution of potassium persulfate (KPS) as the initiator and N,N-methylene-bis-acrylamide (MBA) as a crosslinking agent. The optimum process parameters of lignosulfonate-grafted-polyacrylic acid resin (LS-PAA) were obtained via a single-factor method: AA 30 wt.%, LS 2.67 wt.% (to AA), cross-linker 0.03 wt.% (to AA), initiator 0.43 wt.% (to AA), and neutralization 65%. The optimum reaction temperature was 60 °C. Although lignin is a hydrophobic polymer, it has many reactive functional groups that can react with AA. It has been expected that adding lignins can change the cross-linking density by their three-dimensional structure, thus increasing the water absorbency. The LS-PAA resins were compared to other kinds of lignin derivatives including alkali lignin, lignocresol, lignoresorcinol, and lignopyrogallol under the same reaction conditions. The results showed that changing the types of lignin can change the resulting water absorbency. Lignopyrogallol-grafted-polyacrylic acid resin (LP-PAA) showed the highest water absorbency (2137 g/g).

*Keywords:* Lignin; Acrylic acid (AA); Potassium persulfate (KPS); N,N-Methylene-bis-acrylamide (MBA); Water-absorbent resin; Absorption capacities

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## INTRODUCTION

Water-absorbent resin is a kind of functional polymer that is being developed quickly and widely. It plays an important role in water absorption, water retention in medicine, agriculture, forestry, gardening, desert governance, and many other fields (Shen *et al.* 2016). Due to the recent increase in environmental consciousness, the renewable and biodegradable properties of materials are closely scrutinized. As a result, using biomass resources as raw materials to design and synthesize environmentally friendly water-absorbent resin is becoming a popular research direction (Ma *et al.* 2011). Biomass resources such as starch, cellulose, and chitosan have been used to synthesize water-absorbent resin (Li *et al.* 2007; Shang *et al.* 2008; Dahou *et al.* 2010). The heat-resistant properties of starch-based resins are poor, and they are difficult to store in water due to how easily they corrode. Moreover, cellulose-based resins have poor salt resistance and water absorption performance. The development of a new type of water-absorbent resin

design would be immensely valuable.

Lignin, as a natural aromatic polymer, is rich in lignocelluloses. It is usually used for waste combustion to generate energy in pulping and papering processes. Due to the three-dimensional stereoscopic structure of the aromatic ring of lignin, the properties of the unique polymer have not been fully examined and utilized. In recent years, with the increasing discussion and application of biomass, research investigating the application and detailed structures of lignin has been undertaken. There are some reports on the study of lignin-based resins, but the type of lignin compound was largely limited to lignosulfonates (Hu *et al.* 2013; Hao *et al.* 2016).

In this study, for the purpose of extensive development and application of lignin products, alkali lignin (AL), lignocresol (LC), lignoresorcinol (LR), and lignopyrogallol (LP) were used in the synthesis of water-absorbent resin, and their water absorption capacities were compared with lignosulfonate-grafted-polyacrylic acid resin (LS-PAA). In addition, there are some inherent advantages of lignin-related compounds for the preparation of PAA-based hydrogels: (1) resistance to microbial attack; (b) ability to solubilize and bind oily contaminants present in water; (c) ability to take up heavy metal ions from solution; and (d) potential ability to block the formation of some of the cross-linking within a PAA-based hydrogel.

## EXPERIMENTAL

### Materials

Acrylic acid (AA) was supplied by Kelon Chemical Reagent Co., Ltd. (Chengdu, China). Sodium chloride (NaOH), potassium persulfate (KPS), and N,N'-methylene-bis-acrylamide (MBA) were purchased from Nanjing Advanced Polymer (Nanjing, China).

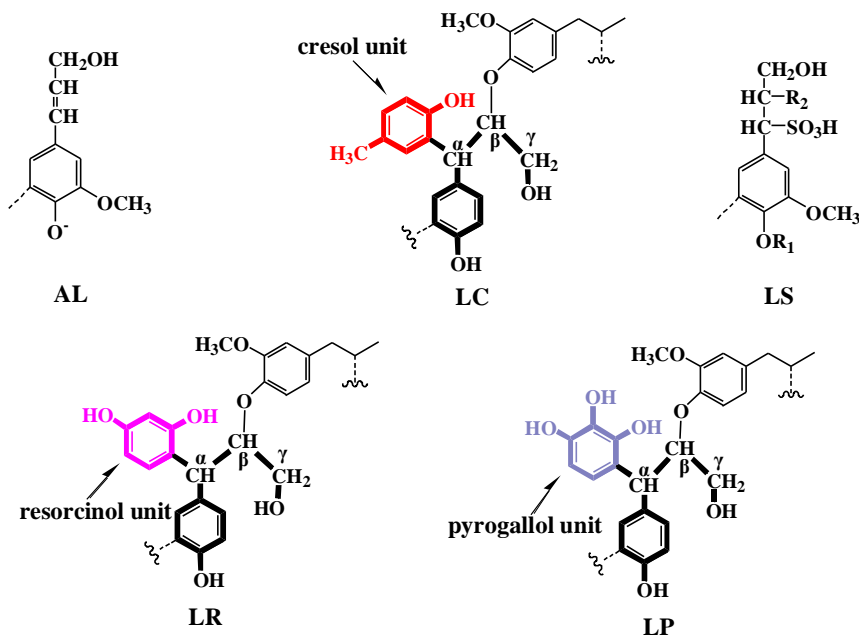


Fig. 1. Molecular structure of lignin types

The bamboo (*Sinocalamus affinis*) was grown in Shaoxing, Zhejiang, China. Alkali lignin (AL) was separated from black liquor from bamboo kraft cooking *via* acid

precipitation (Liu *et al.* 2017). Lignophenols, including LC, LR, and LP, were derived from bamboo mills *via* the phase separation method (Funaoka and Fukatsu 1996) by using 72% sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) as a catalyst and *p*-cresol, resorcinol, and pyrogallol as organic solvents, respectively. Lignosulfonate (LS) was supplied by the Tianjin Institute of Fine Chemicals (Tianjin, China). The structures of five lignin-related compounds are shown in Fig. 1 (Morck 1986; Gargulak and Lebo 2000; Ren and Funaoka 2007).

## Methods

### *Physicochemical characterization analysis of lignins*

Calibration for the weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ), polydispersity ( $M_w/M_n$ ), and the gel permeation chromatography (GPC) of lignins were determined on a PL-GPC50 plus Integrated GPC System (Varian Inc. Company, City, Country) equipped with a Waters 2410 RID detector (City, Country). Sepax Mono-GPC columns (Manufacturer, City, Country) (100 Å, 300 Å, 500 Å, 10 mm ID × 300 mm) were connected in a series, and tetrahydrofuran (THF) was used as an eluent under the flow rate of 1.0 mL/min. The FT-IR spectra of lignins were obtained on a Bruker VERTEX80 Spectroscope (City, Country) using KBr discs. The spectra were recorded in a range from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> over 32 scans.

### *Preparation of water absorbent resin*

A certain amount (5.00 g to 8.00 g) of acrylic acid was put into a 100-mL beaker and then sodium hydroxide (NaOH) solution was gradually added into the beaker under an ice water bath to prepare an acrylic acid sodium within a range of neutralization degree (50% to 70%). Next, a certain amount of lignin (0.30 g to 1.00 g) was dissolved in the acrylic acid sodium solution through stirring. Then, the mixtures were transferred to a four-neck flask setting with a mechanical agitator, a reflux condenser pipe, and a thermometer under nitrogen protection. When the reaction temperature (50 °C to 70 °C) was reached, potassium persulfate (0.0400 g to 0.1000 g) and N,N'-methylene-bis-acrylamide (0.0040 g to 0.0080 g) were added. After the reaction mixture reached a liquid viscosity, it was poured into a 200-mL beaker loaded with 100 mL ethanol. After soaking for 24 h, the products were washed 1 to 2 times until the eluate became colorless. Next, the products were cut and then oven-dried at 60 °C. The dried products were extracted with acetone, and the specimens were vacuum dried in the presence of phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>). The products were used for the following purposes. Lignosulfonate was used as the initial lignin sample, and the synthesis processes were discussed. After achieving optimum process conditions, kraft lignin (AL), lignocresol (LC), lignoresorcinol (LR), and lignopyrogallol (LP) were tested using the same methods.

### *Measurement of deionized water/physiological saline absorbency*

An amount of 0.01 g dry resin powder (accuracy of 0.0001 g) was immersed in 100 mL deionized water or a 0.9% sodium chloride (NaCl) aqueous solution at room temperature. After equilibrium adsorption (10 h), the resins were poured into a known quantity of 200-mesh nylon yarn bags used to remove excess water and then weighed (Bao *et al.* 2011). The absorption capacity ( $Q$ , g/g) was calculated according to Eq. 1,

$$Q = (W_e - W_d) / W_d \quad (1)$$

where  $W_d$  (g) and  $W_e$  (g) were the mass of dried resin and the equilibrium adsorption, respectively.

## RESULTS AND DISCUSSION

### FTIR Spectra of Lignins

Five lignin-related compounds were compared by FTIR analysis (Fig. 2). There were peaks at  $1600\text{ cm}^{-1}$ ,  $1510\text{ cm}^{-1}$ , and  $1430\text{ cm}^{-1}$ , which belong to the vibrations of aromatic nuclei in all spectra. A distinct C=O vibration, belonging to carboxyl or ester group at  $1730\text{ cm}^{-1}$ , was found in all of the lignophenols' spectra, which is attributed to the esterified coumaric acid in bamboo lignin (Ren and Funaoka 2007; Qian *et al.* 2015). The introduced phenols peaks were observed at  $815\text{ cm}^{-1}$ ,  $842\text{ cm}^{-1}$ , and  $802\text{ cm}^{-1}$  for lignocresol, lignoresorcinol, and lignopyrogallol, respectively. The peak at  $980\text{ cm}^{-1}$  was found in LS's FTIR spectra, which belonged to the vibrations of the sulfonic group.

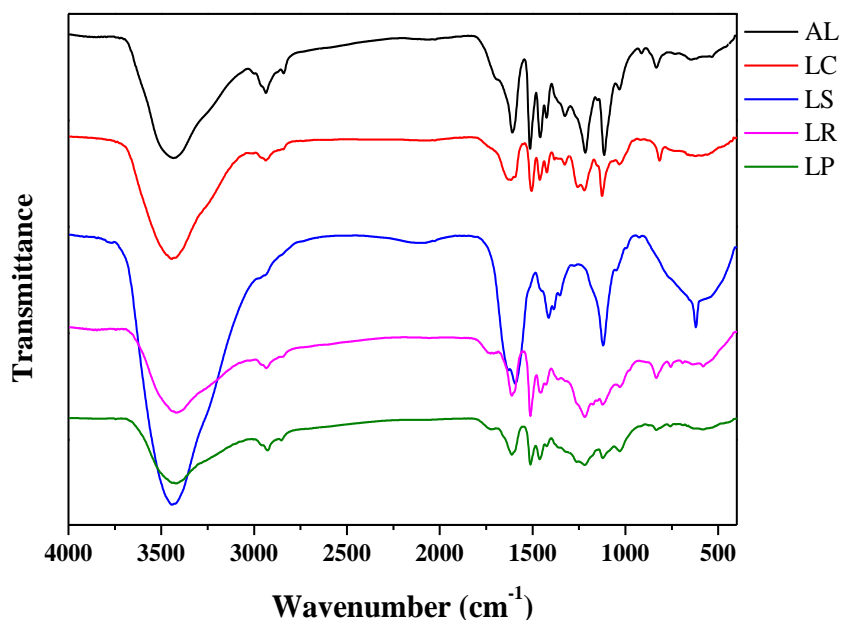


Fig. 2. FTIR spectra of lignins

### Molecular Weight Distribution of Lignins

The molecular weight distributions of lignins were determined using gel permeation chromatography. The results are shown in Table 1. The weight-average molecular weight of alkali lignin was  $2184\text{ g/mol}$ , and the polydispersity was 2.39 units. Compared with alkali lignin, the polydispersities of lignophenols were lower (1.40 units to 1.83 units). These results indicated that the molecular structures of lignophenols were more regular.

Table 1. Molecular Weight Distribution of Lignophenols

Sample	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	$\bar{M}_w/\bar{M}_n$
Alkali Lignin	899	2184	2.39
Lignocresol	3364	6156	1.83
Lignoresorcinol	3401	2562	1.52
Lignopyrogallol	3699	2638	1.40

### Influence of Monomer Concentration on Water Absorption Capacity

The association of water absorption capacity with monomer concentration is shown in Fig. 3. As the monomer concentration was increased from 20% to 40%, water absorption capacity first increased then decreased. When monomer concentration was low, the generated resin had a low molecular weight and an imperfect network structure due to the low polymerization reaction rate of free radicals and its low density. Therefore, water absorption capacity was low. Free radical density increased with monomer concentration, thus the polymerization reaction was accelerated. Therefore, as the molecular weight of the generated polymer increased and the network structure gradually increased, the water absorption rate increased. When the monomer concentration was 30%, the water absorption capacity peaked, then weakened as the monomer concentration further increased. When the monomer concentration was over 30%, heat dissipation in the polymerization process became difficult, which caused an implosion reaction. Finally, the molecular chain of the whole system was shorter and the network structure of resin was imperfect, resulting in a decline in the overall water absorption capacity (Ma *et al.* 2016).

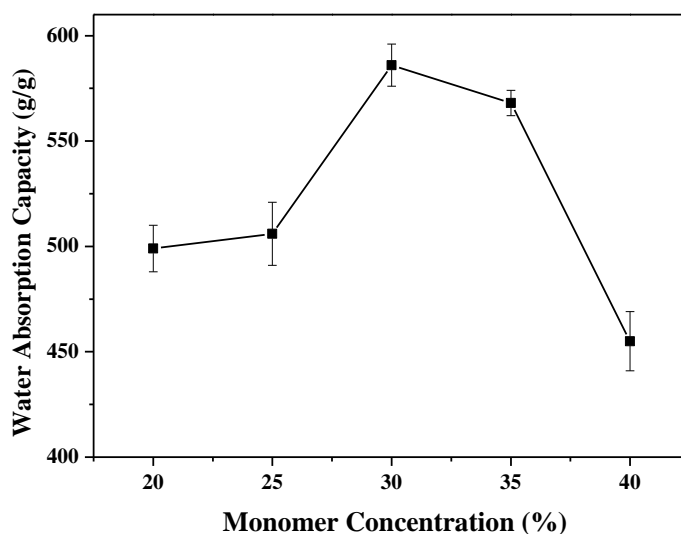


Fig. 3. The influence of monomer concentration on water absorption capacity

### The Influence of Lignosulfonate Content on Water Absorption Capacity

The association of water absorption capacity with the amount of lignosulfonate is shown in Fig. 4. With an increase in lignosulfonate content, the water absorption capacity first increased and then decreased. Lignosulfonate can be classified as an anionic surface active agent because it has both hydrophobic groups (C<sub>3</sub>-C<sub>6</sub> skeleton structure) and hydrophilic groups such as sulfonic and carboxyl groups. When the dosage of lignosulfonate was 2.7 wt.% (to AA, the same below), the water absorption capacity of resin peaked. When the dosage exceeded 2.7 wt.%, excess lignosulfonate could not be grafted by acrylic acid due to self-flocculation. The phase interface configuration of these unreacted lignosulfonate was not arranged as would be expected for low molecular surfactants. Although it could reduce the surface tension, the inhibitory effect was weak. Therefore, micelles could not be formed, resulting in a decline in the overall water absorption capacity (Carr 1992; Yoshinobu *et al.* 1994; Xie *et al.* 2007)

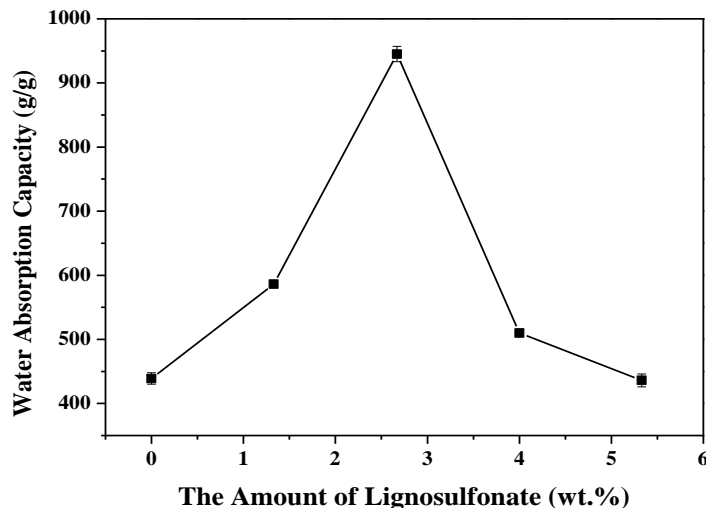


Fig. 4. The influence of lignosulfonate content on water absorption capacity

### Influence of Crosslinking Agent Content on Water Absorption Capacity

The association of water absorption capacity with the amount of crosslinking agent is shown in Fig. 5. With an increase in the amount of crosslinking agent, the water absorption capacity first increased and then decreased. When the dosage of the crosslinking agent was low, the junction was small. Under these conditions, water absorption capacity was good but the soluble part of the resin also increased, which made the overall water absorption capacity low. When the amount of the crosslinking agent was 0.03 wt.% (to AA, the same below), the water absorption capacity peaked. When the dosage of crosslinking agent exceeded 0.03 wt.%, the water absorption capacity decreased. This was because the crosslink density became too large and the molecular weight among network points became too small to expand easily due to the swelling caused by the excessive dosage of the crosslinking agent. Therefore, there was a reduction in the amount of water that the resin could hold (Hu *et al.* 2013), resulting in a decline in the overall water absorption capacity.

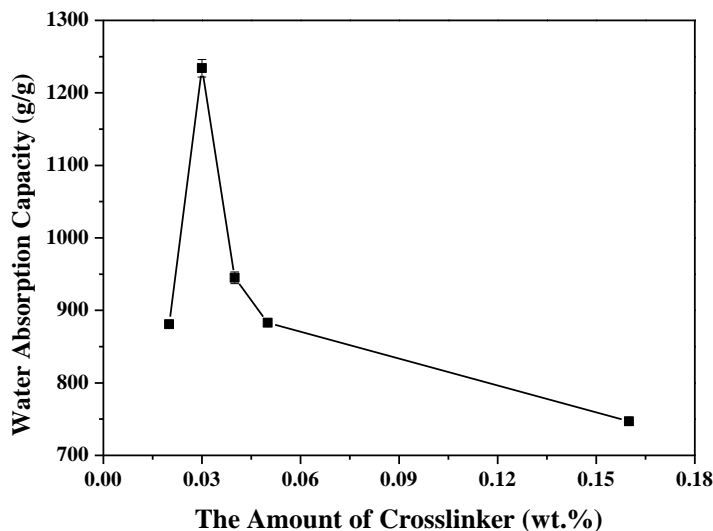


Fig. 5. The influence of crosslinking agent content on water absorption capacity

### Influence of Initiator Content on Water Absorption Capacity

The association of water absorption capacity with the amount of initiator is shown in Fig. 6. As the initiator content increased, water absorption capacity first increased and then decreased. When the amount of initiator was small, the low active center of the polymer reaction resulted in a slow polymerization rate. In that case, the crosslinking degree was too small to form a three-dimensional network structure of polymer, which resulted in a generated product that was water-soluble. Therefore, water absorption capacity was low. As the initiator content increased, the network structure of polymer began to form, which resulted in an increase in the water absorption capacity. When the dosage of initiator was 0.4 wt.% (to AA, the same below), water absorption capacity peaked. When additional initiator content was added, the polymerization reaction rate increased. However, more acrylic radical due to the increase of homopolymerization and the decrease of polymerization reaction. Thus the water absorption capacity began to decline.

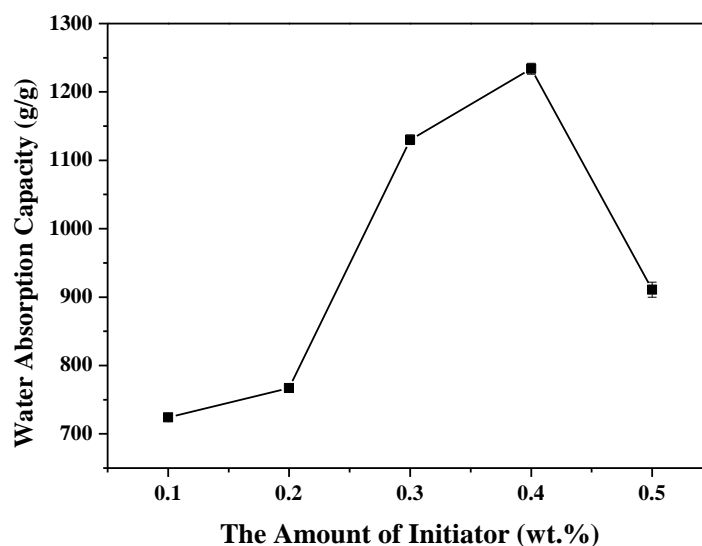


Fig. 6. The influence of initiator content on water absorption capacity

### Influence of Neutralization Degree on Water Absorption Capacity

The association of water absorption capacity with neutralization degree is shown in Fig. 7. As neutralization degree increased, water absorption capacity first increased and then decreased. This was due to the higher hydrophilicity of  $-\text{COONa}$  compared to  $-\text{COOH}$  (Xie *et al.* 2007). When the neutralization degree was low, a crosslinked network structure of monomers formed by self-polymerization, which resulted in better water absorption capacity. When the neutralization degree increased, the rate of the self-polymerization reaction reduced, and the monomers began to graft lignosulfonate. However the quantity of lignosulfonate grafted by monomers was small. Overall, the water absorption capacity decreased. As the neutralization degree increased, the rate of the polymerization reaction increased, which resulted in a higher molecular weight of the polymer and a fully crosslinked structure. Consequently, water absorption capacity gradually improved. When the neutralization degree was 65%, the water absorption capacity of resin peaked. When the neutralization degree was over 65%, polymerization occurred frequently so that the degree of crosslinking was large, which resulted in a decrease in water absorption capacity.

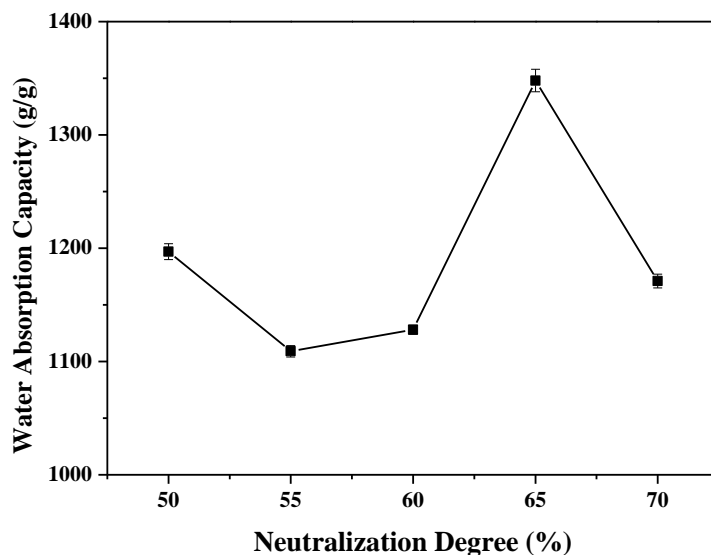


Fig. 7. The influence of neutralization degree on water absorption capacity

### Influence of Reaction Temperature on Water Absorption Capacity

The association of water absorption capacity with reaction temperature is shown in Fig. 8. In the range of 50 °C to 70 °C, the water absorption capacity was stable in the range of 1329 to 1348 g/g. No significant effect of reaction temperature on the water absorption capacity of resins was found. However, the error of water absorption capacity increased notably after 60 °C. This occurred because heat dissipation became difficult at high temperatures, and the reaction process became harder to control. When the reaction temperature was 60 °C, the water absorption capacity was relatively high and the error bar was relatively small. Therefore, the optimal reaction temperature was 60 °C.

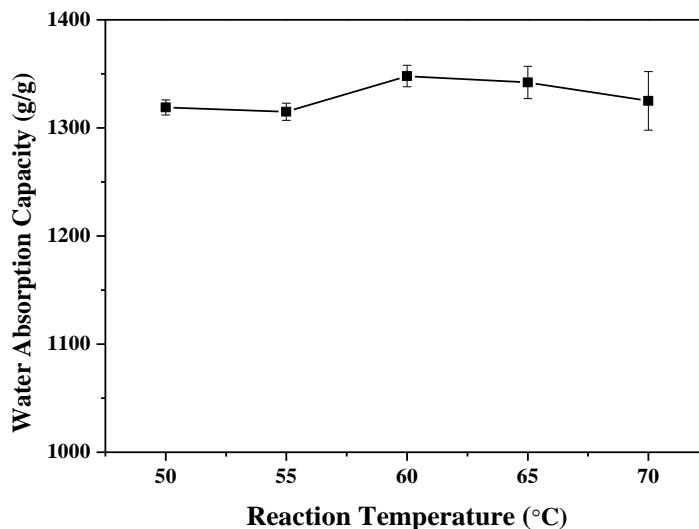


Fig. 8. The influence of reaction temperature on water absorption capacity



## Influence of Lignin Types on Absorption Capacities

The effect of lignin type on the absorption capacities of resins was investigated under the above-described optimum conditions and the results are shown in Fig. 9. In all cases, the addition of a small amount of lignin (approximately 0.5 wt.% to AA) greatly increased the absorption capacities compared with those of PAA resin. This was due to the differences in the structure of the lignin macromolecules. The alkali lignin had fewer functional groups, low solubility in water, and its synthesized resin exhibited lower absorption capacities than the synthesized resins of other lignin types. Lignocresol-grafted-polyacrylic acid resin and liginosulfonate-grafted-polyacrylic acid resin had higher absorption capacities than alkali lignin-grafted-polyacrylic acid resin. This was because lignocresols contained more hydroxyl groups than alkali lignins (Funaoka and Fukatsu 1996; Qin *et al.* 2015); thus more acrylic acid could be grafted on lignocresol than alkali lignin. As a result, the polymerization degree increased, which resulted in higher absorption capacities. However, LS-PAA resin displayed better absorption capacities compared with LC-PAA resin. This was because liginosulfonate had sulfonic and carboxyl groups, which are hydrophilic groups, and the hydrophilic properties of LS-PAA were greater than those of the hydroxyl groups. Additionally, different lignins may act as dispersants in the whole system (Raschip *et al.* 2013), leading to different void size and distribution in resins.

However, lignocresol is a kind of lignophenol that, through a phase separation system, can be changed according to the requirements of a given application. In general, cresol can be replaced by catechol, resorcinol, and pyrogallol, *etc.*, which have one, two, or more phenolic hydroxyl groups. In this study, LR and LP were also tested for grafting by polyacrylic acid to generate resins. In Fig. 9, the absorption capacity of LP-PAA resin was notably higher than that of other lignin types. This was mainly because lignopyrogallol had more phenolic hydroxyl groups and much better water solubility. In the process of absorbing water, lignopyrogallol could absorb multilayer water. As such, its water absorption capacities were greatly increased. These data indicated that modified lignin samples have potential to be used in developing absorbent materials.

It was interesting that modified lignin could be used in the development of water absorbent resin. However, the reaction mechanism and detailed internet structure of the resin still need further study.

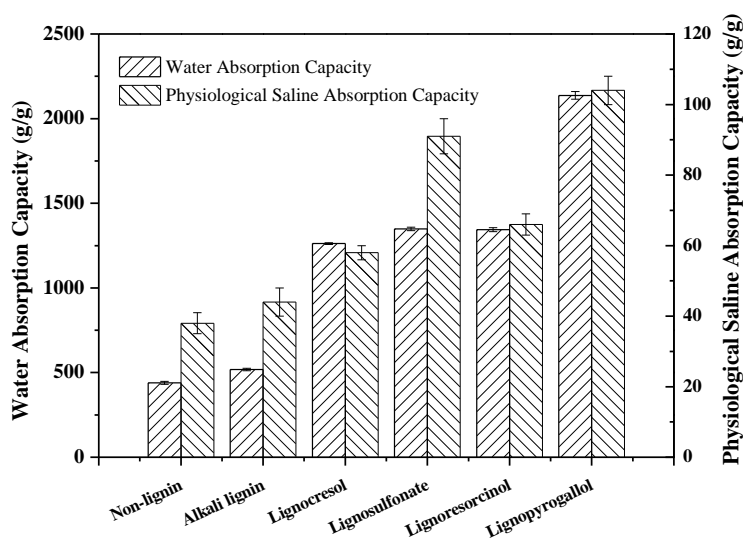


Fig. 9. The influence of lignin types on absorption capacities

## CONCLUSIONS

1. Using a single factor analysis method, the optimum process conditions of lignosulfonate-grafted-polyacrylic acid resin (LS-PAA) were identified: 30% monomer concentration, 2.67 wt.% dosage of lignosulfonate (to AA, the same as below), 0.03 wt.% dosage of crosslinking agent, 0.43 wt.% dosage of initiator, 65% neutralization degree, and a 60 °C reaction temperature. Under the above conditions, the water absorption capacity of LS-PAA resin was as high as 1348 g/g.
2. Alkali lignin, lignocresol, lignoresorcinol, and lignopyrogallol were tested to synthesize the same kind of water absorbent resin under identical conditions. Compared with the default polyacrylic acid resin (PAA), the addition of a small amount of lignin to the synthesized water-absorbent resin increased absorption capacities. Additionally, the degree of cross-linking was not evaluated, under the conditions of preparation, the incorporation of the lignophenols may have resulted in lower cross-linking, which is consistent with the results.
3. Lignopyrogall-grafted-polyacrylic acid resin (LP-PAA) showed the highest water absorption capacity (2137 g/g), which was higher than lignosulfonate-grafted-polyacrylic acid resin (LS-PAA).

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