

Engineering and slow-release properties of lignin-based double-layer coated fertilizer

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ABSTRACT

Chemical fertilizer has become a necessary condition for increasing the production and income of agricultural products in modern agriculture. However, excessive fertilization and fertilizer leakage could cause environmental pollution. To improve the utilization rate of agricultural fertilizers and reduce environmental pollution, the degradability of slow-release fertilizers (SRFs) has become a research hotspot. In this work, a double-layer coating materials of slow-release fertilizer was fabricated using low-cost polyvinyl alcohol (PVA) and methyl cellulose (MC) as the inner coating materials, and attapulgite was doped into super absorbent polymer poly acrylic acid (PAA) and Polyacrylamide (PAM) grafted natural biodegradable lignin as the outer coating materials. We investigated the chemical structures, mechanical properties, hydrophilic properties and water retention properties of the double-layer coating material coated on the surface of urea particles, and optimized the synthesis parameters to obtain the best water

absorption properties of the outer layer water absorbent. Simultaneously, urea release was evaluated in dissolution experiments. The results show that at the PVA concentration of 5% and the MC addition amount of 2.0 g, the performance indicators of the inner coating liquid were better than other contents. At the same time, more urea molecules (>30 days) were released in the single-layer and double-coated fertilizers, and the cumulative release rates of urea molecules were 92.36% and 85.10%, respectively. Therefore, this work provides research ideas for the preparation of double-coated slow-release fertilizers, which can improve soil water retention and improve fertilizer utilization.

Keywords: Slow-release fertilizer (SRF), Coated fertilizer, Lignin, Water absorbent, Double-coated layer

1. Introduction

In areas with scarce rainfall and dry land, the fertilizer utilization rate is generally at a low level. It has become an important issue to increase the utilization rate of chemical fertilizers and effectively improve soil safety with the serious loss of fertilizers and the intensification of soil salinization [1,2]. Therefore, it is of great significance to accelerate the research and development of new fertilizers [3]. Fertilizer slow and controlled release could effectively improve the utilization rate of chemical fertilizers, while reducing the amount of chemical fertilizers and ensuring efficient methods for providing nutrients to crops. The slow and controlled release coating materials had experienced the development process from inorganic coating to organic coating and then to degradable coating [4,5]. With the continuous advancement of agricultural modernization and the development of polymer materials, environmental protection fertilizer has become a new type of functional fertilizer and more and more researchers pay attention to it [6,7].

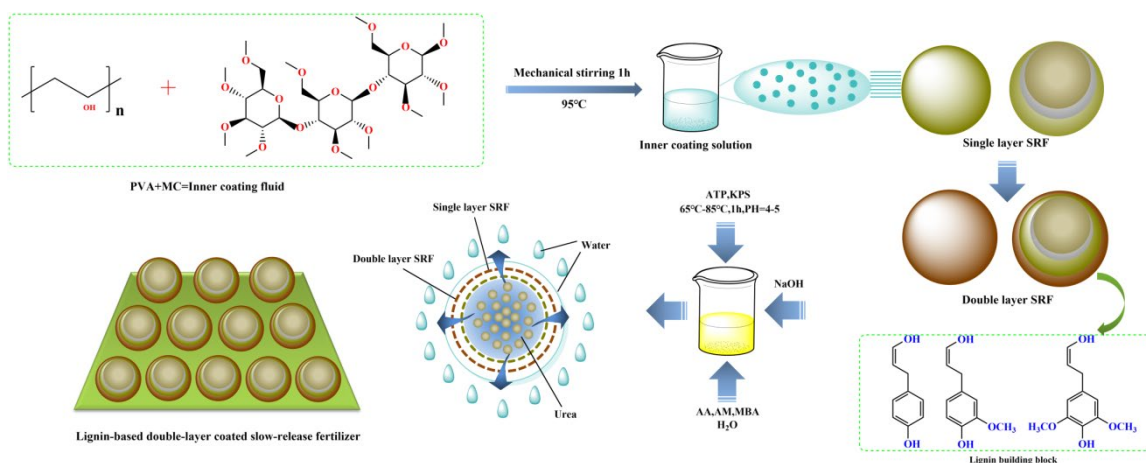
Since 1970s, researchers had concentrated on developing slow-release coated fertilizers [8-10]. Magnesium ammonium phosphate coated fertilizer with better slow-release effect was prepared with polyester compound cover treatment [11]. After 1980s, slow-release fertilizers with polyolefin thermoplastic resin as the main coating material had been widely used. "Nutricote" and "Osmocote" slow-release fertilizers were recognized worldwide [12]. Thereafter, rosin, tung oil and shellac had been added to the coating materials to prepare single-layer slow-release fertilizers [13]. In recent years, the research of double layers coating fertilizer has attracted the attention of researchers. Using ethyl cellulose (EC) as the inner coating and starch-based superabsorbent polymer (SAP) as the outer coating, the fertilizer utilization rate could be increased [14]. Neem seed oil microcapsules were prepared by interfacial polymerization, could slowly release nitrogen and be used as a slow-release nitrogen source for various crops under field conditions [15]. Methyl cellulose (MC) is a renewable resource with low price and good film-forming properties. Polyvinyl alcohol (PVA) contains many hydrophilic groups, which could form hydrogen bonds with MC, improving the water resistance to a certain extent. The addition of PVA could also improve the flexible characteristics of MC. Therefore, the blending of MC and PVA could achieve mutual complement and improve the performance [16].

With the expansion of the use of new coated fertilizers, the issue of soil safety has also attracted people's attention [17]. A large number of researches have been carried out on the

preparation of biodegradable coated slow and controlled release fertilizers by simple and low-cost methods. Black liquor-based hydrogel (BLH) water-retaining and slow-release fertilizers had been shown to significantly promote plant growth and degrade in the soil. Liu X et al. [18] Biodegradable interpenetrating polymer network (IPN) hydrogels based on pre-vulcanized natural rubber (NR) and cassava starch (St) using sulphur (S) and glutaraldehyde (GA) as crosslinkers were developed in a solution form as a coating membrane for slow-release nitrogen fertilizer. Chaiwute V et al. [19]. The lignin-clay nano-hybrid and bio-based alginate cross-linked as the core material, and the super absorbent polymer poly acrylic acid (PAA) as the outer material, the double-layer water-retaining slow-release fertilizer had good controllability, sustainability, cost-effectiveness and environmental stability. Zhang S G et al. [20]. A thermal response-releasing multi-element compound fertilizer was prepared based on dopamine grafted poly(n-isopropylacrylamide) bimolecular layer coated on a salt core, and the effect of environmental temperature on nutrient release was studied. Ma Z et al. [21]. Gelatin microspheres were used as a sustained-release urea carrier and glutaraldehyde (GA) was used as a cross-linking agent, which was prepared by emulsion cross-linking method. Tang J et al. [22] Sodium lignosulfonate and chitosan as natural polyelectrolytes, a biomass-based pH-responsive controlled-release fertilizer was prepared by a simple and environmentally friendly layer-by-layer self-assembly technology, could effectively improve nutrient utilization and promote the growth and development of the corn. Tao Li et al. [23,24]. Because of its high carbon content, biodegradability, hydrophobicity and oxidation resistance and other physical and chemical properties, lignin was always used as an outer water-retaining coating material [20]. In addition, lignin [25] as the substrate of the outer coating of slow-release fertilizer could not only improve the water absorption and retention capacity of soil, delay the release of fertilizer nutrients, but also provide carbon source for soil after degradation.

In this work, a double-layer slow-release fertilizer (SRF), used for slowly released nutrients and improved water retention capacity was prepared through the schemed process (Scheme 1), and the practical operation was illustrated as follows: polyvinyl alcohol (PVA) was mechanically stirred at 95 degrees for 1 hour by solution blending, and then cooled to 50 degrees, methyl cellulose (MC) was added to increase the speed and blended with the PVA solution to obtain the inner layer blending solution, next the inner layer coating solution was sprayed on the surface of

the urea particles to form a single-layer coated fertilizer. Afterwards, N,N'-methylene bis (acrylamide) (MBA) was employed as a crosslinker and Potassium persulfate (KPS) was used as a initiator, the inorganic component attapulgite was doped into super absorbent polymer poly(acrylic acid) (PAA) and Polyacrylamide (PAM) grafted natural biodegradable lignin solution as the outer coating materials. After that, the synthesized materials were characterized by FTIR, DSC, SEM and Contact Angle Test Technology.



Scheme. 1 Synthetic Process of Double-Layer SRFs with Water-Retention Capability Using lignin-based Coating Materials.

2. Experimental

2.1. Materials

Lignin (Alkaline, L, AR) was provided by TCI (Shanghai) Development Co. Ltd., acrylic acid (AA, AR, Tianjin Damao Chemical Reagent Factory Co. Ltd., Tianjin, China) and acrylamide (AM, AR, Tianjin Kaixin Chemical Industry Co. Ltd., Tianjin, China) were used as monomer. N,N'-methylene bis (acrylamide) (MBA, AR, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) was used as a crosslinker. Potassium persulfate (KPS, AR, Tianjin Kaitong Chemical Co. Ltd., Tianjin, China) was used as a initiator. Natural attapulgite (ATP, supplied by Gansu Haozhou ATP Co. Ltd., Gansu, China) was milled and sieved through a 200-mesh screen before use. Methylcellulose (MC, AR) was purchased from Shanghai Macklin Biochemical Co. Ltd., China. Polyvinyl alcohol (PVA, AR, 98%) was supplied by Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Sodium hydroxide (NaOH, AR) was purchased from Tianjin Best Chemical Co. Ltd., Tianjin, China. P-Dimethylaminobenzaldehyde (PDAB, AR) was provided by Zhanyun Chemical Co. Ltd., Shanghai, China. Potassium bromide (PB, SP) was purchased from Damao Chemical Reagent Co. Ltd., Tianjin, China. Urea (AR) was purchased from Tianjin

Guangfu Technology Development Co. Ltd., Tianjin, China. The soil used in this work is a representative sample of Lanzhou, which lies in the northwest of China and is a semiarid region. All of the other chemicals used were analytically pure and without further purification..

2.2. Preparation of double-layer coating material

2.2.1. Preparation of Inner Blend Film

Firstly, 3.0g, 4.0g, and 5.0g polyvinyl alcohol (PVA) were respectively added to the three-necked flask under electric stirring and stirred for 1 h at the water bath temperature of 95°C, stirrer speed of 280 rpm to obtain PVA solution concentration of 3 %, 4 %, and 5 %, respectively. And then the speed of the stirrer was increased to 320 rpm, the temperature was lowered to 55°C and a certain amount of MC was added to obtain PVA/MC blend solution [24]. Pure PVA solution was obtained as the above preparation process without MC.

The above PVA/MC blend solutions were respectively allowed to stand for 24 hours to degas, and then were coated on a glass plate with an adjustable film applicator. The thickness of the film was controlled to 2 mm. The films were dried at room temperature for 24 h and removed for use. Thus, we obtained a series of films.

2.2.2. Preparation of outer lignin-based water absorbent (LPA)

A certain amount of lignin was introduced into 100 mL beaker contained 1 mol/L, 50 mL NaOH aqueous solution under magnetic stirring, and then the beaker was put into a 30°C water bath. And 0.8 g attapulgite was added to the lignin solution. 4.0 g acrylic acid, 4.0 g acrylamide and 0.26 g MBA were dissolved in 25 mL of self-made distilled water to obtain a mixed solution,, and the mixed solution was added to the above lignin solution after the attapulgite was evenly dispersed. When the system was evenly dispersed, and added to a three-necked flask under magnetic stirring, and the rotation speed of the magnetic stirring water bath was adjusted to 30rpm and the temperature was adjusted to 30 °C. The pH value of the mixture was adjusted to 5.0 by adding HCl solution (0.1 mol/L). Afterwards, nitrogen gas was bubbled in the three-necked flask for 30 min to fully displace the atmosphere from air to nitrogen. The temperature was raised to 65 °C, and under the conditions of magnetic stirring and nitrogen protection, 0.065 g potassium persulfate (KPS) was added to the system, and reacted at 65 °C, 76 °C and 85 °C for 1 h, respectively to obtain the hydrogel. Nitrogen protection was still used during the reaction. The hydrogel was soaked in a beaker contained 0.1 mol/L, 200 mL NaOH aqueous

solution for 5 min, washed 3 times with self-made distilled water, and dried at 95 °C for 24 h, crushed and sieved at 100 mesh to obtain dark brown lignin-based water absorbent (LPA) [25]. According to the above steps, a water absorbent (PA) without lignin was prepared as a comparison sample.

2.2.3. Preparation of the PVA-MC SRF Beads (PM-SRF)

Urea particles with 10-12 mesh were placed in a coating machine, the PVA/MC blend solution was evenly sprayed on the surface of the urea particles, and the coating was repeated several times to obtain a single-layer coating fertilizer (PM-SRF).

2.2.4. Preparation of the PM-Coated LPA SRF Beads (PML-SRF)

Anhydrous ethanol (10 mL) was sprayed on the surface of the PM-SRF to obtain uniform wet surfaces, afterwards, the pre-ground LPA powder was evenly coated on the outer layer of the PM-SRF. Finally the fertilizer was dried at 50 °C for 48 h to obtain the double-layer coating slow-release fertilizer (PML-SRF).

2.3. Characterization of samples

The surface micro-area and cross-sectional morphology of the sample were observed by scanning electron microscope (SEM, INSPECT F50). Before the SEM observation, the surface of the sample was coated with gold. Thermal analysis was performed by differential scanning calorimeter (DSC, STA 7000, Shimadzu Corporation, Japan) and thermogravimetric (TG, STA 7000, Hitachi High-Technologies Corporation, Japan). The Fourier transform infrared (FTIR) spectra of the samples were collected with a Bruker IFS66v/s FTIR Spectrometer in the range of 500-4000 cm^{-1} , the sample mass was measured by the dry KBr tableting method (mass ratio 1:100). According to the regression equation of the urea content standard curve, the urea concentration determination in the aqueous solution was calculated by measuring the absorbance of the solution using the ultraviolet-visible spectrophotometer at 426 nm (UV-752N, Shanghai Yoke Instrument, China).

2.4. Performance Testing

2.4.1. Water absorption rate test of outer LPA

LPA was dried and ground into powders (100 mesh sieve), then 0.25 g LPA sample was added in a 250 mL beaker containing 250 mL distilled water to absorb water for 24 h. 100 mesh nylon-net was used to filter the hydrogels [26,27], measuring the weight of sample. The water

absorption rate Q_{eq} (g/g) of sample was calculated by using Eq. (1):

$$Q_{eq}(\text{g/g}) = \frac{M-M_0}{M_0} \times 100\% \quad (1)$$

Where, Q_{eq} (g/g) (%) represented water absorption rate of LPA, M_0 (g) represented the quality of the outer LPA before it absorbs water, M (g) represented the mass of the outer LPA after absorbing water.

2.4.2. Viscosity test of inner coating solution

The NDJ-79 rotary viscometer (NDJ-79, Shanghai Changji Geological Instrument Corporation, China) was used to test the viscosity of the PVA/MC blend solution, and the influence of the viscosity of the blend solution on the fertilizer coating effect was explored.

2.4.3. Mechanical properties test of inner film

A uniaxial stretching measurement was carried out in air using a mechanical testing apparatus (WDW-2008, Jinan Star Corporation, China). The lengths of the tensile samples ranged from 10 mm to 120 mm and the thicknesses of the tensile samples ranged from 0.5 mm to 0.8 mm [28]. Each group of samples was measured three times, and the average value was taken.

2.4.4. Water contact angle test of inner film

The OSA optical surface analyzer (OSA60, Zhejiang Ningbo New Boundary Scientific Instrument Corporation, China) was used to measure the water contact angle of the PVA/MC film to explore the influence of MC dosage and PVA concentration on the hydrophilic and hydrophobic effects of the inner coating [29].

2.4.5. The water-holding and water-retention capacity of soil

The experiment was performed at a relative humidity from 20% to 30% at 20 ± 5 °C. Five different amounts of samples (0, 1.0, 2.0, 3.0, and 4.0 g) and 200.0 g of dry soil (below 20 mesh) were thoroughly mixed well, and the mixtures were carefully placed into PVC pipes (150mm in high, 45mm inner diameter), respectively. The bottom of the tube was sealed with non-woven fabrics net (100 mesh) and weighed the whole (defined as W_0). The mixture was slowly soaked by adding deionized water from the upper port of the tube until water seeped out from the bottom of the tube. Stop adding water, after that there was no more water seepage at the bottom of the tube, the tube was weighed again and marked as W_1 [30]. The water-holding capacity ($W_h\%$) of the soil was calculated from below formula:

$$W_h\% = \frac{W_1-W_0}{200} \times 100\% \quad (2)$$

The water retention properties of PML-SRF was measured for five different treatments. Soil with samples were treated as above. Five groups of soil columns were processed under identical conditions at room temperature and weighed every 2 days (W_d). The soil water-retention rate $W_D\%$ was calculated from below formula [31]:

$$W_D\% = \frac{W_d - W_0}{W_1 - W_0} \times 100\% \quad (3)$$

2.4.6. Slow-release behavior in water

The coated fertilizer (10 g) were immersed in a beaker containing 250 mL of distilled water at room temperature, and the solution in the beaker was sampled after every two days interval. The urea concentration was determined and calculated using a UV-Vis spectrophotometer (UV-752N, Shanghai Yoke Instrument, China) for UV quantitative analysis using the standard curve method [32-34]. Under acidic conditions, urea reacts with p-dimethylaminobenzaldehyde to form a tartrazine complex, which absorbs visible light at 426 nm [35]. Specifically, 0, 0.5, 1, 2, 4, 6, 8, 10, 12, 14 mL of urea solution was placed in 10 50 mL colorimetric tubes, and 10 mL of the p-dimethylaminobenzaldehyde was added. Then, distilled water was further added to make up the volume to 50 mL. The solution was mixed and shaken well first followed by a 10 min rest before measuring the absorbance of the solution at 426 nm with a UV-752N spectrophotometer to obtain a series of concentrations [36]. The release experiments were performed in triplicate to reduce error and the average value was taken as a result. The obtained data were subjected to linear correlation analysis using the concentration as the horizontal coordinate and absorbance as the vertical coordinate to obtain the standard curve and regression equation of the urea content.

3. Results and Discussion

3.1. Characterization analysis

3.1.1. Characterization of SEM

SEM images of the surfaces and cross sections of uncoated, single-layer and double-layer coated fertilizers were shown in Fig. 1. Both the surface and cross-section of the uncoated urea particles showed irregular and rough coating shells, with pits and small holes (Fig. 1a, d). After adding the PVA/MC blend liquid as a single-layer coating material, the micropores were filled to make the surface of the inner coated fertilizer smooth and dense (Fig. 1b). MC acted as a sealant and interspersed with PVA, and many densely distributed rod-like structures had been observed (Fig. 1e), this could effectively extend the time for water molecules to enter the inside of the

fertilizer core, thereby avoiding the excessive release of fertilizer nutrients. After the inorganic component attapulgite was doped with super absorbent polymer poly acrylic acid (PAA) and polyacrylamide (PAM) grafted with natural biodegradable lignin solution, and the adsorbent particles were obviously attached to the surface, and the surface became rough, the network-like structure was presented in outer coated fertilizers (Fig. 1c, f), this not only increased the function of water absorption and retention, but also provided a certain degree of anti-extrusion performance for the fertilizer. As can be seen from the macro digital photo of Fig. 1g, the particle size of the fertilizer after coating increased significantly. As was shown in the macroscopic cross section morphology of single-layer (Fig. 1h) and double-layer (Fig. 1i) coated fertilizers, there was a clear shell structure between the fertilizer matrix and the membrane material after coating, indicating that the two-layer coating the membrane material had a good coating effect on the urea fertilizer.

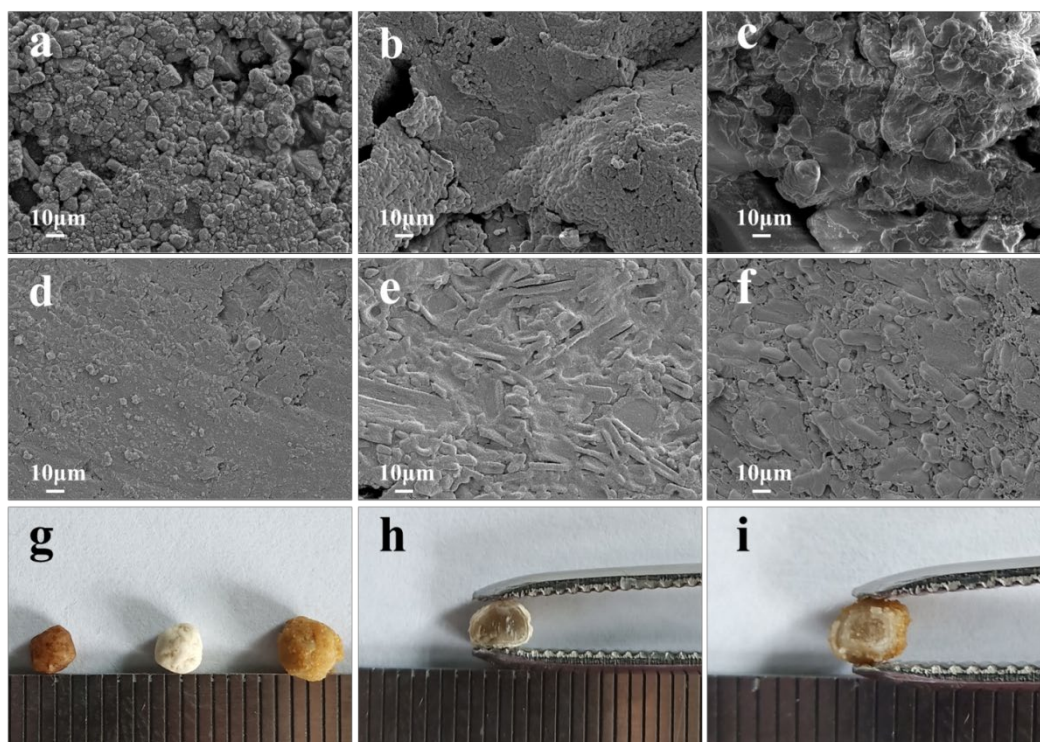


Fig. 1 (a, b, c) SEM morphologies of surface, (d, e, f) SEM morphologies of cross-section, (g, h, i) Macroscopic images of cross-sectional morphology.

3.1.2. Characterization result of FTIR

The FTIR spectra of lignin, attapulgite, lignin-free water-absorbent and lignin-based water-absorbing agent were presented in Fig. 2. In the spectrum of lignin (Fig. 2a), the characteristic absorption peaks are observed at 1610 cm^{-1} (stretching vibration of aromatic rings),

1130 cm^{-1} (C-O stretching vibration peak), respectively. In the ATP spectrum (Fig. 2b), the absorption peak at 3620 cm^{-1} was assigned to Mg-OH stretching vibration peak and Al-OH stretching vibration peak. The peak at 3430 cm^{-1} was ascribed to H₂O stretching vibration, the peak at 1640 cm^{-1} was attributable to -OH bending vibration of absorbed water, the absorption peak at 1030 cm^{-1} was credited with -OH bending vibration. The appearance of these characteristic peaks of H₂O and -OH indicate that there was a thin water film on the surface of the attapulgite, or there was a large amount of structured water between the layer chains. In the spectrum of PA (Fig. 2c), the existence of -COOH, C-H, C=O, C-N bonds in the acrylic acid-acrylamide copolymer corresponded to the representative absorption peaks at 1330, 2940, 1670, 1410 cm^{-1} , respectively. While, a new absorption peak at 1570 cm^{-1} corresponding to the stretching vibration of the aromatic ring of lignin was appeared in the spectrum of LPA (Fig. 2d), which proved that the grafting reaction of acrylic acid-acrylamide copolymer and lignin proceeded successfully, that is, the preparation of lignin-based water absorbent was successful.

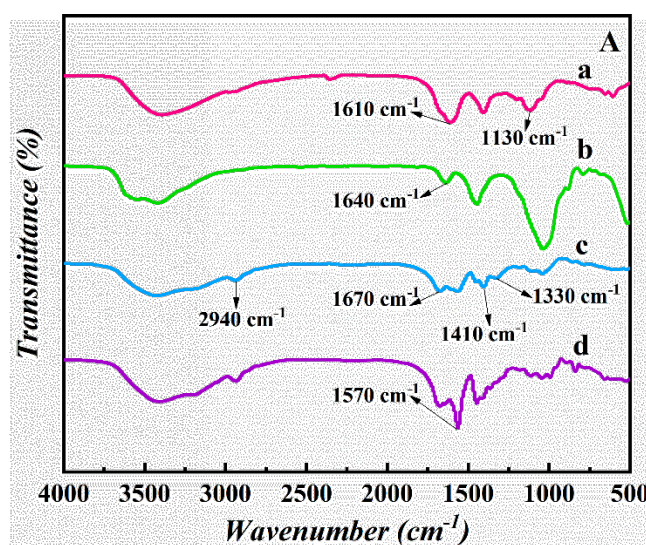


Fig. 2 FTIR spectra of lignin (a), ATP (b), PA (c) and LPA (d)

3.1.3. Characterization result of DSC

DSC analysis of lignin, PA and LPA are displayed in Fig. 3. According to the analysis in (Fig. 3a), the glass transition temperature (T_g) of lignin is about 141 °C, The T_g of PA is approximately 231 °C observed in Fig. 3b. However, the T_g of LPA with lignin is reduced to about 206 °C in Fig. 3c. This shows that the addition of lignin makes the molecular chain of acrylic acid-acrylamide copolymer more susceptible to heat movement.

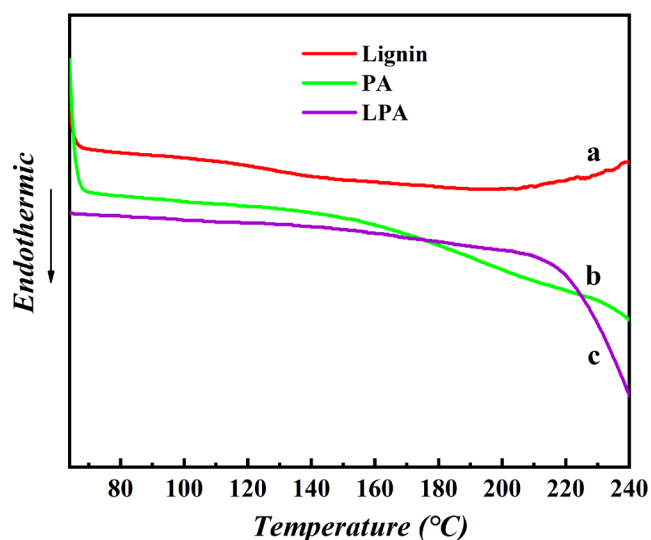


Fig. 3 The DSC curves of lignin (a), PA (b) and LPA (c).

3.1.4. Characterization result of TGA

The TGA tests were performed on lignin, PA and LPA. The test results was shown in Figure 4. In Figure 4a, the thermal weight loss of lignin could be divided into two stages, the vaporization of adsorbed water in the lignin was attributed to 70-140 °C, the thermal decomposition of lignin was attributed to 266-470 °C, thereby the final remaining mass percentage was 40.99%. As observed from the DTG curve in Figure 4a, the weight loss of lignin was maximized at 263 °C, where the weight loss rate is the fastest. As can be seen from Fig. 4b, the thermal weight loss zone at 50-248 °C was corresponding to the loss of adsorbed water in acrylic acid-acrylamide copolymer and bound water in attapulgit. 260-500 °C was due to the thermal decomposition of acrylic acid-acrylamide copolymer, and the final remaining mass percentage was 30.34%. The weight loss of PA was maximized at 409 °C, where the weight loss rate is the fastest. The thermal weight loss process of LPA in Fig. 4c could be divided into three stages, 50-190 °C was corresponding to the loss of adsorbed water and bound water in the LPA, 245-510 °C was corresponding to the thermal decomposition of the lignin skeleton and acrylic acid-acrylamide three-dimensional network copolymer, a complicated reaction was presented in this stage of the LPA. 580-800 °C was corresponding to the further decomposition of organic matter in lignin, and the final remaining mass percentage was 27.24%. The weight loss of LPA was maximized at 369 °C, where the weight loss rate is the fastest. The analysis results indicate that the molecules in the adsorbent decomposed at higher temperatures after adding the lignin and the successful preparation of the above LPA.

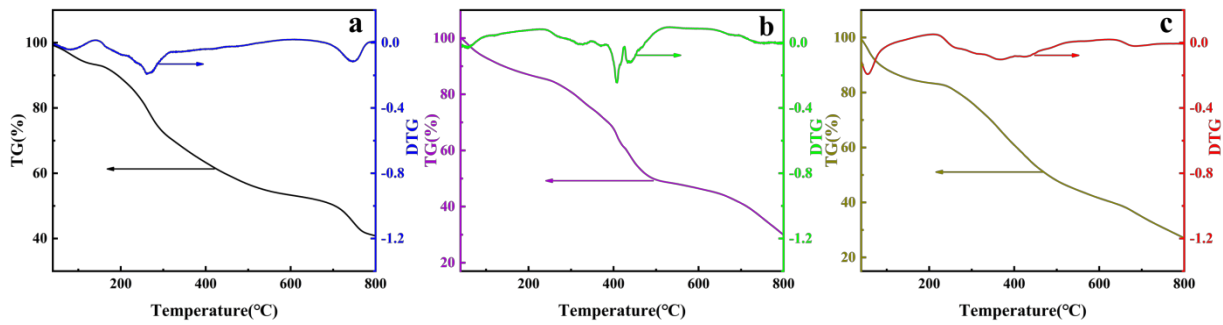


Fig. 4 The TG and DTG curves of lignin (a), PA (b) and LPA (c).

3.2. The influence of synthesis conditions on the water absorbency of LPA

The water absorbent with a three-dimensional network structure formed by cross-linking of polymers containing hydrophilic groups such as hydroxyl and carboxyl groups has a capacity to absorb and hold a large amount of water, and can effectively improve the absorption and slow release of trace elements in crops. Additionally, superabsorbents are potential materials for regulating the release behavior of fertilizer due to electric charges and interconnected channels in the swollen superabsorbent networks. The water absorption rate under different conditions is a key factor for the double-coated urea granular material in the practical production. Therefore, the comprehensive parameters such as lignin, MBA, KPS, and ATP content were optimized.

3.2.1. Influence of the content of lignin

As a natural renewable aromatic resource, lignin is chemically reacted with nutrient elements (N, P, K) in its functional groups with the aid of initiators and cross-linking agents. A number of longer thread-like structures or larger net-like structures are formed and the water retention capacity of the soil can be prolonged. As observed from Fig. 5a, the maximum water absorption was obtained when the added amount of lignin was 4.17 wt%. When the weight ratio was higher than 4.17 wt%, the water absorption decreases rapidly. The main reason was that most of the copolymers could be completely grafted on the lignin backbone when the added amount of lignin was small. As the proportion of added lignin increases, more initiated sites were generated on its molecular backbone, which led to a decrease in the grafting rate of the copolymer, which was not conducive to LPA's absorption of water. Considering that the addition of lignin could improve the biodegradability of LPA in the soil and also provide a carbon source for the soil, it could effectively reduce the cost in the production process of coated fertilizers. Therefore, it is reasonable to select the mass ratio of lignin to acrylic acid and acrylamide as 4.17 wt% to be

added.

3.2.2. Influence of the content MBA

The degree of crosslinking has an enormous influence on the water absorption of LPA. When the crosslinking is too high, it is difficult for the polymer segment to stretch, and it is difficult for water molecules to be retained in the water absorbent. Therefore, the water absorption rate would be reduced. When the crosslinking is too low, it is difficult for the polymer segments to form a three-dimensional network structure, which makes the water absorption rate low. In this work, the amount of crosslinking agent was researched as an optimization parameter. As shown in Fig. 5b, when the ratio of $W_{MBA}/W_{(L+AA+AM)}$ was less than 4 wt%, the water absorption rate of the water-absorbing agent increased with the cross-linking. When the ratio of $W_{MBA}/W_{(L+AA+AM)}$ was greater than 4 wt%, the water absorption capacity was significantly decreased. The maximum water absorbency in distilled water is about 233 g/g when the ratio of $W_{MBA}/W_{(L+AA+AM)}$ is 4 wt%. This shows that if the amount of MBA is too small, less cross-linking points are formed, more soluble copolymer parts are found, and the water absorption rate is not high. When the amount of MBA is too large, the cross-linking density is large, the space between the water-absorbing agent networks is small, it is not easy to expand during swelling, and the amount of distilled water that can be accommodated is reduced. In this experiment, the water absorption rate of the water absorbent is the best when the ratio of $W_{MBA}/W_{(L+AA+AM)}$ is equal to 4 wt%.

3.2.3. Influence of the content KPS

The amount of initiator also has a great impact on the water absorption rate of the water absorbent. Too little initiator dosage makes it difficult to initiate the polymerization reaction. On the one hand, there are more unreacted monomers, and on the other hand, the polymer crosslinking density is small, so the water absorption rate of the water absorbent is low. If the amount of initiator is too large, the polymerization reaction speed is too fast and difficult to control, and the crosslinking density of the polymer is too large, and the oligomers are more, so the water absorption capacity is also low. If the initiator dosage is too large, the polymerization reaction speed is too fast and difficult. In addition, the crosslinking density of the polymer is too large, and the oligomers are more, so the water absorption capacity is also lower. It could be seen from Fig. 5c that when the ratio of $W_{KPS}/W_{(L+AA+AM)}$ was less than 1 wt%, the degree of

incomplete reaction was increased, the average relative molecular mass of the polymer product is large, the self-crosslinking density is small, The water absorption rate is low due to the increase of the soluble part of the water absorbent. The maximum water absorbency in distilled water is about 244 g/g when the ratio of $W_{KPS}/W_{(L+AA+AM)}$ is 1 wt%. When the ratio of $W_{KPS}/W_{(L+AA+AM)}$ is greater than 1 wt%, the polymerization speed is accelerated, the reaction temperature is raised, resulting in an increase in the crosslinking density. Therefore, the relative molecular weight of the polymer is reduced, and the water absorption rate is correspondingly reduced. In this work, when the ratio of $W_{KPS}/W_{(L+AA+AM)}$ was 1 wt%, the water absorption rate of the product was the highest.

3.2.4. Influence of the content ATP

ATP improved the nutrient release efficiency and water retention capacity due to its high specific surface area and the structure of parallel channels running through the internal crystal lattice. The effect of the amount of ATP on the water absorption of LPA was shown in Fig. 5d. When the amount of ATP increased to 12.8 wt%, the water absorption of LPA gradually increased, which may be due to the presence of hydrogen bonds on the surface of ATP, which can react with AM to improve the polymeric network with consequent increase of the water absorbency. Continuing to increase the amount of ATP, Continuing to increase the amount of ATP, the water absorption of LPA was sharply decreased. This is due to more cross-linking points being generated due to the increased ATP content, which the swelling of the LPA network is limited, thereby reducing the size of the voids between the polymer segments and the water absorption and water retention efficiency. Therefore, ATP addition of 12.8 wt% was chosen as the optimal amount.

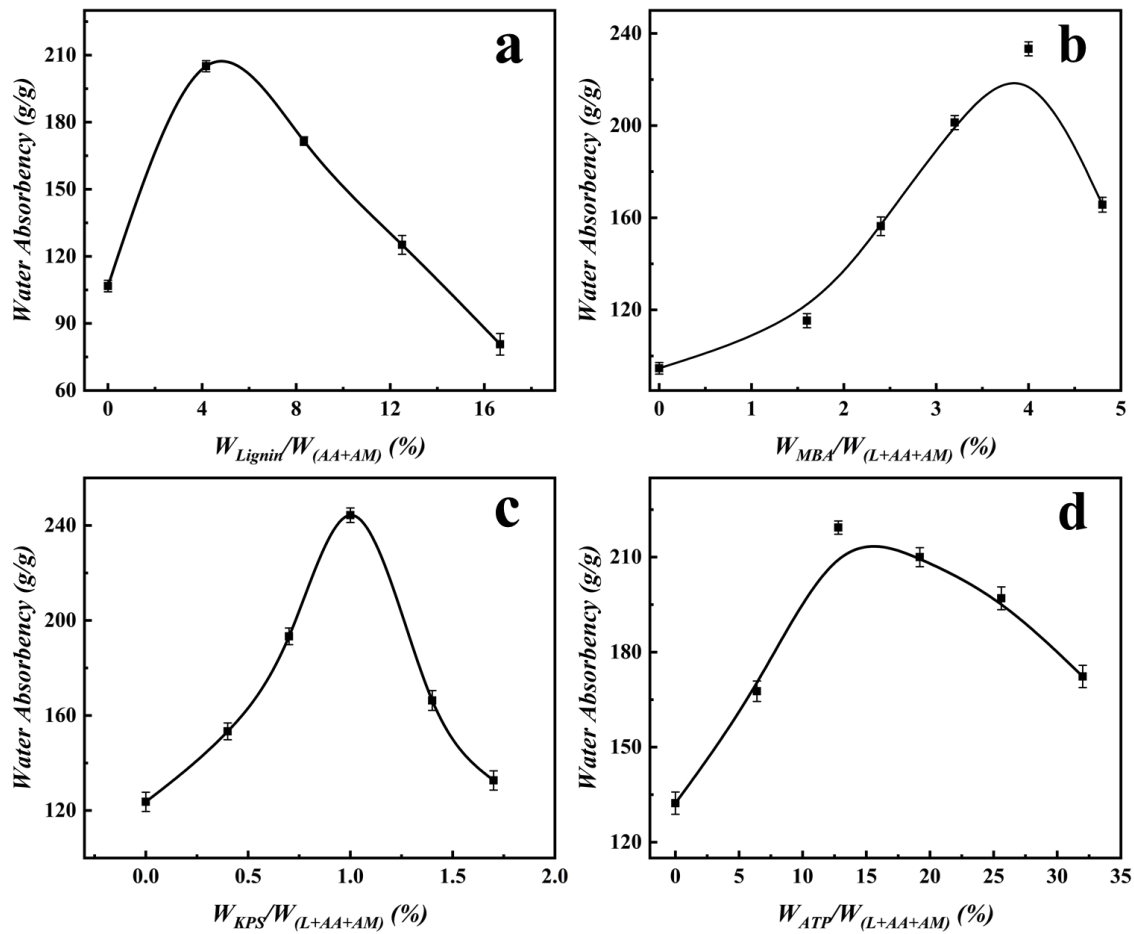


Fig. 5 Effects of the content of lignin (a), MBA (b), KPS (c) and ATP (d) content on water absorption of outer layer.

3.3. Viscosity of blend solution

In this work, a spray gun was used to spray the inner layer coating solution on the surface of urea. If the viscosity is too small, the spray gun will be sprayed a large amount, the sag phenomenon will be easily generated, and the coating film defects such as poor covering power and adhesion will be caused. Excessive viscosity will make it difficult to control the thickness of the coating film, and the cost will be wasted. Poor leveling performance results in uneven coating on the fertilizer surface, and it is easy to generate air bubbles, which will generate large internal stress and easily break down. Therefore, the influence of inner coating solution viscosity on fertilizer coating was investigated in this work. To obtain an objective result, different dosages of MC and different concentrations of PVA were adopted. And the test results were shown in Fig. 6. With the increase of MC content, the viscosity of 3%, 4% and 5% PVA solutions were all showed a gradually increasing trend. When the amount of MC was between 2.0g and 3.0g, a sharp

increase in viscosity occurs. The reason could be that the increase of MC to a certain extent generated intertwining with the molecular chain of PVA and caused the viscosity to increase. The higher the concentration of PVA, the more tangled sites with MC were presented. So that when the viscosity changed suddenly, the added amount of MC should be lower. Take the logarithm of the abscissa and ordinate to find that the linear relationship between $\ln(\eta)$ and $\ln(MC)$ was presented. The average slope of the three curves was 1.9456, and the fit was good. And then the better coating effect on fertilizer was established when the MC addition amount of 5% PVA solution was 2.0 g (at the inflection point).

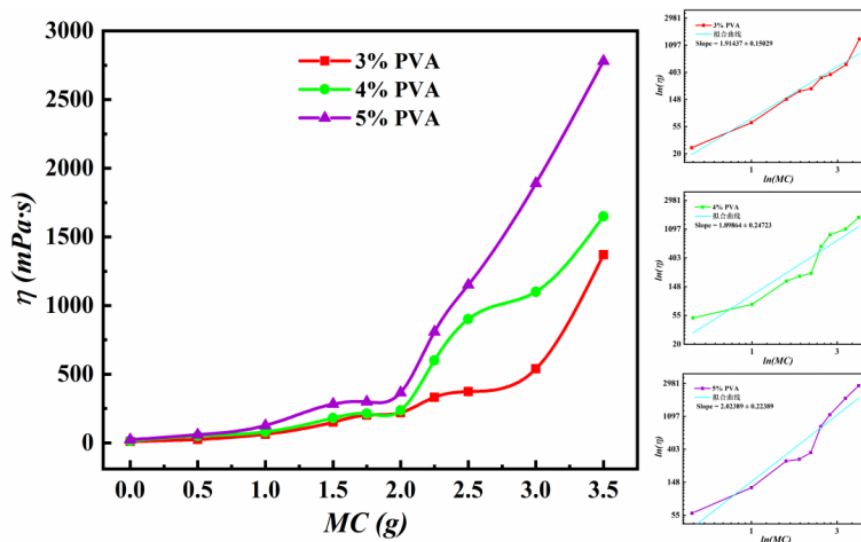


Fig. 6 Effect of MC Dosage and PVA Concentration on the Viscosity of Inner Coating Solution.

3.4. Mechanical properties of inner film

In the actual transportation of slow-release fertilizers, the mechanical properties of the outer film of the fertilizer will have a certain impact. The tensile strength and elongation at break of the inner film were investigated, as shown in Fig. 7. The tensile strength and elongation at break of the films both increased first and then a trend of rising first and then falling was presented with the addition of methylcellulose. When the addition amount of methyl cellulose was 2g, the tensile strength is 60Mpa, the elongation at break was reached 425%. The maximum of both was reached and the mechanical properties are the best. The test results correspond to the viscosity test. The main reason was that similar compatibility between polyvinyl alcohol and methyl cellulose, the hydrogen bonds were formed. Intermolecular forces were increased resulting in improved mechanical properties. However, when the amount of methyl cellulose added was higher than 2g, the sliding of the molecular chain became difficult, the methyl cellulose

molecules were too concentrated, and it is difficult to disperse uniformly in PVA, and the film performance was decreased.

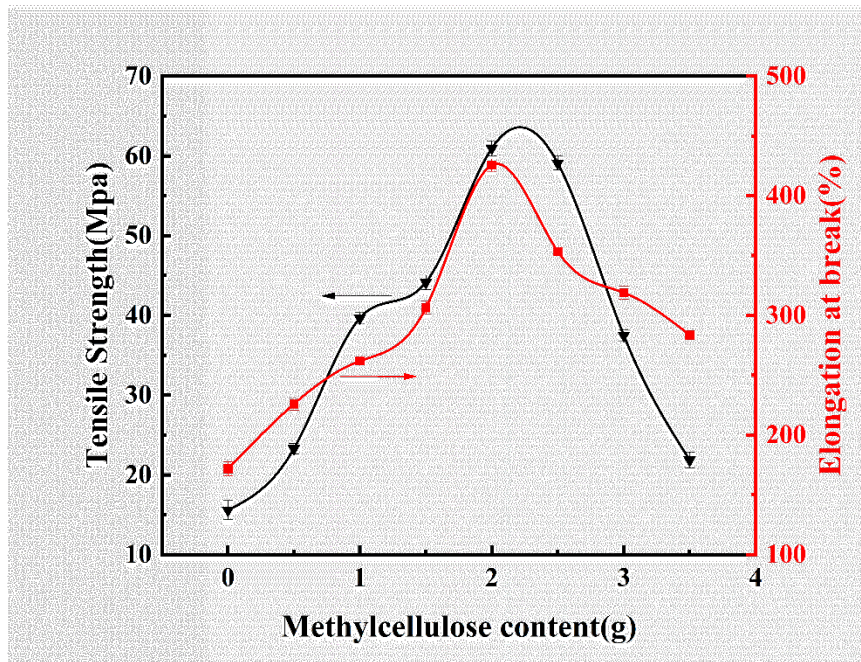


Fig. 7 Mechanical properties of PVA/MC composite.

3.5. Hydrophilic properties of blended film

To clarify the influence of MC on the hydrophilic properties of PVA, the remaining solution after the above viscosity test was coated and dried for 24 h, and then the water contact angle test was performed. And the test results were shown in Fig. 8A. With the gradual increase in the amount of MC, the water contact angle of the inner film was presented a gradually increasing trend. And the concentration of PVA of 3%, 4% and 5% pure PVA film would be inversely proportional to the water contact angle. This is due to the large number of hydroxyl groups on the PVA molecular chain, which make it had good water solubility. With the increase of MC, PVA and MC would intersperse and entangle each other, and a large number of hydroxyl groups on the molecular chain would be wrapped by it, thereby the water contact angle of the blended film would show an increasing trend. Then test the water contact angle of the PVA/MC blend film in all proportions, and the test results were shown in Fig. 8B. The regularity was consistent with the results obtained in Fig. 8A, it showed a sudden increase between 0.5 g and 1.0 g of MC addition, and then showed a steady increase. It could be concluded that the addition of MC effectively improved the hydrophilic properties of PVA, this would help to form a dense coating on the surface of the fertilizer, thereby delaying the entry of water molecules into the fertilizer core, and the utilization rate of the fertilizer was effectively improved.

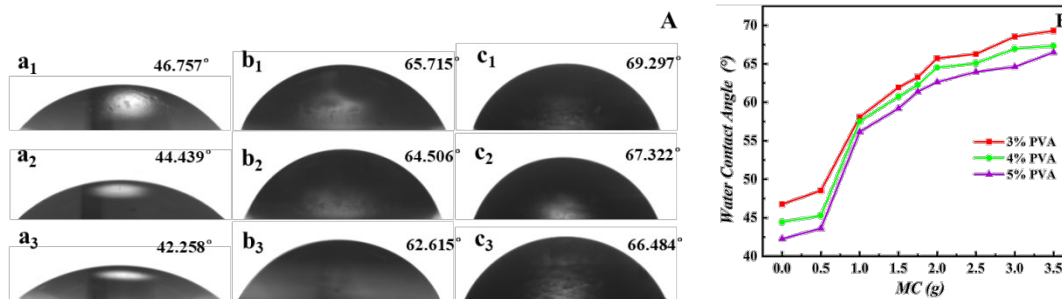


Fig. 8 Image comparison of water contact angle of inner composite film A, the influence of (3% ■), (4% ■), (5% ■) PVA concentration and MC dosage on the water contact angle of the internal mixed film B.

3.6. Water-holding and water-retention capacity of soil

Dry regions have high temperature and low precipitation, due to the large number of deserts and insufficient water sources, resulting in low water retention and water holding capacity of sandy soils and serious soil erosion, the development of agriculture in such areas is limited. Due to its high water absorption rate and water retention capacity, superabsorbents can be applied to such regions to increase the moisture content in the soil. The application of PML-SRF in improving soil water holding and water retention capacity was investigated, and the results were shown in Fig. 9. Fig. 9A shows that the water holding capacity of 200 g dry soil after adding 0, 1.0, 2.0, 3.0 and 4.0 g PML-SRF are 46.57%, 48.5%, 50.97%, 57.67% and 62.46%, respectively. The water-holding capacity of soil increased with the increase of PML-SRF, with a gentle growth trend in the early stage and a rapid growth trend in the later stage. In addition, the water holding capacity of adding 4gPML-SRF was 15.89% higher than that without adding chemical fertilizer. It can be seen that compared with the blank group, the water holding capacity of the soil was effectively improved by adding PML-SRF.

Similar results were also observed from Fig. 9B. The water-holding capacity of soil samples treated with the addition of PML-SRF was greater than that of the blank group (soil only), and the water-holding capacity of soil samples was enhanced with increasing dose of PML-SRF. After 28 days at room temperature, the water in the blank group was almost completely evaporated. However, soil samples b, c, d and e were still able to retain 3.4%, 29.96%, 31.23% and 36.27% of water content, respectively. After adding 1.0, 2.0, 3.0 and 4.0 g of PML-SRF, the water in the soil was completely evaporated after 30, 50, 54, and 64 days, respectively. This is because the moisture equivalent to tens to hundreds of times its own weight can be absorbed by the outer layer water-retaining agent of PML-SRF, and maintain its own moisture for a considerable period

of time. At the same time, its own moisture can be slowly released for a long period of time, and PML-SRF can also slowly released nutrients. The results of this study show that the prepared PML-SRF can provide water to plants for a long time in arid regions, and the frequency of farmland irrigation is reduced, which has broad application prospects in agroforestry.

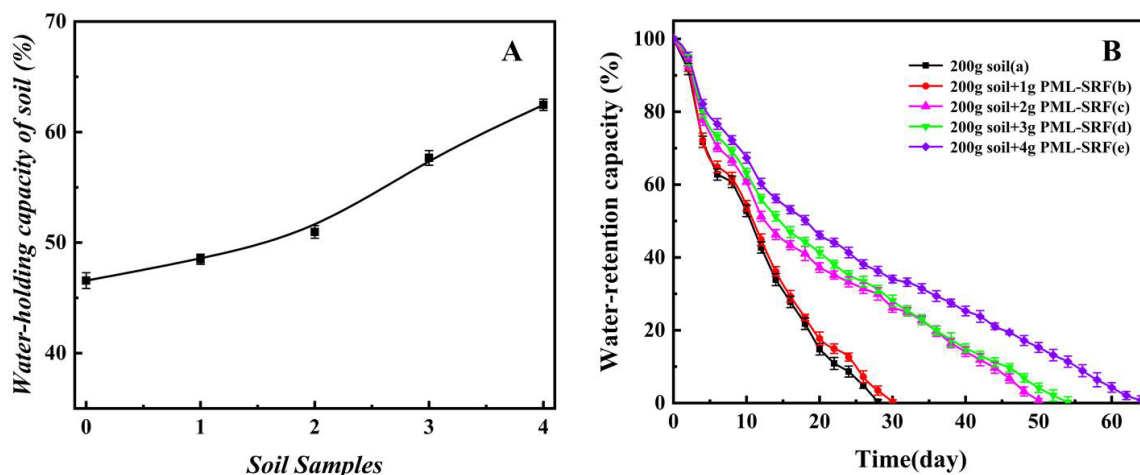


Fig. 9 Maximum water holding capacity of double-coated fertilizers in soil (A), the effect of double-coated fertilizer addition on soil water retention (B): 0g (a); 1g (b); 2g (c); 3g (d); 4g (e).

3.7. Slow release behavior results for SRFs in water

3.7.1. Standard curve for urea content

The standard curve of urea is shown in Fig. 10, there is a significant linear correlation between concentration and absorbance, and the linear correlation coefficient (R^2) was 0.9995, which can meet the experimental requirements. From the standard curve, the linear regression equation of $y=0.00145x+0.13552$ was obtained for further use.

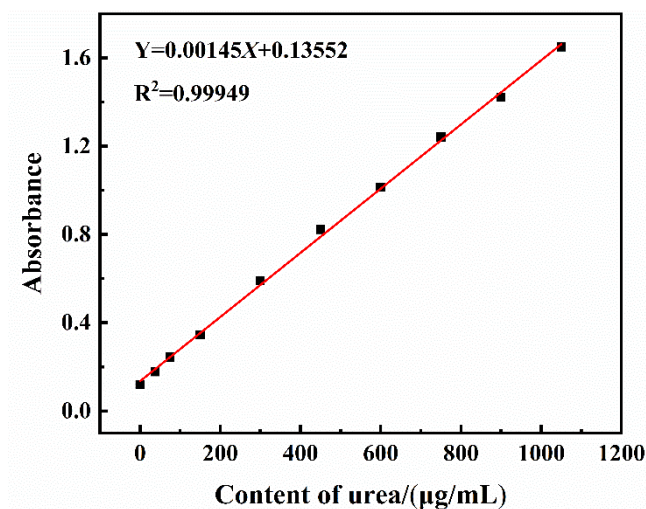


Fig. 10 The standard curve of urea content.

3.7.2. Slow release behavior of coated fertilizers in water

An important criterion for evaluating the coated slow-release fertilizer is its slow-release performance. In this work, based on the effect of the thickness of the coating layer and the water-retaining agent on the release rate, three sets of experiments as shown in Fig. 11 were designed to measure the release rate. As shown in Fig. 10B-a, the encapsulated urea was basically completely released within two days, and the cumulative release rate was 93.97%. PM-SRF (Fig. 10B-a) reached the release equilibrium at 36 days, and the cumulative release rate was about 92.36%. In addition, the cumulative release rates of urea by PM-SRF at 2, 20, and 40 days were 6.9%, 56.47%, and 92.91%, respectively. It indicated that the release rate was significantly slowed down after passing through the monolayer coating. PML-SRF (Fig. 10B-c) reached the release equilibrium at 42 days, and the cumulative release rate was around 85.12%. This is due to the physical barrier effect of the outer coating material and the inner coating layer material, which hinders the diffusive release of nutrients from the fertilizer core.

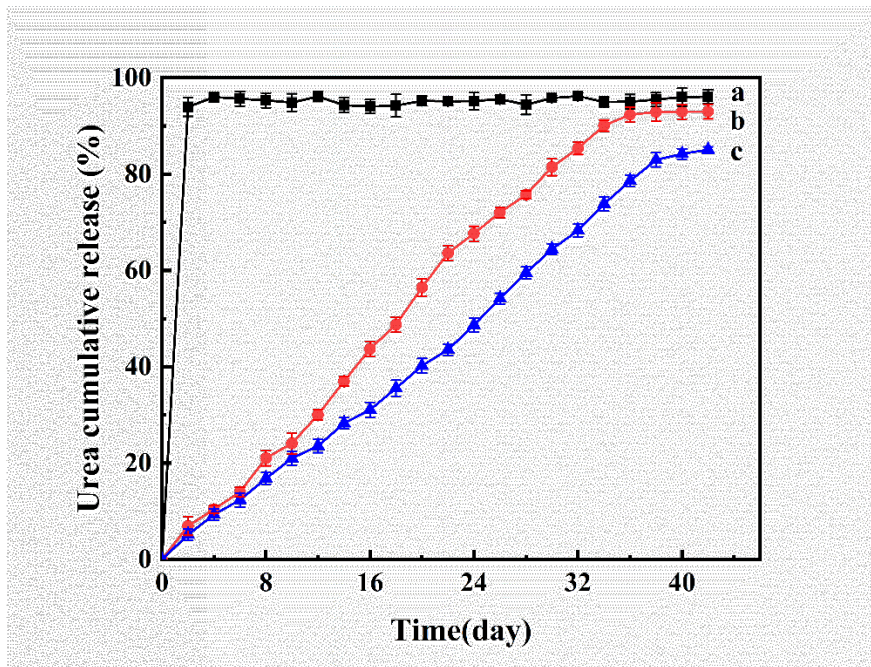


Fig. 10 Slow-release properties of urea granules (a), PM-SRF (b), and PML-SRF (c).

4. Conclusions

Using degradable lignin as the matrix, selecting acrylic acid and acrylamide as monomers, the copolymer of acrylic acid and acrylamide was grafted onto the lignin skeleton by grafting copolymerization method, and the preparation of lignin based water absorbent was proved to be successful by infrared spectrum analysis and thermal analysis. In addition, the PVA/MC blend

solution was prepared by solution polymerization and controlled variable method, and the viscosity was logarithmic related to the amount of MC added. After the solution was coated, the water contact angle and mechanical properties test were performed, and the comprehensive effect was the best when the concentration of PVA was 5% and the amount of MC added was 2.0 g (at the inflection point). Then optimize the synthesis conditions for different parameters of LPA to obtain the best water absorption. The soil structure was improved by adding the prepared PML-SRF, which was beneficial to the circulation of air and the absorption of nutrients in the soil. The slow-release fertilizer had a good sustained release effect. After PM-SRF and PML-SRF reach equilibrium, the cumulative release rates of urea molecules were 92.36% and 85.10%, respectively. Therefore, the double-layer fertilizer could effectively prevent water molecules from entering the fertilizer core, could effectively store water, delaying the release of nutrients, but also improve the water retention capacity of the soil.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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