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Ultrasonic Synthesis and Properties of Sodium Lignosulfonate -grafted Poly (acrylic acid-co-acryl amide) Composite Super Absorbent Polymer

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Abstract: A new method (ultrasound synthesis) has been applied to prepare a sodium lignosulfonate-grafted poly (acrylic acid-co-acryl amide) superabsorbent polymer (SL/P(AA-co-AM) and the success was confirmed by FTIR（Fourier Transform Infrared Spectroscopy）, SEM（scanning electron microscope）and TG/DSC（Thermogravimetry/ Differential Scanning Calorimetry）. The synthetic conditions of SL/P(AA-co-AM) were optimized by L_{16} $(4)^5$ orthogonal experiment. The maximum water absorbency (1350 g/g) and physiological saline absorbency (96 g/g) were achieved under the optimized synthetic conditions. Adjusting pH and existence of metal ions have negative effects on the water absorbency of SL/P(AA-co-AM), while the rising temperature has a positive influence on it. The swelling behaviors of SL/P(AA-co-AM) were also investigated, and the results revealed that the water diffusion in this superabsorbent was non-Fickian transport, and the swelling process fitted Schott model. In additional, both water absorbency and physiological saline absorbency of SL/P(AA-co-AM) were improved versus the P(AA-co-AM) superabsorbent.

Keywords: superabsorbent, lignosulfonate, acrylic acid, acryl amide, orthogonal experiment

1. Introduction

Superabsorbent polymers (SAPs) are lightly cross-linked three-dimensional (3D) networks of flexible polymer chains and can take up a multiple amount of water compared with general water-absorbing materials in which the absorbed water is hardly removable even under some pressure. [1] SAPs are primarily used as an absorbent for water and aqueous solutions for diapers, adult incontinence products, feminine hygiene products, and similar applications. Promisingly, in these applications, superabsorbent materials will replace traditional absorbent materials such as cloth, cotton and cellulose fibre. Therefore, the water absorbency (Q_e) and physiological saline absorbency (Q_s) are two main parameters to evaluate the performances of SAPs. SAPs contain a large number of strongly hydrophilic groups, like carboxyl groups, sulfonic acid groups, hydroxyl groups and so on. SAPs are widely used in agriculture, horticulture, medical care, petroleum industry, and artificial intelligence. [2] These absorbent polymers are mainly fabricated from acrylic acid and a cross-linker (like acrylic acid-acrylamide copolymer (P(AA-co-AM)) by solution or suspension polymerization, which requires quite a long time and relatively high temperature. For example, Rashidzadeh et al. [3] prepared a novel bioabsorbent under the conditions of 70℃ and 4h, Zhu et al. [4] synthesized a PAM/GO superabsorbent under the conditions of 70℃ and more than 3h.

Ultrasound synthesis has been established as a significant and effective technique in Polymer Chemistry.[5] High-intensity ultrasound can be used for the preparation of novel polymers and provides an unusual route to known polymers. Cavitations-induced sonochemistry provides a unique interaction between energy and matter, with hot spots inside the bubbles of roughly 5000 K, pressures of about 1000 bar, heating and cooling rates of >1010K s^{-1} , which causes the formation of free radicals. [6-7] With the assist of ultrasound, a large amount of polymerization reactions can be carried out in shorter reaction time, and higher yields can be obtained under milder conditions. [8-10] More and more works have been reported due to the advantages of sonochemical synthesizing method .[11-12]

Recently, a lot of attentions have been paid to the superabsorbents prepared with biomass like starch [13], chitosan [14], cellulose [15] and cultured auricularia auricula [16] by reasons of their low cost, abundant resources and biodegradability. [17] Lignin is the most abundant aromatic compound on earth and co-exists with cellulose in wood biomass. Nowadays, most lignin applications are based on technical lignin (such as lignosulphonate), which are mostly separated during the pulping process. [18-20] Lignosulphonate is functionalized with lots of hydrophilic groups such as sulfonic, carboxyl, and hydroxyl groups as well as hydrophobic aromatic and aliphatic groups (like sodium lignosulphonate (SL)) which make it a suitable material in the modification of superabsorbents. For instants, Wu et al. [21] and Peng et al. [22] have prepared lignosulphonate grafted superabsorbents with magnesium lignosulphonate and calcium lignosulphonate, respectively. While compared with these two papers, the reaction time cost in this study is much shorter (T=2h in this study versus T=8h in Wu's work) and sodium lignosulphonate (RMB ¥ 900/t) is much cheaper than magnesium lignosulphonate (RMB ¥ 1800/t) and calcium lignosulphonate (RMB ¥ 1400/t).

In this paper, the rapid synthesis of lignin-grafted poly (acrylic acid-co-acrylamide) superabsorbent polymer (SL/P(AA-co-AM)) with sodium lignosulphonate was described, the water absorbing properties of SL/P(AA-co-AM) was discovered and the kinetic model of SL/P(AA-co-AM) absorbent was discussed.

2. Materials and Methods

2.1 Material

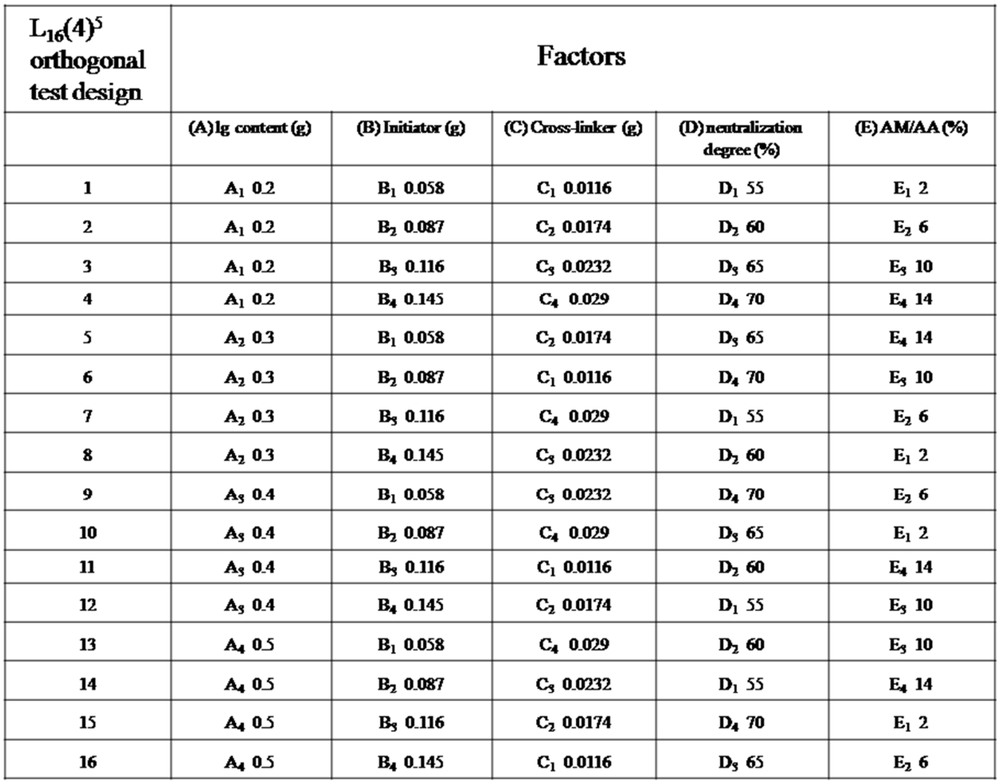
Sodium lignosulphonate was purchased from the Fuchen chemical reagent factory (Tianjin, China). Other reagents used in this experiment including acrylic acid (AA), acrylic amide (AM), ammonium persulfate (NPS), N, N’ - methylene double acrylamide (MBA), sodium hydroxide (NaOH), absolute ethyl alcohol and inorganic reagents were of analytical grades and they were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were used without further purification.

2.2 Orthogonal Experimental Design

The Orthogonal Experimental Design [23-24] was applied to determine the optimal synthetic conditions for SL/P(AA-co-AM). Deionized water absorbency was selected as the response. 5 factors were considered to be the most effective in the preparation of SL/P(AA-co-AM) based on some previous papers [25] and our preliminary experiments: mass of sodium lignosulphonate (A.lignin content), mass of ammonium persulfate (B.initiator), mass of N, N’ - methylene double acrylamide (C.cross-linker), neutralization degree of acrylic acid (D. neutralization degree), the mass ratio of AM to AA (E.AM/AA).

Based on the maximum dosage of sodium lignosulphonate in the pre-experiments, four levels were chosen for each selected factor. Therefore, the $L_{16}(4)^5$ orthogonal array was selected for experimental design (Tab.1). The “$L_{16}(4)^5$ design” is an orthogonal experimental design which contains 5 factors and each factor has 4 levels. The total experiment number is 16 (calculated by the orthogonal table).Based on this orthogonal array, 16 samples were prepared and marked as SL/P(AA-co-AM)-1~16. For each synthesis, mean value of the three replications was the response of this synthesis. Tab.2 shows the experimental design and the Responses (Water absorption rate).

Tab 1. Orthogonal test design. 16 experiments were carried out based on this table.



$L_{16}(4)^5$ orthogonal test design	Factors				
	(A) lg content (g)	(B) Initiator (g)	(C) Cross-linker (g)	(D) neutralization degree (%)	(E) AM/AA (%)
1	A_1 0.2	B_1 0.058	C_1 0.0116	D_1 55	E_1 2
2	A_1 0.2	B_2 0.087	C_2 0.0174	D_2 60	E_2 6
3	A_1 0.2	B_3 0.116	C_3 0.0232	D_3 65	E_3 10
4	A_1 0.2	B_4 0.145	C_4 0.029	D_4 70	E_4 14
5	A_2 0.3	B_1 0.058	C_2 0.0174	D_3 65	E_4 14
6	A_2 0.3	B_2 0.087	C_1 0.0116	D_4 70	E_3 10
7	A_2 0.3	B_3 0.116	C_4 0.029	D_1 55	E_2 6
8	A_2 0.3	B_4 0.145	C_3 0.0232	D_2 60	E_1 2
9	A_3 0.4	B_1 0.058	C_3 0.0232	D_4 70	E_2 6
10	A_3 0.4	B_2 0.087	C_4 0.029	D_3 65	E_1 2
11	A_3 0.4	B_3 0.116	C_1 0.0116	D_2 60	E_4 14
12	A_3 0.4	B_4 0.145	C_2 0.0174	D_1 55	E_3 10
13	A_4 0.5	B_1 0.058	C_4 0.029	D_2 60	E_3 10
14	A_4 0.5	B_2 0.087	C_3 0.0232	D_1 55	E_4 14
15	A_4 0.5	B_3 0.116	C_2 0.0174	D_4 70	E_1 2
16	A_4 0.5	B_4 0.145	C_1 0.0116	D_3 65	E_2 6

Tab 2. The results of $L_{16}(4)^5$ test results.

$L_{16}(4)^5$ test results	Parameters					Water absorbent rate (Deionized water/Aqueous solution of 0.9% NaCl)
	A	B	C	D	E	
1	A_1	B_1	C_1	D_1	E_1	667/64
2	A_1	B_2	C_2	D_2	E_2	321/36
3	A_1	B_3	C_3	D_3	E_3	292/40
4	A_1	B_4	C_4	D_4	E_4	239/37
5	A_2	B_1	C_2	D_3	E_4	454/54
6	A_2	B_2	C_1	D_4	E_3	614/68
7	A_2	B_3	C_4	D_1	E_2	272/43
8	A_2	B_4	C_3	D_2	E_1	403/51
9	A_3	B_1	C_3	D_4	E_2	617/70
10	A_3	B_2	C_4	D_3	E_1	334/41
11	A_3	B_3	C_1	D_2	E_4	239/34
12	A_3	B_4	C_2	D_1	E_3	679/58
13	A_4	B_1	C_4	D_2	E_3	281/39
14	A_4	B_2	C_3	D_1	E_4	410/50
15	A_4	B_3	C_2	D_4	E_1	1002/76
16	A_4	B_4	C_1	D_3	E_2	1270/96

2.3 Preparation of the SL/P(AA-co-AM) Composite Superabsorbent

In each experiment, a known mass (depending on the $L_{16}(4)^5$ design in section 2.2) of NaOH was dissolved in 20 mL deionized water in a 50 mL beaker. Then, AA was pre-neutralized by dropwise addition of 5mL AA into the NaOH solution in an ice-water bath with stirring. After the solution was cooled to room temperature, AM, NMBA, NPS and sodium lignosulphonate were orderly added into the pre-neutralized AA solution on the basis of Table 1. The whole solution was stirred for another 10 min, and then the beaker was sealed and transferred into a KQ-250 ultrasonic reactor (Kunshan, China, P=250W, f=40kHz) to finish the synthesis. The water temperature in the reactor was maintained around 53℃ and the reaction time was set as 2h (2h is the longest reaction time during the orthogonal experiment to make sure all samples can be successfully synthesized. Actually, some samples can be prepared within 30min (like SL/P(AA-co-AM)-16, SL/P(AA-co-AM)-17 and so on)). When the copolymerization was completed, 30 mL anhydrous ethanol was poured into the beaker to remove the water and un-reacted monomers. After soaking in the anhydrous ethanol for 24h, the sample was dried in vacuum oven at 60°C until its mass was constant. In the end, the dried product was ground thoroughly.

2.4 Measurement of Deionized Water/Inorganic Ions Aqueous Solution Absorbency

In the experiment of determining the water absorption capability, 0.01g samples were immersed in 200 mL deionized water, 0.9% NaCl aqueous solution or 0.15 mol·L^{-1} metal ion solution for water swelling equilibrium test at room temperature, respectively. Then the swollen samples were filtered through a 120-mesh nylon tea bag to remove non-absorbed water and weighed again to measure the amount of absorbed water. The water absorbency (Q_e) and physiological saline absorbency (Q_s) of SL/P(AA-co-AM) were calculated by the following equations:

$$Q_e = \frac{m_2 - m_1}{m_1} \quad (1)$$

$$Q_s = \frac{m_2 - m_1}{m_1} \quad (2)$$

Where m_1(g) and m_2(g) are the weights of dry and swollen samples, respectively. Q_e (g/g) or Q_s (g/g) were calculated as the mass of water divided by the mass of the sample. All experiments were carried out three times repeatedly, and the averages were reported in this paper.

2.5 Characterization of the SL/P(AA-co-AM) Composite Superabsorbent

A certain mass (about 0.005g) of SL/P(AA-co-AM) sample was ground thoroughly with dried KBr (mass ratio≈1:100). The FTIR spectra of SL/P(AA-co-AM) sample was obtained with a Nicolet Nexus 470 spectrometer (Nicolet, USA); the surface morphology was studied by a Field Emission Scanning Electron Microscope JSM-7001F (Jeol Ltd., Japan). Dried SL/P(AA-co-AM) powders were coated with a thin gold layer and imaged at an accelerating voltage of 15.0 kV.

TG/DSC analysis was performed with an STA 449C integrated thermal analyzer (Netzsch, Germany) under a nitrogen atmosphere at a heating rate of 5℃·min^{-1}. The temperate ranged from 25℃ to 800℃.

3. Results

3.1 Results and Analysis of Orthogonal Experimental Design

In this experiment, the polymerization reaction was initiated by ultrasonic cavitation, free radicals are produced in cavitating liquid. Thus, ultrasound caused and accelerated the polymerization of monomers. The results of orthogonal experimental design were shown in Tab.2. The mean value of three replications of each Q_e was selected as the result for each run, and the mean value of three replications of each Q_s was also listed in Tab.2. The optimal levels of the factors indicated by mean responses (according to Tab.3) are A_4 (lignin content), B_4 (initiator), C_1 (cross-linked), D_4 (neutralization degree) and E_2 (AM/AA). SL/P(AA-co-AM)-17 was synthesized by this combination, and it was chosen for the further characterization. SL/P(AA-co-AM)-18 was prepared as SL/P(AA-co-AM)-17 only without the addition of sodium lignosulphonate. The Q_e (Q_e=1350) and Q_s (Q_s=96) of SL/P(AA-co-AM)-17 were selected as the maximum water absorbency (Q_{em}) and maximum physiological saline absorbency (Q_{sm}). In addition, the Q_e and Q_s of SL/P(AA-co-AM)-18 was 1140 and 52, respectively.

Tab 3. Analysis of the $L_{16}(4)^5$ test. The optimal level was $A_4B_4C_1D_4E_2$

Analysis of $L_{16}(4)^5$ test results	A	B	C	D	E
K_1	1519	2019	2870	2028	2406
K_2	1743	1679	2456	1244	2560
K_3	1869	1805	1722	2430	1866
K_4	3043	2671	1126	2472	1342
k_1	379.75	504.75	717.5	507	601.5
k_2	435.75	419.75	614	311	640
k_3	467.25	451.25	430.5	607.5	466.5
k_4	760.75	667.75	281.5	618	335.5
R	381	248	436	307	304.5
Optimal level	A_4	B_4	C_1	D_4	E_2

3.2 FT-IR

It can be confirmed that sodium lignosulphonate was successfully grafted onto AM/AA copolymer by comparing the FT-IR spectrum of lignosulphonate with that of SL/P(AA-co-AM)-17. Fig.1 shows the FTIR spectrum of sodium lignosulphonate (a), SL/P(AA-co-AM)-17 (b) , acrylamide (c) and acrylic acid (d). The band at about 3420 cm^{-1} is assigned to the hydroxyl stretching vibrations. The band at 1686 cm^{-1} is related to carbonyl stretching. Asymmetric stretching in carboxylate anion is confirmed by the peak at 1459 cm^{-1} which is attributed to the symmetric stretching mode of the carboxylate groups. [26] The peak at 2,500 cm^{-1} was probably due to atmospheric moisture and carbon dioxide [27]. The peaks from 3300 cm^{-1} to 3500 cm^{-1} were assigned with –OH of AA and N-H of AM, and the peak at 2943 cm^{-1} was assigned with –CH of AA, the peak of C=O of AA and AM appeared at 1686 cm^{-1} and the peak appeared at 1459 cm^{-1} was assigned to COO- of sodium polyacrylate. The peak at 1125 cm^{-1} was assigned with syringyl unit which is a unique phenylproane unit exists in lignin. Therefore it proves that sodium

175 lignosulphonate was successfully grafted onto AM/AA".

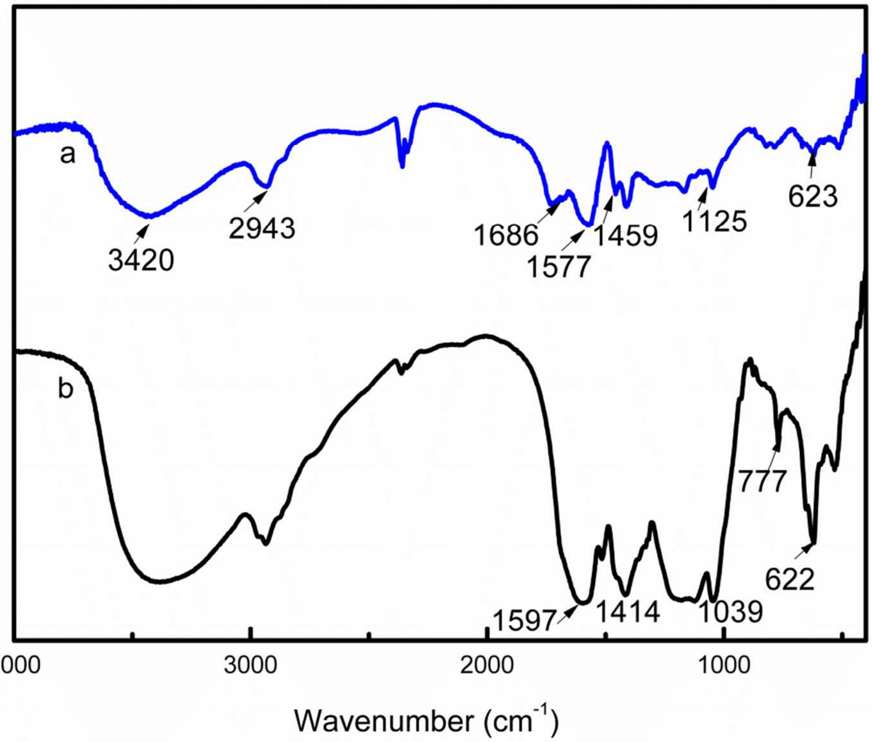


Fig.1 The FTIR spectrum of lignin (a) and SL/P(AA-co-AM) (b). The success of grafting can be confirmed.

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3.3 TG/DSC

TG and DSC curves of SL/P(AA-co-AM)-17 and SL/P(AA-co-AM)-18 are presented in Fig.2. Both two samples have three weight loss ranges. In Fig.2a, the weight loss before 300℃ is the

185 loss of free water and bound water. Between 300℃~500℃, the weight loss is mainly attributed to the decomposition of AA/AM copolymer. And after 500℃ the TG curve represents the end of

decomposition. The decomposition after 700 °C can be attributed to the decomposition of the backbone of polymer molecules. In Fig.2b, the TG curve is mostly consistent with that in Fig.2a. While in Fig.2b, the maximum exothermic peak appears at 237.3℃ during the first weight loss range, which is much later than 157.2℃ in Fig.2a. This observation has clearly indicated that grafting of sodium lignosulphonate has improved the thermal stability of SL/P(AA-co-AM) at lower temperature region.

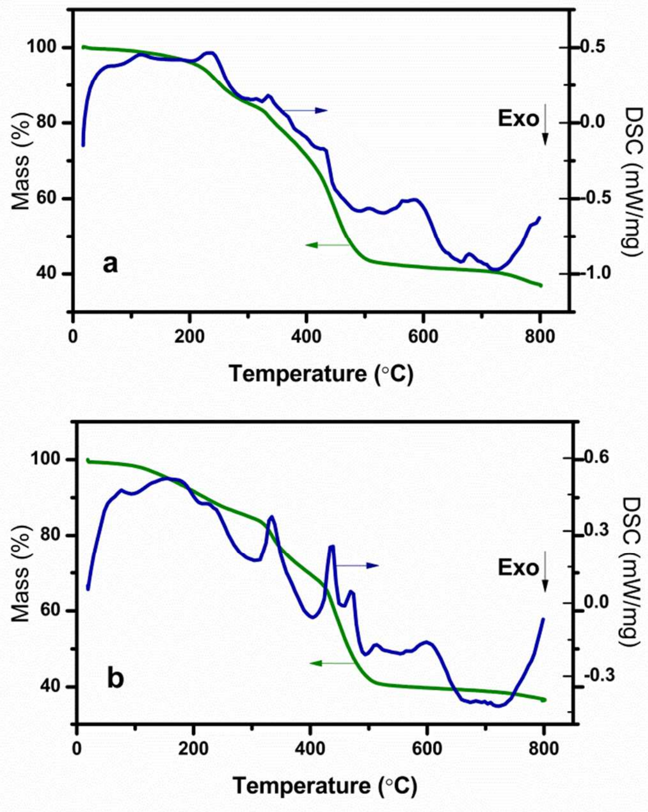

Fig.2 The TG and DSC curves of SL/P(AA-co-AM)-17 (a) and SL/P(AA-co-AM)-18 (b). The addition of sodium lignosulphonate improved the thermal stability at lower temperature region.

3.4 SEM

Fig.3 are the SEM images of SL/P(AA-co-AM)-18 (a) and SL/P(AA-co-AM)-17 (b). The super absorbent polymer synthesized by ultrasound method usually has more pores than those conventional products. It may be resulting from the washing process by ethanol, which remove the homo-polymers with low molecular mass and then form many pores. And it is very obvious that the micro pores in Fig.3b are more and smaller than those in Fig.3a. This can be attributed to the addition of sodium lignosulphonate, of which the grafted short chain made the micro pores dense and the surface rough. In additional, the difference of water absorbency (Q_w17=1350 and Q_w18=1140) may be attributed to the micro pore structure. Tinier micro pores enhanced the structure of SL/P(AA-co-AM)-17 and made the polymer more stable to hold more water, which significantly improved the water absorbency.

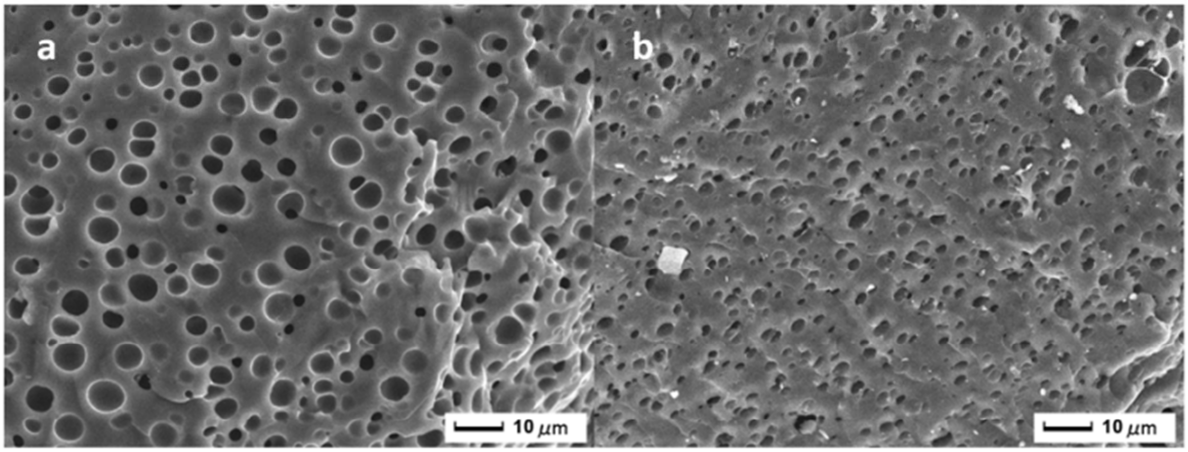

Fig.3 The SEM images of SL/P(AA-co-AM)-18 (a) and SL/P(AA-co-AM)-17 (b). The addition of sodium lignosulphonate made the polymer more stable to hold more water, which significantly improved the water absorbency.

4. Discussion

4.1 Effect of pH

The effect of pH on Q_w is presented in Fig.4a. It is quite clear that either increasing or decreasing the pH will reduce Q_w. This phenomenon can be well interpreted by known theories. The Flory [28] equation is widely used in the explanation of the relationship between swelling ratio and network structure parameters.

$$q_m^{\frac{5}{3}} \cong \frac{\left(i/2\nu_u S^{*1/2}+\right)^2+\left(\frac{1}{2}-\chi_1\right)/\nu_1}{\nu_e/V_0} \qquad (3)$$

where q_m is the swelling ratio; i/ν_u is the concentration of the fixed charge of the no swollen networks; S^* is the ionic strength of the swollen solution; V_0 is the volume of polymer after swelling, ν_e/V_0 is the cross-linking density which refers to the number of effectively cross-linked chains in unit volume. The term $(1/2-\chi_1)/\nu_1$ stands for the network-medium affinity.

Before discussing the influence factors of water absorbency of superabsorbent polymers it is first necessary to understand the reasons why SAPs swell. Sodium carboxylate groups are dissociated in water. The neutralized chains contain same charges that repel each other. Overall electrical neutrality is maintained due to the negative carboxylate groups are balanced by the positive sodium ions. The sodium ions are hydrated upon contact with water, which reduces their attraction to the carboxylate ions (due to the high dielectric constant of water). This allows the sodium ions to move freely within the network, which caused the osmotic pressure within the gel. The mobile positive sodium ions, however, cannot leave the polymer because they are still weakly attracted to the negative carboxylate ions along the polymer backbone and so act like they are trapped by a semi-permeable membrane. Therefore, the driving force for swelling is the difference between the osmotic pressure inside and outside the polymer. Cross-links between polymer chains form a three-dimensional network and prevent the polymer swelling to infinity (i.e. dissolving). This is due to the elastic retraction forces of the network, and is accompanied by a decrease in entropy of the chains, as they become stiffer from their originally coiled state. In the end, when the repulsive force of carboxylate groups and the elastic retraction forces of the network are equal, SAP reaches its maximum water absorbency point. And the maximum swelling of the gel will occur in deionized water.

Therefore, change the pH of solution will significantly increase the value of S* and reduce the difference between the osmotic pressure inside and outside the gel, finally, the more the pH changed, the more the value of q_m will be reduced as shown in Fig.4a. Also SL/P(AA-co-AM)-17 can be considered as a pH responsive material.

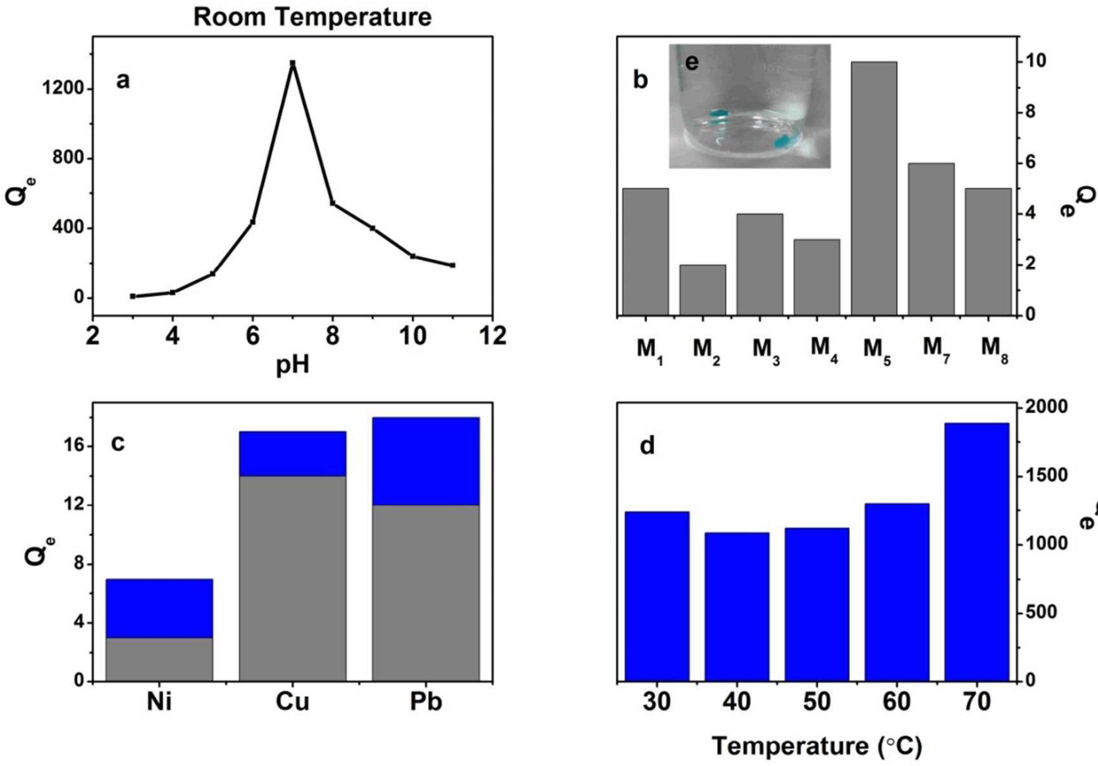

Fig.4 The influence of pH (a), species of metal ions, [M_1, M_2, M_3, M_4, M_5, M_6, M_7 and M_8 respectively represent $ZnCl_2$, $FeCl_3$, $NiCl_2$, $CuCl_2$, $MgCl_2$, $Pb(NO_3)_2$, $Zn(NO_3)_2$, and $Cu(NO_3)_2$] (b), concentration of metal ions, C=0.15mol•L^{-1} (The blue bars) and C=0.005 mol•L^{-1} (c) and temperature (d) on Q_e. The raise of ion strength will reduce the water absorbency of SL/P(AA-co-AM)-17.

4.2 Effect of ions

The effects of other cationic or anionic ions are depicted in Fig.4b and Fig.4c. In Fig.4b, it is clear that the concentration of ions is an important factor in the determination of Q_w. It also can be explained by the Flory equation (discussed in 3.5). For a given superabsorbent polymer, i/ν_u , ν_e/V_0, $(1/2-\chi 1)/\nu 1$ is constant, with the increase of S^* (related to the concentration of ions) , the q_m decreases. However, the main influence may attribute to the chelating activity of different metal ions. It is known that there are a large amount of carboxy groups and amino groups in the SL/P(AA-co-AM)-17 (discussed in 3.2). Therefore, the carboxy groups will combine with metal ions in the aqueous solution, which may impede the spread of molecular chains and reduce Q_w. The absorption capability of SL/P(AA-co-AM)-17 towards metal ions is effective (Fig.4e) and the details of metal ions adsorption of SL/P(AA-co-AM)-17 will be studied in our further research.

4.3 Effect of temperature

Fig.4d depicts the effect of temperature on Q_w. The absorbency decreased from 30℃ to 40℃ and then increased when increasing the temperature from 40℃ up to 70℃. Temperature has two main influences on the thermal motion of polymer. Firstly, it can activate the motor unit and the thermal motion energy of the polymer chain will increase with the rise of temperature. Secondly, the polymer will swell with the rise of temperature; the volume of polymer will increase accordingly and there is more room to store H_2O molecules. It fits the pattern in Fig.4d very well.

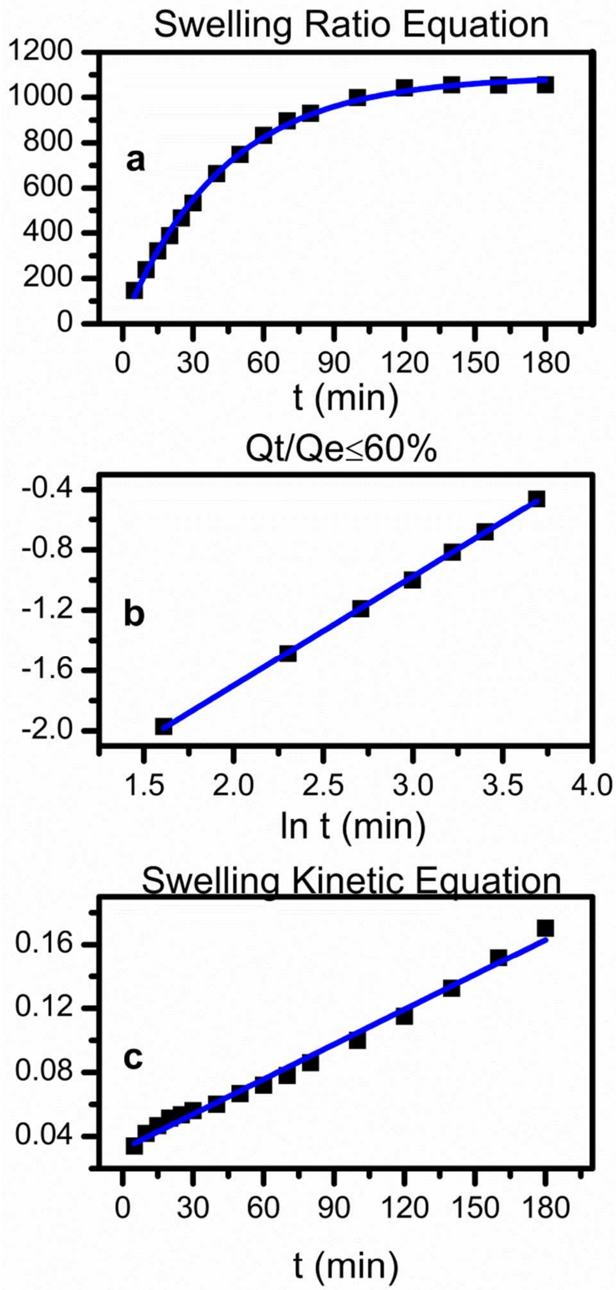

Fig.5 The analysis of the swelling behavior. The swelling behaviors of SL/P(AA-co-AM) is non-Fickian transport, and the swelling process fits Schott model.

280 4.4 Swelling behaviors of SL/P(AA-co-AM)

When a glassy polymer is immersed in a solvent, the solvent diffuses into the polymer matrix, which caused it to swell. This diffusion process involves migration of water into dynamically formed or pre-existing spaces between macromolecular chains. Swelling of hydrogel involves larger scale segmental motion resulting ultimately into an increased distance of separation between macromolecular chains. [29] Firstly, the relationship between Q_t (water absorbency at time t) and t was investigated. Fitting analysis was performed (in Fig.5a) and the equitation $Q_t=1093.78\times\exp(-0.02331\times t)$ was obtained. It can be concluded that the swelling equilibrium was achieved at t=120min. Due to the systemic and random errors, Q_e in this experiment is correspondingly small.

Then the portion of the water absorption curve with a fractional water uptake ($M_t/M_\infty<0.60$) was analyzed with the following equation [30]:

$$\frac{M_t}{M_\infty} = kt^n \quad (4)$$

where M_t is the mass of water absorbed at time t, M_∞ is the mass of water absorbed at equilibrium, k is a characteristic constant of the hydrogel, and n is a swelling exponent describing the mode of the penetrant transport mechanism. Plot of $\ln(M_t/M_\infty)$ versus lnt is depicted in Fig.5b. The constants n and k were calculated from the slop and interception of the plot, respectively. For a cylindrical gel, n=0.45~0.50 corresponds to Fickian-type diffusion process, while 0.50<n<1.0 indicates non-Fickian or anomalous transport and n=1 implies case II (relaxation controlled) transport. For SL/P(AA-co-AM)-17, the swelling exponent n=0.7246, thus suggesting the anomalous or non-Fickian type diffusion.

The kinetics of a hydrogel can be described with Schott's second-order swelling kinetics [31]

$$\frac{t}{Q_t} = \alpha + \beta t \quad (5)$$

In this equation, α and β are two coefficients with physical meaning which are interpreted in the following manner: for long treatment times, β_t »α and the pending β will be the reciprocal of the swelling in the equilibrium ($\beta=1/Q_{equ}$). On the contrary, at a very short treatment time, α»β_t so β_t can be rejected, and in this case α is equal to the inverse of the initial swelling speed

$$\lim_{t\to 0}\left(\frac{t}{Q_t}\right)=\frac{1}{\alpha} \quad (6)$$

Therefore, the ordinate at the origin (α) represents the inverse of the initial swelling. And equation obtained from Fig.5c is $t/Q_t=0.0321+7.272\times10^{-4}t$, the Q_{equ} was calculated as 1375. While Q_{wm} is 1350, it fits the theoretical value (Q_{equ}) very well.

5. Conclusion

In this paper, ultrasound synthesis has been successfully applied to prepare a sodium lignosulphonate (SL) grafted acrylic acid-acrylamide (AA-AM) copolymer superabsorbent. Both Q_e (1350 g/g) and Q_s (96 g/g) of SL/P(AA-co-AM) were improved versus the P(AA-co-AM) superabsorbent. The Q_e of SL/P(AA-co-AM) was affected by the pH, temperature, species and concentration of ions. The swelling behaviors of SL/P(AA-co-AM) is non-Fickian transport, and the swelling process fits Schott model. In addition, SL/P(AA-co-AM) is a promising green absorbent, this ultrasonic method could be a convenient and efficient way to prepare a green superabsorbent material. The applications of SL/P(AA-co-AM) superabsorbent are various and its application will make a significant contribution to the utilization of industrial waste lignin.

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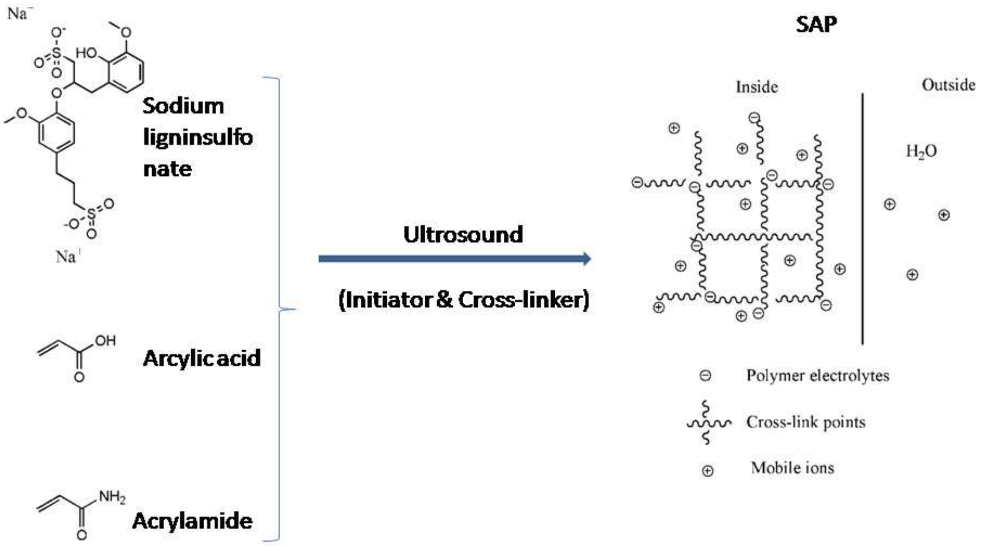

We presented a quick and efficient way (ultrasonic method) to prepare a green and high quality superabsorbent.