

PREPARATION OF BIODEGRADABLE FLAX SHIVE CELLULOSE-BASED SUPERABSORBENT POLYMER UNDER MICROWAVE IRRADIATION

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Superabsorbent polymer was prepared by graft polymerization of acrylic acid onto the chain of cellulose from flax shive by using potassium persulfate (KPS) as an initiator and N,N'-methylenebisacrylamide (MBA) as a crosslinker under microwave irradiation. SEM photographs were also studied for more information about the shive, cellulose from shive, and the superabsorbent polymer. The structure of the graft copolymer was confirmed by FT-IR spectroscopy and thermogravimetric analysis (TGA). The biodegradability in soil was measured at 32 and 40 °C. The polymer was porous, and thermal stability of the polymer was observed up to approximately 200 °C. FT-IR analysis indicated that acrylic acid in polymer was successfully grafted onto the cellulose. The graft copolymer was found to be an effective superabsorbent resin, rapidly absorbing water to almost 1000 times its own dry weight at pH around 7.3. The water absorbency in 0.9% NaCl, KCl, FeCl₃ solutions and urine were 56.47 g/g, 54.71g/g, 9.89g/g and 797.21g/g, respectively. The product biologically degraded up to 40% at 40 °C in 54 days, which shows good biodegradability.

Keywords: Superabsorbent polymer; Graft copolymerization; Flax shive cellulose; Acrylic acid; Microwave irradiation; Biodegradability

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INTRODUCTION

Superabsorbent polymers are highly swollen, hydrophilic polymer networks, capable of absorbing large amounts of water or saline solution (Lu et al. 2003; Zhao et al. 2005). For these properties, they are widely utilized in various applications such as sanitary napkins, disposal dippers additives for drug delivery systems, and soil in agriculture (Li et al. 2007; Zhang et al. 2007). At present, more attention is being paid to sodium acrylate homopolymer or copolymers of starch graft polyacrylates. So far, most of the superabsorbent resin based on cellulose mainly comes from the carboxymethyl-cellulose (CMC) derivative (Nie et al. 2004; Abd El-Mohdy 2007; Chang et al 2010). Less research has been done on cellulose directly grafted polymer to prepare superabsorbent resin, which can offer better salt resistance than other kinds of superabsorbent material (Zheng et al. 2007; Feng et al. 2009). This approach is more difficult than CMC because of the inhomogeneous reaction. Cellulose is a promising natural polymer material, because of its renewability, biodegradability, biocompatibility,

and abundance in nature (Dong et al. 2008; Zhu et al. 2009). It is widely applied in many fields.

Microwave irradiation has received increasing interest in organic synthesis due to the great enhancement of the reaction speed over conventional reaction conditions (Cao et al. 2001; Shao et al. 2003). Microwave can heat the system rapidly and evenly (Danke 1999; Ge et al. 2006) so that it has been successfully applied to the synthesis of superabsorbent resin of starch-acrylic acid grafted copolymer (Xu et al. 2004).

Flax (*Linum usitatissimum* L.) is a widely used crop that supplies fiber and seed for domestic and important industrial applications (Sankari 2000). Flax stems constitute the source of bast fibers, which are utilized in textiles, composites, specialty papers, etc. (Domier 1997). To obtain these bast fibers, flax straw needs to be retted, a process in which gums are removed and fibers are separated from the other part of the stem, called shive. Shive is woody, lignified inner tissues of the stem and is a by-product of flax fiber production. It constitutes about 70% of the stem. Therefore, a large amount of flax shive is available in fiber processing. In North America, the amount of flax shive can be estimated at 2.1 million tons annually (Thomas 2009). The amount in China is about 1.0 million tons. In fiber processing plants, the large amount of flax shive requires value-added uses, which attract more interest of researchers. However, shive is traditionally used as a waste in some low-value applications such as burning for thermal energy, animal bedding, and particle-board. In recent years, it has been used as training material for edible mushrooms. Cox et al. (1999, 2000) and El-Shafey et al. (2002) studied the carbonaceous material remaining from flax shive after sulfuric acid treatment. Other references demonstrated that flax shive can be used as bio-absorbent to absorb metal ions. Flax shive constitutes about 46 to 48% cellulose, which is approximately equal to the content of cellulose in polar wood. The content of lignin in it is about 24 to 27% (Wayne 2007), which is lower than that in most softwood species and higher than that in most hardwood species. Therefore, flax shive is also a potential cellulosic resource. So far there has not been significant research on superabsorbent from flax shive cellulose

In this paper we report the synthesis of superabsorbent by graft copolymerization reaction of cellulose from flax shive and acrylic acid using N,N'-methylenebisacrylamide as a crosslinker and potassium persulfate as an initiator in an aqueous solution under microwave irradiation. The system was characterized by Fourier transform infra-red spectrometry (FT-IR), thermo-gravimetry(TG/DTG), and scanning electronic microscopy (SEM). The water absorbency properties and degradability were also analyzed.

EXPERIMENTAL

Materials

Flax shive was collected after processing retted flax stems from the Keshan Flax fiber plant, Helongjiang province, China. Acrylic acid (AA, analytical reagent (AR)), sodium hydroxide (AR), absolute alcohol (AR), and potassium persulfate (KPS, AR) were purchased from Tianjin Kermel Chemical Reagent Development Center. N,N'-methylenebisacrylamide (MBA, AR) was purchased from Tianjin Aoran Institute of Fine

Chemical. AA was purified by active carbon and stored in a refrigerator before use. All other chemicals were of analytical grade and used without further purification.

Preparation of Cellulose from Flax Shive

Flax shive cellulose samples prepared in our own laboratory via alkali cooking method and the cooking conditions were as follows: NaOH concentration 18 wt%, ratio of flax shive to volume of NaOH solution 1g:4.5mL, and 160°C for 2.5 h. Cooking trials were made in a batch type digester rotating four times per min with automatic temperature control. After cooking, the cellulosic fibers so obtained were rinsed with tap water to remove residual NaOH and degraded lignin. The rinsed cellulosic fiber were dried and ground to a size lower than 250 μm , then hydrolyzed in 2.5mol/L hydrochloric acid solution for 30 min at 105°C. The hydrolyzed product was rinsed with distilled water to neutral pH value, dried, and ground to powder with size less than 120 μm .

Preparation of Superabsorbent

An LWMC-205 adjustable microwave reactor (made in Nanjing Lingjiang Science and Technology Development Co., Ltd., China) was employed in these studies. 0.01g of MBA, 7.15g of AA, and the desired amount of NaOH solution and de-ionized water were mixed and kept in an ice bath until use. A two-neck reactor with beater and condenser pipe was first assembled on the microwave reactor. A certain amount (1.0g) of flax shive cellulose and some deionized water were added to the two-neck reactor and stirred to get the cellulose suspension into solution for 30 min under N_2 atmosphere. Then, KSP was added and continuously stirred for 15min, and next, the blend above was added to the system to react for 7min. The whole process was conducted under N_2 atmosphere and 160W microwave irradiation. After completing the reaction, the product was taken out and cooled to room temperature. Then it was cut into small pieces and immersed into absolute ethanol for 30 min. Subsequently, it was dried at 60°C until the weight became constant. After being ground and sieved with steel screens, superabsorbent powder in size of 120 to 180 μm was obtained.

Characterization

IR spectra of samples as KBr pellets were taken using a Nicolet 560 spectrometer (Nicolet Co., USA). The thermal stability of samples was studied on a Pyris 6 thermogravimetric analyzer (TGA) (Perkin Elmer, USA) with a temperature range of 50 to 600°C at a heating rate of 10°C/min under nitrogen atmosphere. Morphology observation was performed on a scanning electron microscope (SEM) (Quanta 200, Philips-FEI Co., Netherlands). The scanned surfaces were coated with a thin gold layer before observation to avoid charging under the electron beam.

Measurement of Water Absorbency

The amount of 0.2g of the superabsorbent polymer was placed into a 200-mesh sieve pouch. The pouch was then immersed into 250mL of distilled water. After a period of time, the pouch with swollen superabsorbent polymer in it was taken out from the water and hung in air for 30 min, allowing the excess water to be removed as much as

possible. After removing the excess water, the weight of the swollen polymer was measured. The swelling ratio (Q , g/g) was calculated by the equation below:

$$Q(\text{g/g}) = (m_1 - m_0) / m_0 \quad (1)$$

where m_0 and m_1 are the weight of the dry and swollen superabsorbent polymer, respectively.

Biodegradability Measurement

Soils for planting flowers were used in the biodegradation tests. A certain amount (0.4g) of the superabsorbent polymer was wrapped with two layers of nylon screen cloth and embedded 10 cm depth under the soil surface. The samples embedded in soils were placed in two temperature humidity chambers at 32°C and 40 °C, respectively. The biodegraded samples were weighed at intervals of 6 days for 8 times. The biodegradability can be calculated with the below equation:

$$\text{Biodegradability}(\%) = (m_s - m_d) / m_s \times 100\% \quad (2)$$

where m_s is the weight of the un-degraded superabsorbent polymer, and m_d is the weight of the biodegraded superabsorbent polymer.

RESULTS AND DISCUSSION

Morphological Analysis

SEM micrographs of untreated shive, cellulose from shive, and the superabsorbent polymer are shown in Fig. 1. The differences are obvious. The untreated shive is the woody part and characterized by ordered rows of tubular structures involved in water and nutrient transport in the stem of the flax plant. Cellulose from shive did not retain the structure of shive, showing characteristics of woody fiber with a row of pits. Shortening in fibers occurred and resulted in small particle size. This can be attributed to the effect of hydrolysis of fibers by the HCl solution. The superabsorbent polymer shows a porous surface. The pores are connected with each other. This surface morphology may accelerate the penetration of water into the polymeric network. It can also be clearly seen in the enlarged view (Part F) that cellulose is wrapped by the polymer and there exists silk-like bonding between them.

FT-IR Analysis

The IR spectra of the flax shive cellulose and the graft polymer prepared are shown in Fig. 2. Figure 2(a) shows that the main characteristic peaks of cellulose are at 1163 cm^{-1} , 1114 cm^{-1} , 1062 cm^{-1} (pyran structure), 3434 cm^{-1} (O-H stretch), and 2906 cm^{-1} (C-H stretch). The small peaks at 1639 cm^{-1} and 1431 cm^{-1} result from -C=O stretching and amorphous cellulose, respectively.

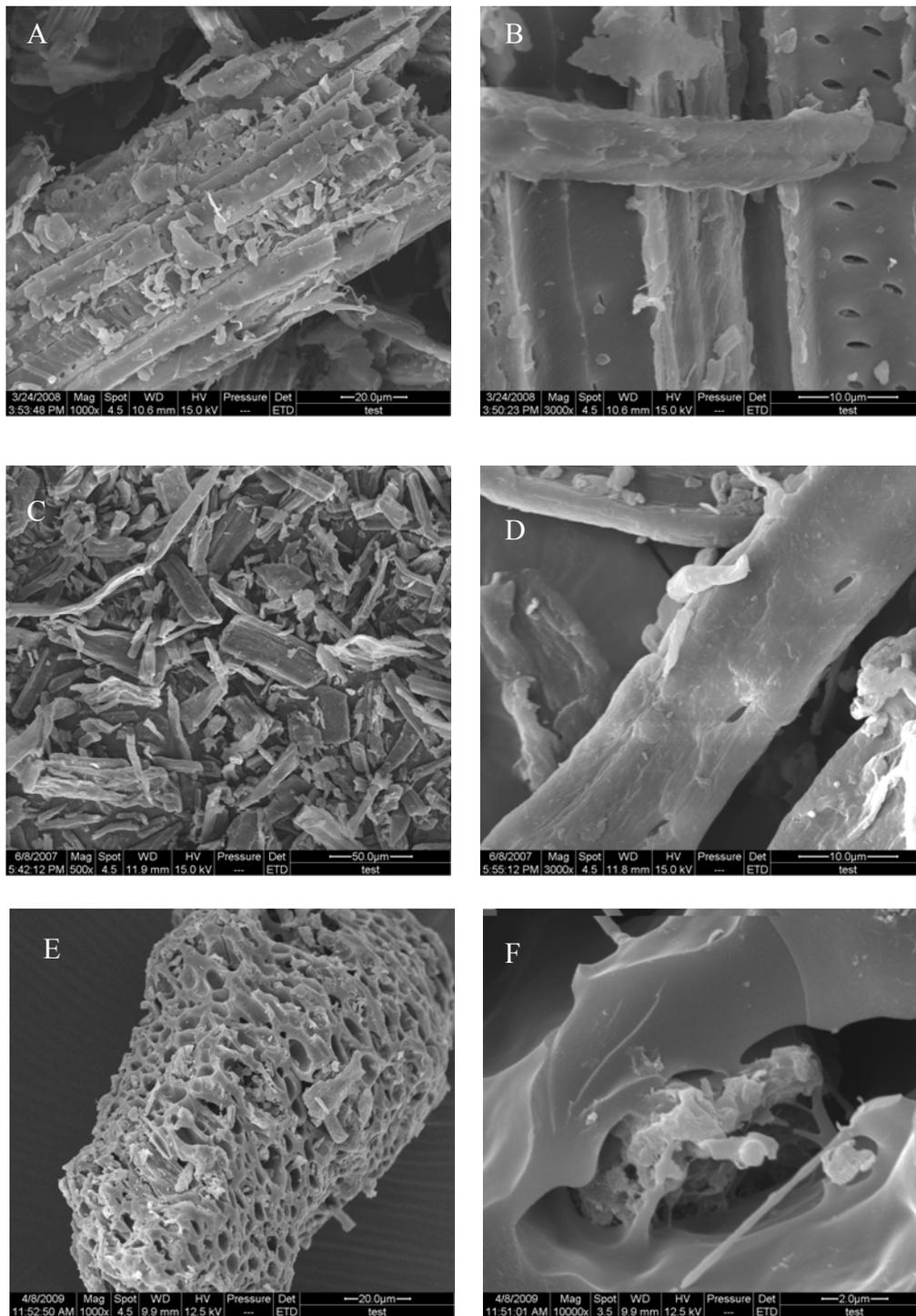


Fig. 1. SEM micrographs of untreated shive, cellulose from shive, and the superabsorbent polymer. A. Untreated fragment of shive. $\times 1,000$. B. Enlarged area of untreated lignified cell wall. $\times 3,000$. C. Fragment of cellulosic fiber from shive. $\times 500$. D. Enlarged area of cell wall of the fiber with pores. $\times 3,000$. E. Fragment of the superabsorbent polymer. $\times 1,000$. F. Enlarged area of the pore. $\times 10,000$.

The absorption bands at 1372 cm^{-1} and 898 cm^{-1} are ascribed to C-H bending vibration. The peak at 1318 cm^{-1} is attributed to O-H bending vibration. In the spectrum of PAA(Na) shown in Fig.2(b), the peak at 1702 cm^{-1} corresponds to the carboxyl absorption from grafted poly(acrylic acid) (PAA), and the peak at 809 cm^{-1} is also characteristic of PAA. Furthermore, the bands at 1571 and 1408 correspond to the sodium carboxyl group. In the spectrum of grafted cellulose shown in Fig.2(c), in addition to the cellulose peaks, some characteristic absorption peaks from acrylic acid and polyacrylate appear. The peak at 1716 cm^{-1} corresponds to the carboxyl absorption from grafted poly(acrylic acid) (PAA), and the wide peak at 809 cm^{-1} is also characteristic of PAA. Furthermore, the bands at 1584 and 1408 correspond to the sodium carboxyl group. These indicate that PAA(Na) has been grafted onto cellulose.

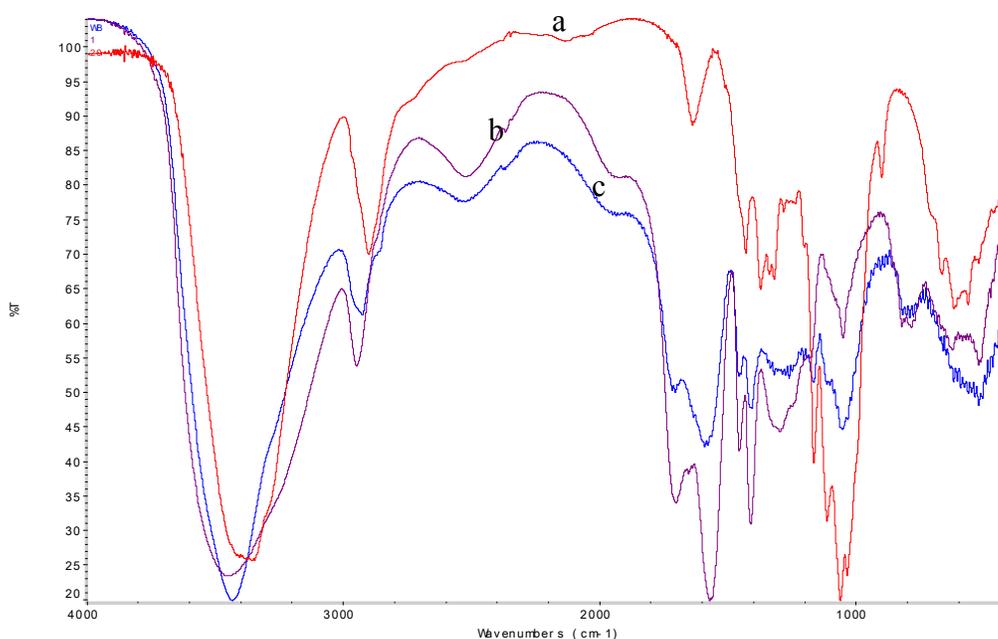


Fig. 2. FT-IR spectra of (a) cellulose,(b) PAA(Na) and (c) PAA(Na)-g-cellulose superabsorbent polymer

Thermal Stability

The grafting was also supported by thermo-gravimetric analysis, as shown in Fig. 3. TGA of flax shive cellulose (a) showed a weight loss in two stages. The first stage ranged between 10 and $100\text{ }^{\circ}\text{C}$ and showed about 2.5% loss in weight. This may be due to the loss of absorbed and bound water. The second stage of weight loss started at $320\text{ }^{\circ}\text{C}$ and continued to $400\text{ }^{\circ}\text{C}$, during which 78% weight loss may correspond to the degradation of cellulose (Zheng et al. 2007). Curve (b) of PAA(Na) revealed two main stages of weight loss from $50\text{ }^{\circ}\text{C}$ to $540\text{ }^{\circ}\text{C}$. The first stage started at $50\text{ }^{\circ}\text{C}$ and continued up to $425\text{ }^{\circ}\text{C}$, and the second stage started at $435\text{ }^{\circ}\text{C}$ and continued up to $540\text{ }^{\circ}\text{C}$, in which about 27% and 29% of weight lost, respectively. The resin (c) showed three stages of weight loss between 50 and $520\text{ }^{\circ}\text{C}$. The first stage of weight loss started at $50\text{ }^{\circ}\text{C}$ and

continued up to 245 °C, during which there was about 12% weight loss due to the absorbed water. The stage from 320 to 420 °C and the third one from 420 to 520 °C may correspond to the decomposition of cellulose and polyacrylate (PAA(Na)). The degradation profile of the resin contains three steps, which also were present in the degradation curve of cellulose and pure PAA(Na). These observations confirm that the graft polymerization was completed. Below 400 °C the resin had lower loss than cellulose, which indicates that the grafting of cellulose increased the thermal stability of cellulose to a certain extent. In short, thermal stability of the polymer was observed up to approximately 200 °C.

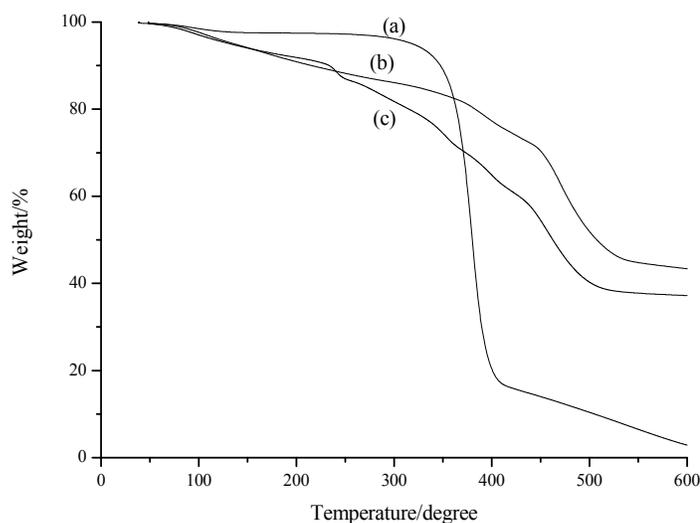


Fig. 3. TGA curves of (a) cellulose, (b) PAA(Na), and (c) cellulose-g-PAA(Na) superabsorbent resin

Water Absorption of the Grafted Copolymer

The water absorption rate of the superabsorbent polymer is shown in Fig. 4. It can be seen that it took about 10 min to reach the swelling equilibrium. Because the superabsorbent polymer synthesized according to the procedures used in this study is full of pores, the Na^+ ions move to the outside of the polymer more easily, and the hydrophilic $-\text{COO}^-$ groups attract more water molecules. Therefore, the water absorption rate was higher. Moreover, with the swelling of the polymer, the distance between polymer chains was increased, which accelerated the water absorption rate.

In order to investigate the sensitivity of the grafted polymer to pH, the equilibrium swelling of the resin was investigated at various pHs ranging from 1 to 13.7. As shown in Fig. 5, the maximum swelling was achieved at a pH value near 7.3. At pH 7.3, the carboxylic acid groups became ionized and the electrostatic repulsive force between the charged sites ($-\text{COO}^-$) caused an increase in swelling. At lower pHs, the carboxylic acid groups were protonated, so that the main anion-anion repulsive forces were eliminated and consequently swelling values decreased (Pourjavadi 2006). At higher pHs, a screening effect of the counter ions shielded the charge of the carboxylate anions and prevented an efficient repulsion. Thus, an obvious decrease in swelling was observed.

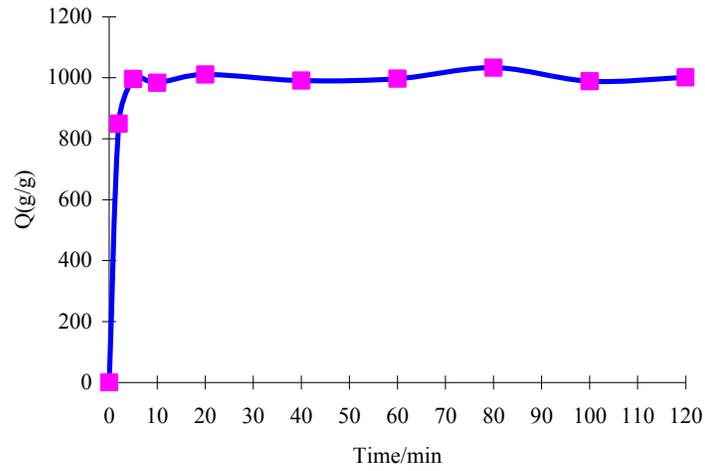


Fig. 4. Water absorption rates of the superabsorbent polymer

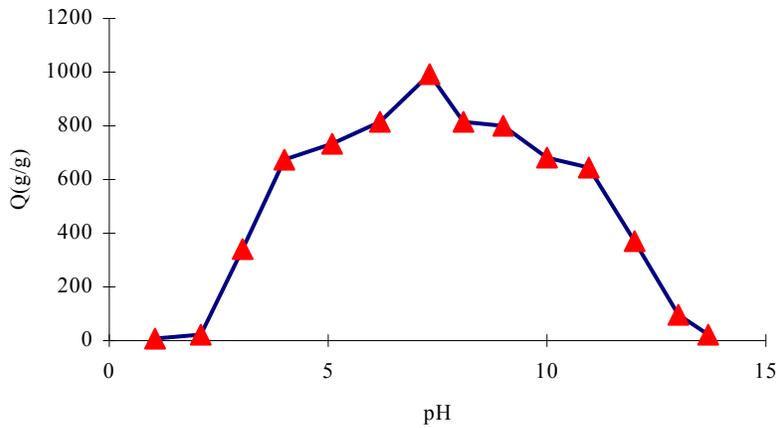


Fig. 5. The effect of pH value on water absorbency

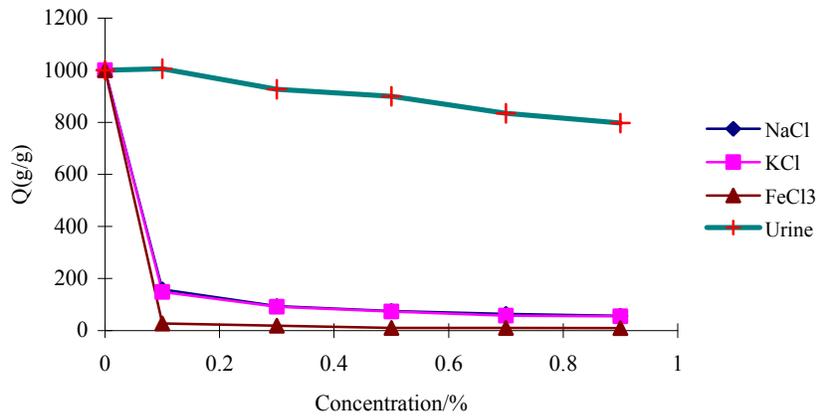


Fig. 6. Water absorption of the resin in various solutions

Figure 6 shows the effects of the concentration of saline and urine solutions on water absorbency of the resin. The water absorbency decreased with the increase of the concentration of all four solutions. It was also found that the water absorbency in NaCl solution was almost equal to that of in KCl solution, but far higher than that of in FeCl₃ solution. It decreased with increase of ionic strength of the external solution. Moreover, the multivalent cationic solution effects could be due to the complexing ability of the carboxylate groups, which result in an increase in the crosslinking density of the network (Castal et al 1990). However, the water absorbencies in the three saline solutions were significantly lower than that of in the urine solution. Urine is a non-ionic matter, and the effect is relatively small. The water absorbency in 0.9% NaCl, KCl, and FeCl₃ solutions and urine were 56.47 g/g, 54.71 g/g, 9.89 g/g, and 797.21g/g, respectively.

Biodegradation Analysis

Biodegradability of superabsorbent resin under 32 °C and 40 °C is shown in Fig. 7. Biodegradation at temperature below 40 °C was faster. The material was degraded by almost 40% at 40 °C, and approximately 20% at 32 °C in 54 days. Slightly slower biodegradability of the polymer is beneficial to its longer application. Higher temperature may improve the activation of some microorganisms and accelerate the biodegradation. Furthermore, the porous structure allows microorganisms to go more easily inside the network, which also favors its biodegradation.

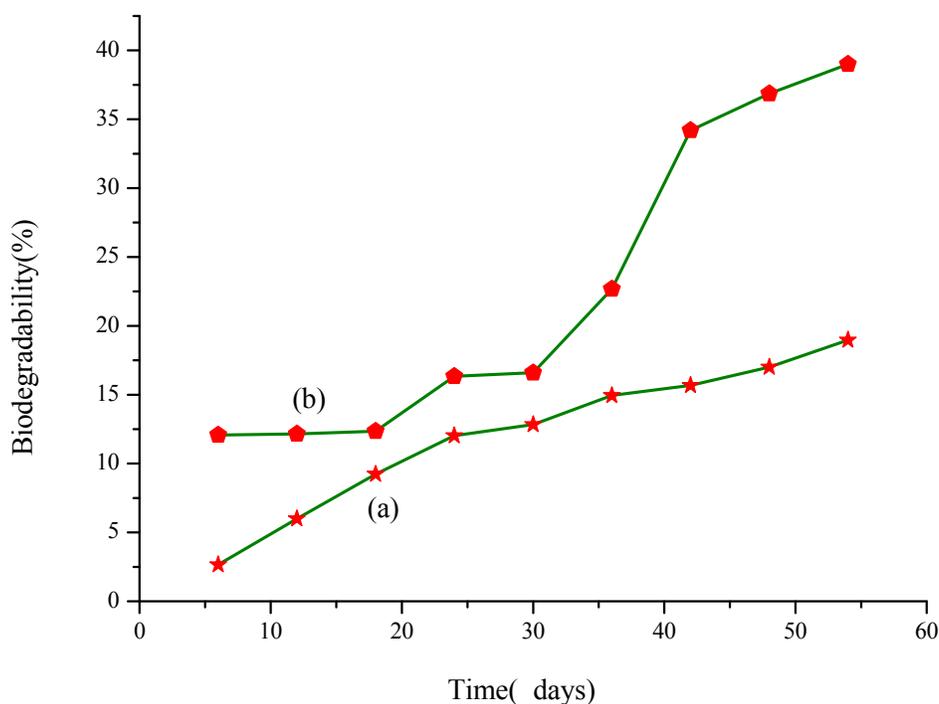


Fig. 7. Biodegradability of cellulose-g-PAA superabsorbent resin at (a) 32 °C and (b) 40 °C

CONCLUSIONS

1. Superabsorbent polymer was prepared by graft polymerization of acrylic acid onto the chain of cellulose from flax shive by using $K_2S_2O_8$ as an initiator in the presence of N,N' -methylenebisacrylamide (MBA) as a crosslinker under microwave irradiation.
2. The superabsorbent was a graft copolymer of acrylic acid and cellulose and had a porous structure. Thermal stability of the polymer was observed up to approximately 200 °C.
3. It took less than 10min to reach swelling equilibrium and rapidly absorb water almost 1000 times its own dry weight. The maximum swelling was achieved at a pH value near 7.3. The water absorbency in 0.9% NaCl, KCl, and $FeCl_3$ solutions and urine were 56.47 g/g, 54.71g/g, 9.89g/g, and 797.21g/g, respectively.
4. The product was observed to decompose 40% at 40 °C in 54 days; therefore, it can be considered to be an environmentally friendly product. Thus, the present superabsorbent polymer is expected to be useful for agricultural applications. This study also provides a novel method for high value-added utilization of a by-product that is high in cellulose.

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