

Synthesis and Urea-Loading of an Eco-Friendly Superabsorbent Composite Based on Mulberry Branches

Xiying Liang, Yong Zhang, Lin Liu, and Juming Yao*

Mulberry branch, consisting of bark and stalk, was used as raw skeleton material without any chemical pre-treatment to synthesize an eco-friendly mulberry branch-g-poly(acrylic acid-co-acrylamide) (PMB/P(AA-co-AM)) superabsorbent composite. The synthesis conditions and properties of the PMB/P(AA-co-AM) superabsorbent composite were investigated. The results showed that under the optimal synthesis conditions, the water absorbency of the prepared PMB/P(AA-co-AM) reached 570.5 g/g in deionized water, 288.0 g/g in tap water, and 70.0 g/g in 0.9 wt% aqueous NaCl solution. The PMB/P(AA-co-AM) composite also exhibited excellent water retention capacity as well as a rapid water absorbency rate. The urea loading percentage of the PMB/P(AA-co-AM) composite was controlled by the concentration of aqueous urea solution. The release of urea from the loaded PMB/P(AA-co-AM) composite in deionized water initially exhibited a high rate of release for 60 min, followed by a rapid decline. Meanwhile, the PMB/P(AA-co-AM) superabsorbent composite with larger particle size achieved a better sustained release of urea.

Keywords: Mulberry branch; Superabsorbent composite; Synthesis condition; Water absorbency and retention; Urea loading and release

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INTRODUCTION

Superabsorbents make up a category of new functional polymer materials with a three-dimensional network structure (Ma *et al.* 2011). The existence of a large number of hydrophilic groups endows it with excellent water absorbency, which can absorb as much as hundreds or thousands of times its own weight in water. The loose, three-dimensionally cross-linked structure provides it with good water retaining capacity that can prevent fluid loss under a certain pressure. Based on this performance, superabsorbents are widely used in the fields of agriculture and horticulture (Wu and Liu 2008; Islam *et al.* 2011), in sanitary products (such as sanitary napkins and disposable diapers) (Kosemund *et al.* 2009; Zhao *et al.* 2005), and for drug delivery (Wu *et al.* 2008; Mahdavinia *et al.* 2004). At present, global demand for superabsorbents is increasing steadily. However, most superabsorbents are based on synthetic polymers like pure poly(sodium acrylate), which is expensive and nonbiodegradable (Liang *et al.* 2009). The monomers are mainly derived from increasingly exhausted oil resources and have poor

biodegradability. As a consequence, efforts in developing new superabsorbents from natural resources have been carried out. Eco-friendly biological resources, such as starch (Lu *et al.* 2003; Li *et al.* 2007; Peng *et al.* 2008), cellulose and its derivatives (Dahou *et al.* 2010; Sadeghi and Hosseinzadeh 2008), hemicelluloses (Peng *et al.* 2011; Peng *et al.* 2012), chitosan (Ge *et al.* 2006; Wu *et al.* 2008), humic acid (Chu *et al.* 2006), carrageenan (Pourjavadi and Amini-Fazl 2007; Salimi *et al.* 2010), and even the waste of biological material like wheat straw (Ma *et al.* 2011; Liu *et al.* 2009) and flax yarn waste (Wu *et al.* 2012) are gradually being introduced into the synthesis process of superabsorbent composites.

In recent years, there has been an unprecedented increase in interest in the efficient utilization of agro-industrial residues (Wang *et al.* 2008). As an economically important plant, mulberry is extensively planted in Asia, Europe, North and South America, and Africa (Wasano *et al.* 2009). However, mulberry is primarily cultivated to obtain the leaves to support silkworm rearing. Masses of mulberry branches have been removed as a by-product that is currently used as firewood or discarded as agricultural waste (Liu *et al.* 2010) and has not been efficiently utilized. Much progress has been made in this field in recent years. Cellulose whisker was extracted from the bark of mulberry branches for the potential application as a reinforcing phase (Li *et al.* 2009). Pectin was obtained from the bark of mulberry with and without epidermis (Liu *et al.* 2010). Additionally, natural fibers were separated from the endothelium of mulberry branch (García *et al.* 2012).

Mulberry branch, consisting of bark and stalk and mainly containing cellulose, hemicelluloses, and lignin, can be used as a skeletal material. Monomers such as acrylic acid (AA) and acrylamide (AM) can then be grafted onto it to form a superabsorbent composite for potential applications in agriculture and horticulture. Therefore, in this study, a novel method for the utilization of whole mulberry branch, *i.e.*, incorporating it into superabsorbent polymer was provided. Here, mulberry branch, including both bark and stalk, was used directly without any chemical pre-treatment to synthesize an eco-friendly superabsorbent composite by grafting AA and AM onto it. The synthesis conditions and properties of the pulverized mulberry branch-g-poly(acrylic acid-co-acrylamide) (PMB/P(AA-co-AM)) superabsorbent composite were investigated. The urea loading and sustained release behavior of the PMB/P(AA-co-AM) were also characterized for its potential for agricultural and horticultural applications.

EXPERIMENTAL

Materials

Mulberry branch was obtained from the mulberry plantation of Zhejiang Sci-Tech University in Hangzhou, China. Acrylic acid (AA, analytical grade; Aladdin Chemistry Co. Ltd., China) was distilled under reduced pressure before use. Acrylamide (AM, analytical grade; Yingguangtai Biotechnology Co. Ltd., China) was used as received. Ammonium persulfate (APS, analytical grade; TianjinYongda Chemical Co. Ltd., China) was recrystallized from water before use. N,N-methylenebisacrylamide (MBA, analytical grade; Guoyao Chemical Reagent Co. Ltd., China), ammonium bicarbonate (analytical

grade; Beijing Solarbio Science Technology Co. Ltd., China) and urea (analytical grade; Beijing Solarbio Science Technology Co. Ltd., China) were used as purchased. All other agents used were analytical grade and all solutions were prepared with deionized water.

Preparation of PMB/P(AA-co-AM) Superabsorbent Composite

Preparation of pulverized mulberry branch

The mulberry branch was cut up and washed, then dried at 105 °C. The dried mulberry branch was smashed by a disintegrator and screened to collect the pulverized mulberry branch (PMB) between 100 to 200 mesh (0.072 to 0.143 mm).

Grafting of PMB with AA and AM

PMB (1.0 g) was dispersed in 20 mL deionized water. The solution was then added into a 250 mL three-necked flask equipped with a magnetic stirrer, reflux condenser, and nitrogen line. The reactor was immersed in a water bath kept at 70 °C (Liang *et al.* 2009; Wu *et al.* 2012). Simultaneously, oxygen-free nitrogen gas was bubbled into the solution for 30 min before adding the initiator. A deionized water solution containing a certain amount of APS was added. After 15 min of stirring, the AA solutions with a certain degree of neutralization by ammonium bicarbonate, AM, and MBA were added to the reaction mixture in turns. The whole volume of solution in the reactor was controlled at 40 mL. After reaction for 2 h, the obtained gel (PMB/P(AA-co-AM)) was washed with deionized water and ethyl alcohol several times. Then, it was cut into small pieces and dried at 60 °C to a constant weight. The dried gel was milled into different particle size powders for use.

Water Absorbency Measurement

Water absorbency at various temperatures

The accurately weighed PMB/P(AA-co-AM) superabsorbent composite powder (0.1 ± 0.0001 g) was immersed in 500 mL deionized water, 500 mL saline solution, and 500 mL tap water at various temperatures to reach swelling equilibrium (about 2 h). The swollen samples were then separated from the unabsorbed water by being filtered over a 100-mesh nylon screen. The weight of the swollen samples was measured. The equilibrium swelling Q_{eq} was calculated by the following equation,

$$Q_{eq} = \frac{M_2 - M_1}{M_1} \quad (1)$$

where M_1 and M_2 are the weights of the dry and the swollen sample (g), respectively, and Q_{eq} is the water absorbency per gram of dried sample (g/g).

Water absorbency at various pH values

The determination of water absorbency in various pH solutions was the same as described in the previous section on water absorbency at various temperatures. The desired pH values were achieved via diluting NaOH (pH 13.0) and HCl (pH 1.0) solutions.

Water absorbency in different salt solutions

The measurement of water absorbency in different salt solutions (NaCl, KCl, NH₄Cl, MgCl₂, and CaCl₂) with different concentrations was also the same as the method presented in the section, “water absorbency at various temperatures.”

Water Absorbency Rate Measurement

The accurately weighed PMB/P(AA-co-AM) superabsorbent composite powder (0.1 ± 0.0001 g) was swelled in 500 mL deionized water. At set intervals, the sample was picked out and the excess water was removed. The water absorbency was measured immediately. The sample was immersed into the same deionized water again for the next measurement.

Water Retention Measurement

Water retention at various temperatures

The prepared PMB/P(AA-co-AM) superabsorbent composite was immersed in deionized water at room temperature to reach swelling equilibrium. Then, the swollen gel was weighed (M_0) after the excess water was removed and placed at the temperatures 10, 25, and 45 °C. The sample was weighed every hour (M_i) for 12 h. The water retention capacity of the PMB/P(AA-co-AM) at various temperatures was determined by Equation (2):

$$R_{iT} = \frac{M_i}{M_0} \times 100\% \quad (2)$$

Water retention at various centrifugal forces

The prepared PMB/P(AA-co-AM) superabsorbent composite was immersed in deionized water at room temperature for swelling equilibrium. The swollen gel without excess water was placed in a weighed tea bag (200-mesh nylon screen). The tea bag containing the swollen gel was then centrifuged at different rotation speeds for 30 min. The water retention capacity of the PMB/P(AA-co-AM) at various centrifugal forces was determined by the following equation,

$$R_i = \frac{M_i - M'}{M_0 - M'} \times 100\% \quad (3)$$

where M_0 and M_i are the weights of the swollen and centrifuged PMB/P(AA-co-AM) superabsorbent composite with tea bag (g) and M' is the weight of the tea bag (g).

Loading and Release of Urea

Loading of urea

The loading of urea was carried out by immersing the pre-weighed dry gel into 500 mL of aqueous urea solution for 12 h. Subsequently, the swollen gel was dried at 37 °C for 3 d. The loading percentage was calculated by Equation (4),

$$\text{Loading\%} = \frac{W_1 - W_0}{W_1} \times 100\% \quad (4)$$

where W_0 and W_1 are the weights of unloaded and loaded dry gels (g).

Release of urea in water

Urea-loaded (0.2 g), dry PMB/P(AA-co-AM) composite was placed in beakers containing 400 mL deionized water (release medium) without stirring. At various intervals, 2 mL solution was drawn out from the medium to detect the quantity of urea released, which was determined by an ultraviolet spectrophotometer (Watt and Chrisp 1954). Subsequently, the extra 2 mL fresh deionized water was added into the release medium for the next test.

RESULTS AND DISCUSSION

Optimization of PMB/P(AA-co-AM) Synthesis Conditions

Superabsorbent composites prepared under different synthesis conditions have different water absorbencies due to their different structures. In order to find the best synthesis conditions for the PMB/P(AA-co-AM) superabsorbent composite, an orthogonal experiment with five factors and four levels was conducted (Wu *et al.* 2012; Zhang *et al.* 2013). The letter A stands for the mass ratio of AA+AM and PMB, which has four levels: 4, 6, 8, and 10 g/g. B, C, D, and E stand for the mass ratio of AA and AM, neutralization degree of AA, the mass ratio of APS and PMB, and the mass ratio of MBA and PMB, respectively. The following experiments were performed according to the orthogonal array $L_{16}(4)^5$ (Table 1) and the results of range analysis is shown in Table 2. The results of the range analysis indicated that the order of degree of influence of each factor on the water absorbency was $E > B > D > A > C$ in deionized water. MBA is the most important factor, and the mass ratio of AA and AM followed, then APS, AA+AM, and neutralization degree of AA. According to the results of the orthogonal experiment, the optimal combination $A_2B_4C_1D_1E_1$ was obtained, which corresponded to the following optimal synthesis conditions: the mass ratio of AA+AM and PMB was 6 g/g, AA/AM = 4:1, 60% neutralization degree of AA, the mass ratio of APS and PMB was 0.05 g/g, and the mass ratio of MBA and PMB was 0.02 g/g. The prepared PMB/P(AA-co-AM) superabsorbent composite presented a maximum water absorbency of 570.5 g/g deionized water, 288.0 g/g tap water, and 70.0 g/g 0.9 wt% aqueous NaCl solution. Figure 1 presents the SEM images of surface morphologies of the PMB/P(AA-co-AM) superabsorbent composite. It displays a coarse surface with distribution of scallops and asperities because of the existence of PMB, which structurally increases the surface area, facilitating water into the polymeric network. The excellent water absorbency capability of the prepared PMB/P(AA-co-AM) preliminarily exhibits its potential applications for agriculture and horticulture.

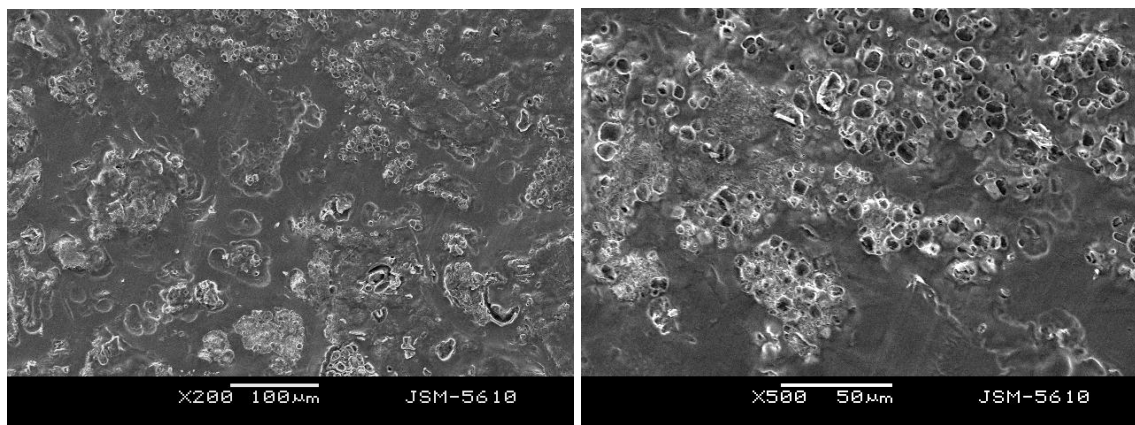


Fig. 1. SEM images of surface morphologies of the PMB/P(AA-co-AM) superabsorbent composite.

Table 1. The Orthogonal $L_{16}(4)^5$ Experiment for PMB/P(AA-co-AM) Synthesis

Sample no.	A (g/g)	B	C (%)	D (g/g)	E (g/g)	Q_{eq} (g/g)
1	4	1 : 1	60	0.05	0.02	402.7
2	4	2 : 1	70	0.10	0.03	255.6
3	4	3 : 1	80	0.15	0.04	245.2
4	4	4 : 1	90	0.20	0.05	256.8
5	6	1 : 1	70	0.15	0.05	248.7
6	6	2 : 1	60	0.20	0.04	238.2
7	6	3 : 1	90	0.05	0.03	439.8
8	6	4 : 1	80	0.10	0.02	536.3
9	8	1 : 1	80	0.20	0.03	300.8
10	8	2 : 1	90	0.15	0.02	360.4
11	8	3 : 1	60	0.10	0.05	365.5
12	8	4 : 1	70	0.05	0.04	366.1
13	10	1 : 1	90	0.10	0.04	349.1
14	10	2 : 1	80	0.05	0.05	322.3
15	10	3 : 1	70	0.20	0.02	334.5
16	10	4 : 1	60	0.15	0.03	420.6

A: mass ratio of AA+AM and PMB; B: mass ratio of AA and AM; C: neutralization degree of AA; D: mass ratio of APS and PMB; E: mass ratio of MBA and PMB; Q_{eq} : water absorbency in deionized water

Table 2. Analysis of The Orthogonal L₁₆(4)⁵ Experiment

	A	B	C	D	E
K ₁ ^a	290.1	325.3	356.8	382.7	408.5
K ₂	365.8	294.1	301.2	376.6	354.2
K ₃	348.2	346.3	351.2	318.7	299.7
K ₄	356.6	395.0	351.5	282.6	298.3
R ^b	75.7	100.8	55.5	100.2	110.2
Order of influence	E>B>D>A>C				
Optimal combination	A ₂ B ₄ C ₁ D ₁ E ₁				
^a K = (∑ the water absorbency in deionized water of single-factor) /4					
^b R = max K – min K					

A: mass ratio of AA+AM and PMB; B: mass ratio of AA and AM; C: neutralization degree of AA; D: mass ratio of APS and PMB; E: mass ratio of MBA and PMB

Water Absorbency of PMB/P(AA-co-AM)

Water absorbency of PMB/P(AA-co-AM) at various temperatures

Figure 2a presents the water absorbency of the prepared PMB/P(AA-co-AM) superabsorbent composite at 5, 25, and 45 °C, which stands for the typical soil temperatures in four seasons (25 °C represents the average temperature of spring and autumn). When the temperature was 5 °C, the water absorbency of PMB/P(AA-co-AM) was about 481.7 g/g in deionized water, 313.6 g/g in tap water, and 61.3 g/g in 0.9 wt% aqueous NaCl solution. When the temperature reached 25 °C, the water absorbency ascended to 531.5 g/g in deionized water, 314.9 g/g in tap water, and 64.9 g/g in 0.9 wt% aqueous NaCl solution. When the temperature was increased to 45 °C, the water absorbency climbed to 542.3 g/g in deionized water, 300.0 g/g in tap water, and 60.3 g/g in 0.9 wt% aqueous NaCl solution. The results indicated that although the temperature changed, the water absorbency of the prepared PMB/P(AA-co-AM) superabsorbent composite was similar in the same solution, which makes the practical utilization of PMB/P(AA-co-AM) possible either in cool winter or in hot summer.

Water absorbency of PMB/P(AA-co-AM) in various saline aqueous solutions

The swelling capacity of superabsorbent polymer depends on its physical and chemical structure as well as the external environment (Zhao *et al.* 2005). Figure 2b exhibits the water absorbency of the prepared PMB/P(AA-co-AM) superabsorbent composite in various aqueous saline solutions, including NaCl, KCl, NH₄Cl, MgCl₂, and CaCl₂. It was found that the Q_{eq} of the PMB/P(AA-co-AM) composite clearly decreased with an increase of the aqueous saline solution concentration. This is because the swell capacity of superabsorbent polymer is related to the osmotic pressure between the polymer network and external solution (Li and Wang 2005). With an increase of saline concentration in the swelling medium, the difference in osmotic pressure between the polymer networks and the external solution reduced, which resulted in a decrease of water absorbency. Furthermore, it can also be seen that the Q_{eq} of PMB/P(AA-co-AM) decreased with an increase of cationic charge of the aqueous saline solution (multivalent < univalent). This may be attributed to the complexes formed by the multivalent ions in the aqueous saline solution and the carboxylate groups on the surface of superabsorbent

polymer, which prevented water from entering into the network of the superabsorbent polymer (Zhao *et al.* 2005).

Water absorbency of PMB/P(AA-co-AM) at various pH values

The swelling capacity of the prepared PMB/P(AA-co-AM) superabsorbent composite was investigated at various pH values, ranging from 2 to 13. The results in Fig. 2c show that in the pH range of 4 to 10, the water absorbency of PMB/P(AA-co-AM) was high. The maximum water absorbency appeared at pH 9, which was 570 g/g in deionized water. The water absorbency decreased sharply at pH values less than 3 and greater than 9. The water absorbency was only able to reach 17.3 g/g at pH 2 and 81.1 g/g at pH 13 in deionized water. This can be ascribed to the protonation of $-\text{COO}^-$ groups to $-\text{COOH}$ groups in the strongly acidic solution, which weakens the mutual repulsion of the polymeric network and prevents water molecules from entering it (Pourjavadi *et al.* 2007). Moreover, in an extremely acidic solution, more Cl^- are ionized from the HCl solution, which reduces the osmotic pressure between the external solution and internal network. As a result, there is low water absorbency in the range of $\text{pH} < 2$. Additionally, in a highly alkaline solution ($\text{pH} > 9$), the charge-screening effect of the Na^+ counterions in the swelling medium shields more $-\text{COO}^-$ groups and prevents an efficient repulsion, which also leads to a decrease of water absorbency (Kabiri *et al.* 2005; Zheng *et al.* 2008). Generally, the pH of agricultural soil is between 5 to 8 (Zheng *et al.* 2008), in which the water absorbency of the PMB/P(AA-co-AM) composite remains roughly constant. This characteristic makes it a suitable candidate for use in an agricultural or horticultural setting.

Water Absorbency Rate of PMB/P(AA-co-AM) with Different Particle Sizes

A high swelling rate is one of the most important characteristics of a superabsorbent polymer applied in agriculture and horticulture, as it can absorb more water in the same amount of time, during either raining or irrigating (Wu and Liu 2008). Figure 2d represents the dynamic swelling behavior of the prepared PMB/P(AA-co-AM) superabsorbent composite with various particle sizes in deionized water. The curves indicate that the PMB/P(AA-co-AM) with different particle sizes had different swelling rates. The smaller the particle size, the faster its swelling rate. The PMB/P(AA-co-AM) composite with particle size ranging from 16- to 20-mesh achieved swelling equilibrium in 20 min and the water absorbency was 445.8 g/g in deionized water. However, another sample with particle size greater than 80-mesh could complete this process in less than 2 min and its water absorbency reached 516.7 g/g in deionized water. The reason may be that the initial swelling properties of the PMB/P(AA-co-AM) composite are determined by the capillary effect and the amount of hydrophilic groups on its surface. When water is introduced into the inside of the polymer, it impels the hydrolysis of ionic groups. The repulsion among ionization groups leads to the extension of the polymeric network and osmotic pressure is created. The extension of the polymeric network and the presence of osmotic pressure promote more water moving into the polymeric network. With a decrease of superabsorbent polymer particle size, its surface area increases and results in an increase of the capillary effect and the hydrophilic group interacts with water more easily (Li *et al.* 2012).

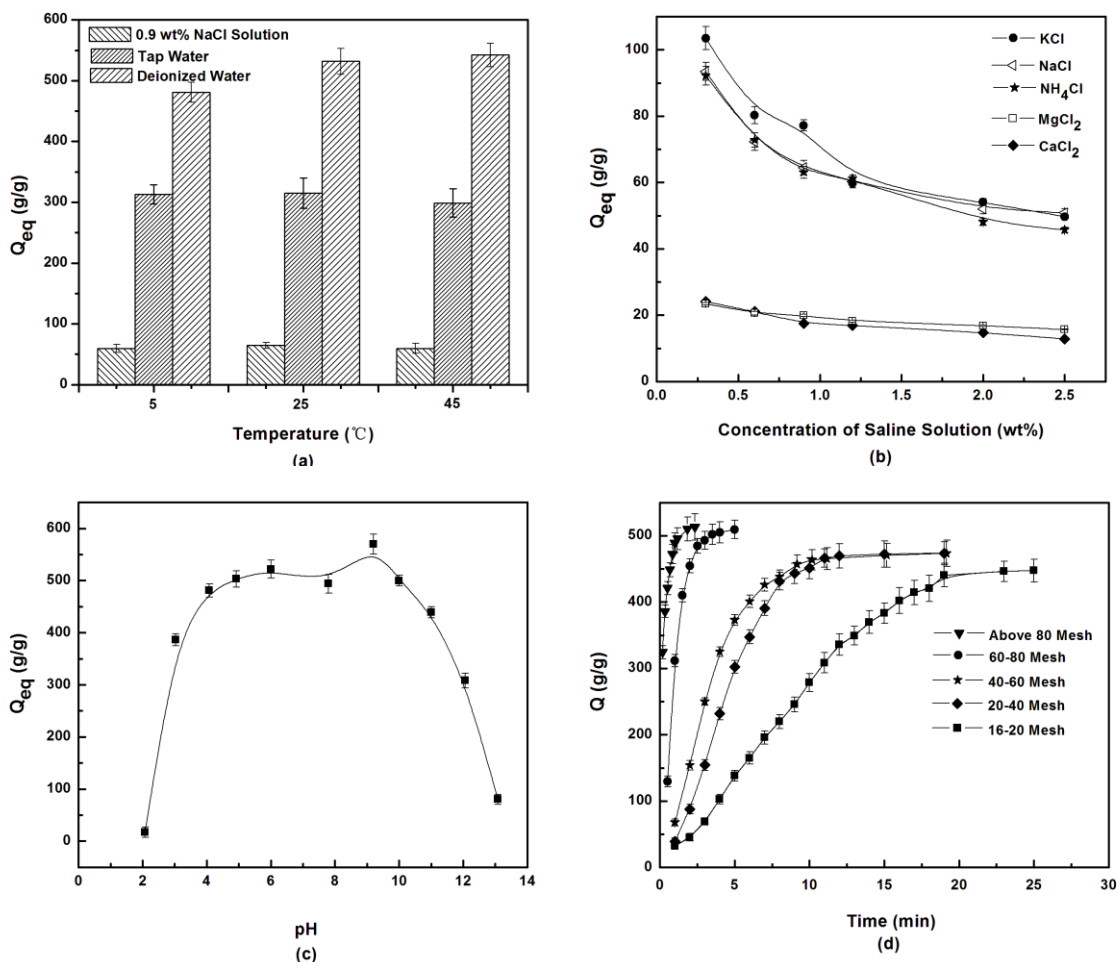


Fig. 2. Water absorbencies of the prepared PMB/P(AA-co-AM) composite (a) at different temperatures, (b) in different saline aqueous solutions, (c) at different pH values, (d) with different particle sizes

Water Retention of PMB/P(AA-co-AM)

Water retention of PMB/P(AA-co-AM) at various temperatures

Figure 3a shows the water retention capacity of the prepared PMB/P(AA-co-AM) superabsorbent composite at different temperatures. The results implied that the water retention of PMB/P(AA-co-AM) decreased, accompanying increases in temperature and time. The PMB/P(AA-co-AM) composite reserved 74.6% and 50.8% of the absorbed water at 25 and 45 $^{\circ}\text{C}$ for 12 h, respectively. While at 10 $^{\circ}\text{C}$ for 12 h, almost all the absorbed water was preserved in the PMB/P(AA-co-AM). The decrease in water retention of the superabsorbent composite at a high temperature can be explained by the fact that the hydrogen bonds that capture water molecules in polymeric chains were broken (Roy *et al.* 2009).

Water retention of PMB/P(AA-co-AM) at various centrifugal forces

The water retention capacity is also an important property for a superabsorbent polymer. Hence, the water retention of the prepared PMB/P(AA-co-AM) superabsorbent composite was determined using a simple centrifugal test at a certain rotation speed. Figure 3b displays the water retention of the PMB/P(AA-co-AM) at various centrifugal forces. As the rotation speed was increased, more pressure was generated and the water retention of PMB/P(AA-co-AM) decreased. The water retention reduced to 79% when the rotation speed reached 4200 rpm for 30 min. The main reason is that the increasing pressure leads to the water molecules on the surface or in the polymeric network losing links with hydrophilic groups and then running out from the PMB/P(AA-co-AM).

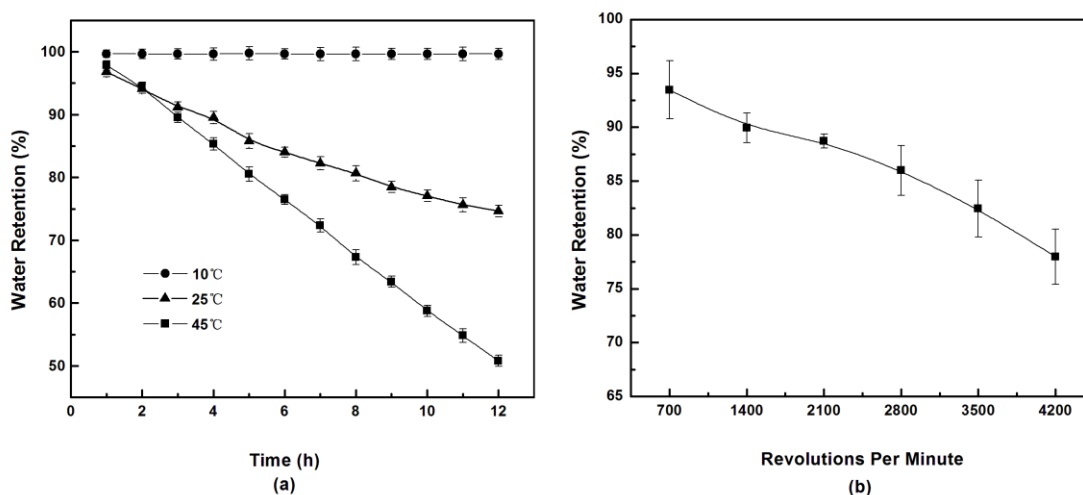


Fig. 3. Water retention capacity of the PMB/P(AA-co-AM) composite (a) at various temperatures, (b) at various centrifugal forces.

Loading and Release of Urea

Swelling of PMB/P(AA-co-AM) in aqueous urea solutions

To load urea, the prepared PMB/P(AA-co-AM) superabsorbent composite was swollen in the aqueous solutions with different urea concentrations. The results are presented in Fig. 4a. Different urea concentrations had less of an impact on Q_{eq} but a greater effect on urea loading percentage, which attained 26.0%, 52.3%, 63.5%, 69.5%, and 76.1% when the concentrations of the urea aqueous solutions were 2, 4, 6, 8, and 10 g/L, respectively. The different urea concentrations in aqueous solutions hardly changed the equilibrium swelling degree of PMB/P(AA-co-AM). This may be attributed to the fact that the urea molecule is neutral, which does not affect the electrostatic repulsion force of $-\text{COO}^-$ on polymer chains (Liang *et al.* 2009). However, while the PMB/P(AA-co-AM) was swollen in the aqueous urea solution with a high concentration, more urea molecules entered into the extended polymer network and were left in the three-dimensional network after drying. The urea loading percentage of PMB/P(AA-co-AM) can be modulated effectively by changing the concentration of the aqueous urea solution.

Release of urea from loaded PMB/P(AA-co-AM) in water

The release profiles of urea from the loaded PMB/P(AA-co-AM) composite with different urea loading percentages in deionized water at 25 °C (swollen in aqueous urea solutions with different concentrations) are depicted in Fig. 4b. The release of urea showed a typical first-order release behavior, which consists of an initially high release rate followed by a rapid decline. The period of the high speed release lasted for 60 min. After this process, the samples that were swollen in the 2 and 4 g/L aqueous urea solutions attained 75% of the whole release, while the rest achieved 85% to 95%. The release of urea is closely related to the swelling characteristics of the PMB/P(AA-co-AM) composite. Firstly, the PMB/P(AA-co-AM) composite has a high water absorbency and the polymer network extends immediately. Then, the urea molecules release from it rapidly. When PMB/P(AA-co-AM) swells to a certain degree, the extension of the polymer network is restricted, resulting in the slow release of urea molecules. Figure 4 also showed that the higher the urea loading percentage was, the faster the release of urea molecule appeared to be. This may be due to the fact that the high load of urea accelerates the movement of water molecule towards the interior of the loaded sample, which facilitates the relaxation of macromolecular chains (Bajpai and Giri 2002). Therefore, swelling in aqueous urea solutions with different concentrations is an effective way to regulate the load and release of urea from the superabsorbent composite.

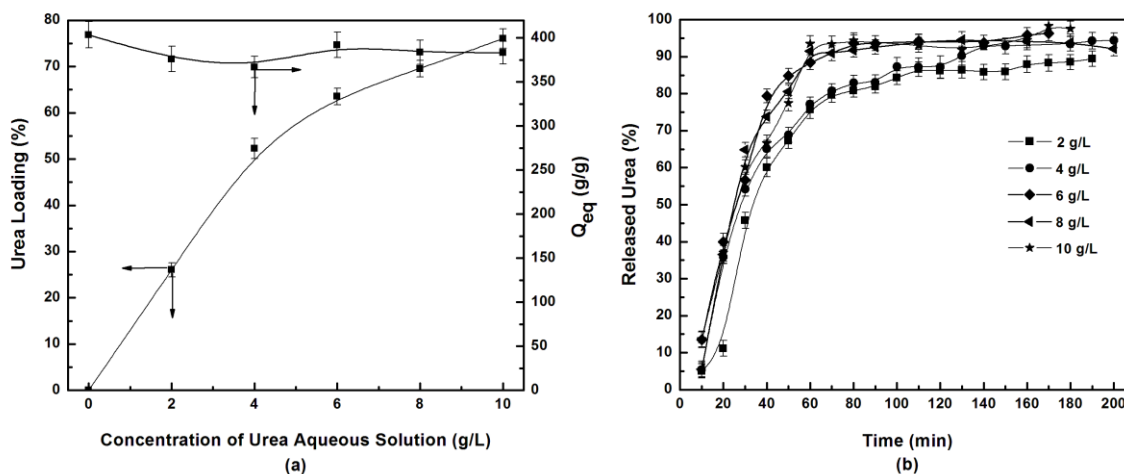


Fig. 4. Equilibrium swelling degree and urea loading percentage of the PMB/P(AA-co-AM) composite swollen in aqueous urea solutions with different concentrations (a) and their release behaviors of urea in deionized water (b).

Release of urea from loaded PMB/P(AA-co-AM) with different particle sizes

Figure 5a presents the release trends of urea from the loaded PMB/P(AA-co-AM) composite with different original particle sizes (16-20 mesh, 20-40 mesh, and 60-80 mesh) in deionized water at 25 °C. The results showed that the urea release of the 16- to 20-mesh particles was similar to others within the first 15 min, when the release of urea reached about 40%. As time went on, the release rate slowed down. This may be ascribed to small particles being held together to form a large particle when they were dried after loading, which led to the decrease in water absorbency rate and the urea release in water. But after some degree of swelling, the cohesive particles were divided and the dispersed

small particles absorbed water molecules quickly. Therefore, the urea release of these dispersed small particles is faster than the larger particles. The results also implied that the use of a superabsorbent composite with larger particle size as a carrier of urea could achieve a better effect in terms of the sustained release of urea.

Release of urea from loaded PMB/P(AA-co-AM) at various temperatures

Figure 5b compares the release profiles of urea from the loaded PMB/P(AA-co-AM) composite with 76.1% urea loading percentage in deionized water at 5 and 45 °C. The urea release increased with the increase of temperature. The proportion of released urea was 95% at 45 °C, while it was 68% at 4 °C for 45 min. The dependence of urea release on temperature is due to the molecular motion of urea being enhanced at higher temperatures, and it is therefore easier for urea molecules to diffuse in the polymer network. Moreover, the increase of temperature was more beneficial for water molecules to permeate into the three-dimensional network of the PMB/P(AA-co-AM) composite, which facilitated the release of urea. Concerning the water absorbency at different temperatures, it can be concluded that temperature has a slight influence on the water absorbency of PMB/P(AA-co-AM), but a considerable effect on its urea release, as well as water absorbency rate.

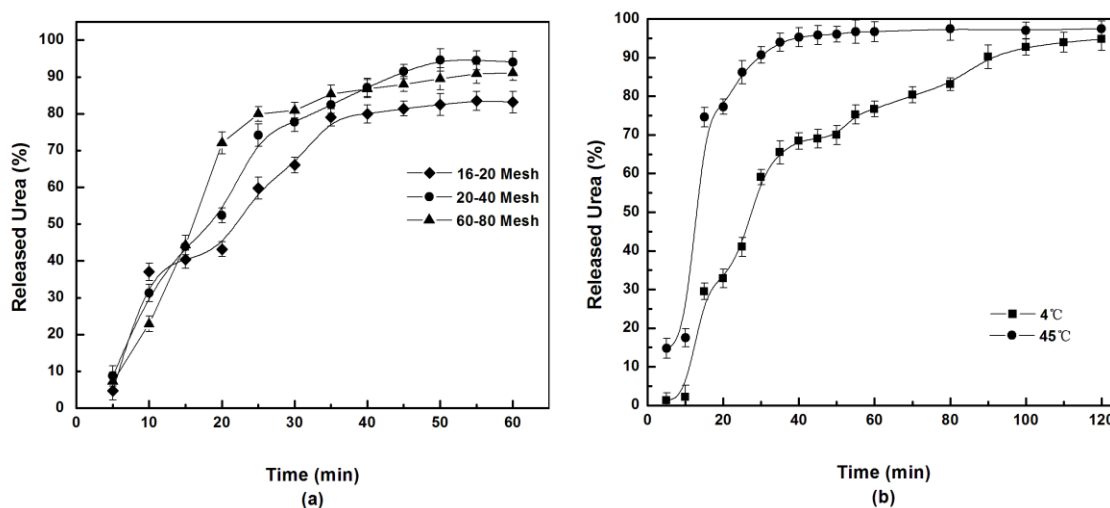


Fig. 5. Release trends of urea from the loaded PMB/P(AA-co-AM) composite with different original particle sizes in deionized water at 25 °C (a) and at different temperatures (b).

CONCLUSIONS

1. An eco-friendly superabsorbent composite was prepared by graft copolymerization of acrylic acid (AA), acrylamide (AM), and pulverized mulberry branch (PMB). The synthesis conditions and properties of the PMB/P(AA-co-AM) superabsorbent composite were studied. The obtained optimal synthesis conditions were 6 g/g mass ratio of AA+AM and PMB, AA/AM = 4:1, 60% neutralization degree of AA, 0.05 g/g mass ratio of APS and PMB, and 0.02 g/g mass ratio of MBA and PMB.

2. The product attained the best water absorbency of 570.5 g/g in deionized water, 288.0 g/g in tap water, and 70.0 g/g in 0.9 wt% aqueous NaCl solution. The PMB/P(AA-co-AM) composite also presented excellent water retention capacity as well as a rapid water absorbency rate. The concentration of aqueous solution had less impact on the Q_{eq} of PMB/P(AA-co-AM), but a greater effect on the urea loading percentage.
3. The release of urea from the loaded PMB/P(AA-co-AM) composite showed a typical first-order release behavior, which meant an initially high release rate followed by a rapid decline. This work is only a preliminary study on the synthesis and properties of the PMB/P(AA-co-AM) superabsorbent composite. Investigation into its biodegradability and application will be done in future research.

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