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Photopolymerisation and characterization of maleylatedcellulose-g-poly(acrylic acid) superabsorbent polymer

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ABSTRACT

A novel biodegradable superabsorbent polymer has been prepared from maleylated cotton stalk cellulose (MCSC) crosslinker and acrylic acid (AA) by ultraviolet (UV) photopolymerization in aqueous solution at room temperature, and irgacure 651 as a photoinitiator. The resulting superabsorbent was characterized by FT-IR, ^{1}H NMR, SEM and TGA. The effects of preparation conditions such as degree of substitution (DS), amount of maleylated cotton stalk cellulose, exposed time, photoinitiator amount and monomer concentration on the water absorbency and the monomer conversion in graft were evaluated. The swelling kinetics, salt-resistance, water retention capacity and biodegradability of the MCSC-g-PAA superabsorbent were investigated. It was found that, the obtained superabsorbent have good swelling degree that greatly affected by its composition and preparation conditions. Owing to its considerable good water retention capacity, being economical and environment-friendly, it might be useful for its application in agriculture field.

1. Introduction

Superabsorbent polymers (SAPs) are lightly crosslinked hydrophilic functional polymers with three-dimensional network structures, which have the ability to absorb large quantities of water, ranging from hundreds to thousands of times of their mass in a relatively short time and retain water even under pressure (Liu, Wang, & Wang, 2007). The hydrophilic groups and domains in their structure play the key role in having the superabsorbent properties. These excellent characteristics allow the application of SAPs as functional materials in the field of hygiene (Kamat & Malkani, 2003), drug delivery (Pourjavadi, Barzegar, & Zeidabadi, 2007), water treatment (Dalaran, Emik, Güçlü, İyim, & Özgümüş, 2011), concrete (Song, Wei, & He, 2009), food additive (Zohuriaan-Mehr, Omidian, Doroudiani, & Kabiri, 2010), agriculture and horticulture (Tian et al., 2012; Xie, Liu, Ni, & Wang, 2012). However, SAPs are mainly petroleum-based synthetic polymers with high production cost and poor biodegradability, widespread use of those polymers may lead to environmental pollution (Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002; Marc, Mele, Palmisano, Pulito, & Sannino, 2006).

Cotton is one of the most abundant crops in the northwestern China. The increase in cotton planting has permitted production of a huge amount of cotton stalks. These big quantities of stalks become an environmental problem, because of loosing their importance as fuel and ending with bad quality results in paper making industries (El-Hendawy, Alexander, Andrews, & Forrest, 2008). Currently, cotton stalks are mostly burned on the ground since they are harboring diseases that could affect future cotton crops (Reddy & Yang, 2009). However, cotton stalks which mainly contain cellulose are abundant, cheap, biodegradable and annually renewable sources, and some attempts have been made to study on the potentials of utilizing cotton stalks (Nahil & Williams, 2012; Reddy & Yang, 2009; Shi, Sharma-Shivappa, Chinn, & Howell, 2009; Silverstein, Chen, Sharma-Shivappa, Boyette, & Osborne, 2007). The mass utilization of this agricultural waste and converting them into a value-added product can provide an environmentally sound method of disposal. Moreover, the development of biodegradable/bio-based superabsorbent materials from renewable sources is nowadays being viewed as a strategic research area (Chang & Zhang, 2011; Sannino, Demitri, & Madaghiele, 2009).

Recently, several researches on the preparation of cellulose based SAPs have been reported, the highest water absorbencies of the obtained superabsorbent hydrogels were 417 g/g (Liu, Miao, Wang, & Yin, 2009), 620 g/g (Wang & Wang, 2010), 680 g/g (Bao, Ma, & Li, 2011), and 875 g/g (Wu, Zhang, Liu, & Yao, 2012), respectively. However, the major drawbacks of these methods are (a) the presence of a considerable amount of ungrafted cellulose in the hydrogel due to the lack of reactive groups of the cellulose chains, (b) using costly divinyl crosslinker such

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as N,N-methylenebisacrylamide (MBA) which can crosslink vinyl monomers but the conventional crosslinker may not improve the grafting extent of cellulose, and (c) commonly used thermal polymerization which causes energy consumption and pollution of environment. Preparing SAPs from modified cotton stalk cellulose with acrylate via UV photopolymerization method could be attractive alternatives to overcome some of the above-mentioned drawbacks. The main reasons are as follows: Modifying cellulose through the use of maleic anhydride (De Melo, da Silva Filho, Santana, & Airoldi, 2009; Zhou, Jin, Hu, Zhang, & Ma, 2012) produces degradable ester bonds, reactive carbon–carbon double bond and hydrophilic carboxylic acid end groups. Therefore, the modified cotton stalk cellulose has the better hydrophilicity and is easier to graft monomer than cellulose. The raw materials and reagents are abundant and cheap. Furthermore, compared with time-consuming thermally induced polymerization, UV photopolymerization has many advantages such as solvent free, time-saving, low energy consumption, high efficiency and less pollution (Wan, Wang, Yuan, & He, 2006; Weiqing, Xiaogong, Yanqing, Yuli, & Aijie, 2006).

In this study, cotton stalk cellulose (CSC) was separated from cotton stalks by alkali pretreatment method, and reacted with maleic anhydride at different feed ratio synthesizing MCSC. Preparation of maleylatedcellulose-g-poly(acrylic acid) (MCSC-g-PAA) superabsorbent polymer by photopolymerization with MCSC and AA was investigated. We predict that the maleate groups on the cellulose backbone in cotton stalks lead to the crosslinking of polymer chains during photopolymerization process. The effects of various factors on the water absorbency of the synthesized superabsorbent and monomer conversion in graft were investigated. The structure and properties of the superabsorbent materials were evaluated.

2. Experimental

2.1. Materials

Cotton stalks were obtained from the waste residue after 2009/2010 harvesting season in cotton farms of Korla, Xinjiang Uygur Autonomous Region. The stalks were air dried, milled and passed through a 100-mesh screen prior to further experiments. The composition of the cotton stalks in terms of cellulose, hemicellulose, lignin and ash content were determined according to standard biomass analytical methods (Sluiter et al., 2008), the cotton stalks predominantly contains cellulose (41.2 ± 0.6%), hemicellulose (23.8 ± 0.7%), acid insoluble lignin (19.6 ± 0.5%), acid soluble lignin (2.2 ± 0.5%) and ash (1.6 ± 0.3%). Acrylic acid (AA, 99.5%, Damao Chemical Industry, Tianjing, China) was distilled under reduced pressure before use. Maleic anhydride (MA, analytical grade, Chemical Reagent Subsidiary Industry, Shanghai, China) was used as received. The sodium hydroxide (98.0%, Baishi Chemical Industry limited company, Tianjin, China) was used as neutralistic reagent. The photoinitiator (PI): Irgacure 651(2,2-dimethoxy-2-phenylacetophenone) was supplied from Ciba-Geigy Co (New Jersey). Other All reagents used in the experiment were all of analytical grade and all solutions were prepared by using distilled water.

2.2. Pretreatment of cotton stalk

CSC was separated from cotton stalks by a microwave heating alkali-cooking method. The dissolution process of cellulose was carried out according to the literature (Zhang, Zhang, Deng, & Sun, 2011). At the pretreatment step, the cotton stalk in 12% alkali solution with the ratio of 1:9 was heated under 200 W microwave for 6 min. After filtration, cellulose was bleached with 10% NaClO for 3 h at 35 °C, and extracted for 10 min by 5% HCl at room temperature. Finally, The product was washed with distilled water until neutralized, then dried at 60 °C for 6 h.

2.3. Synthesis of maleylated cotton stalk cellulose

The dried CSC (5.0 g) was dispersed in acetone with constant magnetic stirring, an appropriate amount of maleic anhydride and pyridine (act as catalyst) were added. The CSC was reacted with maleic anhydride at different mass ratio (CSC:Maleic anhydride = 5:1; 5:2; 5:3) under acetone reflux in the reaction flask which immersed in the oil bath at 65 °C for 4 h. The products were precipitated and washed with distilled water, and finally with acetone, respectively. After that, the modified cotton stalk cellulose was dried at 90 °C for 24 h.

The degree of substitution of MCSC was determined by the back titration method (Zhou et al., 2012). This method is based on adding an excess of NaOH solution which reacted with carboxyl group of MCSC in the test solution, the remaining NaOH solution was titrated with HCl solution. According to this, 0.1000 g MCSC was treated with 0.0100 mol L^{-1} NaOH solution (100.00 mL) in round bottom flask at room temperature for 2 h with constant stirring. Then, 25.00 mL supernatant fluid was treated with 0.0100 mol L^{-1} HCl solution after the materials were filtered. The experiment was carried out in parallel three times. The degree of substitution (DS) was calculated as Eq. (1)

$$DS = \frac{1/2(C_{NaOH} \times V_{NaOH} - 4 \times C_{HCl} \times V_{HCl}) \times M_{MA}}{m_{MCSC}} \quad (1)$$

where C_{NaOH} is the concentration of NaOH solution (mol L^{-1}), C_{HCl} is the concentration of HCl solution (mol L^{-1}), V_{NaOH} is the volume of NaOH solution (L), V_{HCl} is the volume of HCl spent in the titration of excessive non-reacted NaOH solution (L), M_{MA} (g mol^{-1}) is the molecular weight of maleic anhydride and m_{MCSC} (g) is the mass of the MCSC in this experiment.

2.4. Synthesis of MCSC-g-PAA superabsorbent polymer

3.6 g of AA and adequate volume of 5 M sodium hydroxide solution (to 75% of neutralization) were introduced into 50 mL double quartz tube equipped with a magnetic stirrer, and the total monomer concentration was adjusted with adequate volume of water. The mixture was stirred and cooled until the room temperature completely, and then appropriate amount of MCSC and PI were fully dispersed in the mixed solution. UV irradiations were performed for a certain period of time in a dark box using unfiltered light of medium pressure mercury lamp (300 W, the main wavelength 365 nm, average intensity of 12.3 mW/cm^2) which was placed in the axial position of double quartz glass cylinder which was cooled by water circulating in order to avoid overheating. The solutions were thoroughly degassed by bubbling oxygen-free nitrogen during the reaction. The temperature was kept always below 25 °C to ensure a minimum contribution of the thermal process. Polymers thus formed and were stirred in 100 mL acetone water mixture (volume ratio of 3:7) to remove the soluble fraction. The polymers were dried at 80 °C for 48 h in vacuum oven and then was milled.

2.5. Characterizations

The FTIR spectra were recorded on BRUKER EQUINOX-55 FTIR spectrometer in 4000–500 cm^{-1} region using KBr pellets.

Liquid state nuclear magnetic resonance (^{1}H NMR) spectroscopy was used to determine the chemical structures of the modified cotton stalk cellulose and the superabsorbent. ^{1}H NMR spectra were

obtained using a VARIAN INOVA-400 spectrometer (400 MHz) with D_2O as solvents.

The thermogravimetric (TGA) measurement was carried out using the STA449F3GA simultaneous thermal analyzer (NETZSCH Corporation, Hanau, Germany) with the temperature ranging from 30 to 650 °C under a nitrogen atmosphere. The nitrogen flow was 30 mL/min and heating rate was 5 °C/min.

The surface morphology of the superabsorbent was investigated using the scanning electron microscopy (SEM, JSM-5600LV, JEOL, Ltd. Japan). Sample was swollen in distilled water, frozen in liquid nitrogen and lyophilized, and then mounted on an aluminum stub and coated with a thin layer of palladium gold alloy.

2.6. Measurement of monomer conversion in grafts

Sample of the prepared superabsorbent was washed with non-solvent methanol several times. After filtration, the sample was dried in vacuum oven at 80 °C to constant weight. The monomer conversion was calculated by following equation:

$$\text{Monomer conversion in grafts } (\%) = \frac{W_g - W_c}{W_m} \times 100 \quad (2)$$

where W_g is the weight of graft copolymer isolated after several extraction with methanol, W_c is the weight of MCSC before grafting, and W_m is the total weights of acrylic acid and sodium acrylate used for the grafting reaction.

2.7. Measurement of water absorbency

The accurately weighed superabsorbent powder (0.1 ± 0.0001 g) with average particle sizes between 40 and 60 mesh were immersed in excess distilled water or saline solutions at room temperature to reach the swelling equilibrium (about 80 min). The swollen sample was separated by filtration through a tea bag (100 mesh nylon screen). The tea bag was hung for 10 min to remove the excess solution. The equilibrium swelling Q_{eq} was calculated using the following equation:

$$Q_{eq} = \frac{m_2 - m_1}{m_1} \quad (3)$$

where m_1 and m_2 are the weights of the dry sample and the swollen sample, respectively. Q_{eq} is calculated as grams of water per gram of sample.

2.8. Swelling rate

Swelling rate of the superabsorbent was measured according to the following process: a certain amount of sample (40–60 mesh, 0.10 ± 0.0001 g) was poured into a weighed tea bag and immersed in excess distilled water at room temperature. At consecutive time intervals, the water absorbency of the sample was calculated according to Eq. (3).

2.9. Absorbency in different salt solutions

Absorbency of the superabsorbent was evaluated in different concentrations of NaCl, $CaCl_2$, and $FeCl_3$ salt solutions according to the above-described method, except that salt solutions were used instead of distilled water.

2.10. Soil burial degradation

Biodegradability of the samples in soil was studied by weight loss (Wang, Song, & Shang, 2008). Samples were weighed and then buried in the soil for up to 120 days. The soil was maintained at 20% moisture by weight, and samples were buried at a depth of 15 cm. The burial samples were dug out in certain time intervals, washed with distilled water, dried in a vacuum oven at 60 ± 2 °C for 24 h, then equilibrated in a desiccator for at least a day. The samples were then weighed to determine the weight loss.

2.11. Measurement of water retention in soil

Different amounts (0.2, 0.5, and 0.8 g) of the superabsorbent were well-mixed with 200 g of dry soil and kept in 500 mL glass beakers, then 80 g of tap water was slowly added into the beaker and the beaker was weighed (W_0). A control experiment without the superabsorbent was also carried out. The beakers were maintained at room temperature and weighed every day (W_i) for 30 days. The water retention in the soil (Wr%) was calculated by the following equation:

$$Wr\% = \frac{W_i}{W_0} \times 100\% \quad (4)$$

3. Results and discussion

3.1. Mechanism of MCSC-g-PAA superabsorbent formation

The MCSC-g-PAA superabsorbent was prepared by UV photopolymerization of AA and MCSC in the presence of initiator. The proposed mechanism for the grafting and chemically crosslinking reactions is described in Fig. 1. UV photoinitiated polymerization is mediated by photoinitiators. In principle, photoinitiators (PI) are required to absorb light in the ultraviolet–visible spectral range, generally 250–550 nm, and convert this light energy into chemical energy in the form of reactive intermediates, such as free radicals. The photoinitiator radicals would be added to one side of the acrylic acid double bond leading to the formation of an unpaired spin on the other side of a vinyl bond, it reacts with acrylic acid molecule, then acrylic homopolymerization (R_1) starts. At the same time the initiating radicals attacks vinyl fraction of MCSC, resulting in the formation of some active macroradicals (R_2). These free radicals reacts with MCSC or AA leads to growth of branched macroradicals (R_3 and R_4), following the network would be formed via combination of these branched macroradicals (R_2–R_5) each other.

3.2. Characterization of MCSC-g-PAA superabsorbent

3.2.1. FT-IR

The FTIR spectra of the CSC, MCSC and MCSC-g-PAA are shown in Fig. 2. As can be seen in the spectrum of CSC (Fig. 2a), a broad absorption band at 3436 cm^{-1}, due to the stretching frequency of the —OH group and a band at 2920 cm^{-1} attributable to C—H stretching vibration. The characteristic absorption bands of CSC at 1056 and 1158 cm^{-1} (stretching vibration of C—OH groups) were shifted to 1059 and 1162 cm^{-1} for MCSC. In the spectrum of MCSC (Fig. 2b) as compared to the CSC (Fig. 2a), the additional absorption bands appear at 1732(for —COOR), 1716(for —COOH) and 1635 cm^{-1} which can be ascribed to the bounds >C═O and to >C═C<, respectively, providing evidence of a modifying CSC with maleic anhydride. Compared the FTIR spectrum of MCSC-g-PAA (Fig. 2c) with MCSC (Fig. 2b), the spectrum of MCSC-g-PAA shows four new characteristic absorption bands at 1728, 1716, 1569, and 1405 cm^{-1}. These peaks attributed to carbonyl stretching of the ester and carboxylic acid groups and symmetric and asymmetric stretching modes of carboxylate groups, respectively.

3.2.2. ^1H NMR

Fig. 3 presents the comparison of the ^1H NMR spectrum of MCSC-g-PAA with the assignments of all the protons. The spectrum

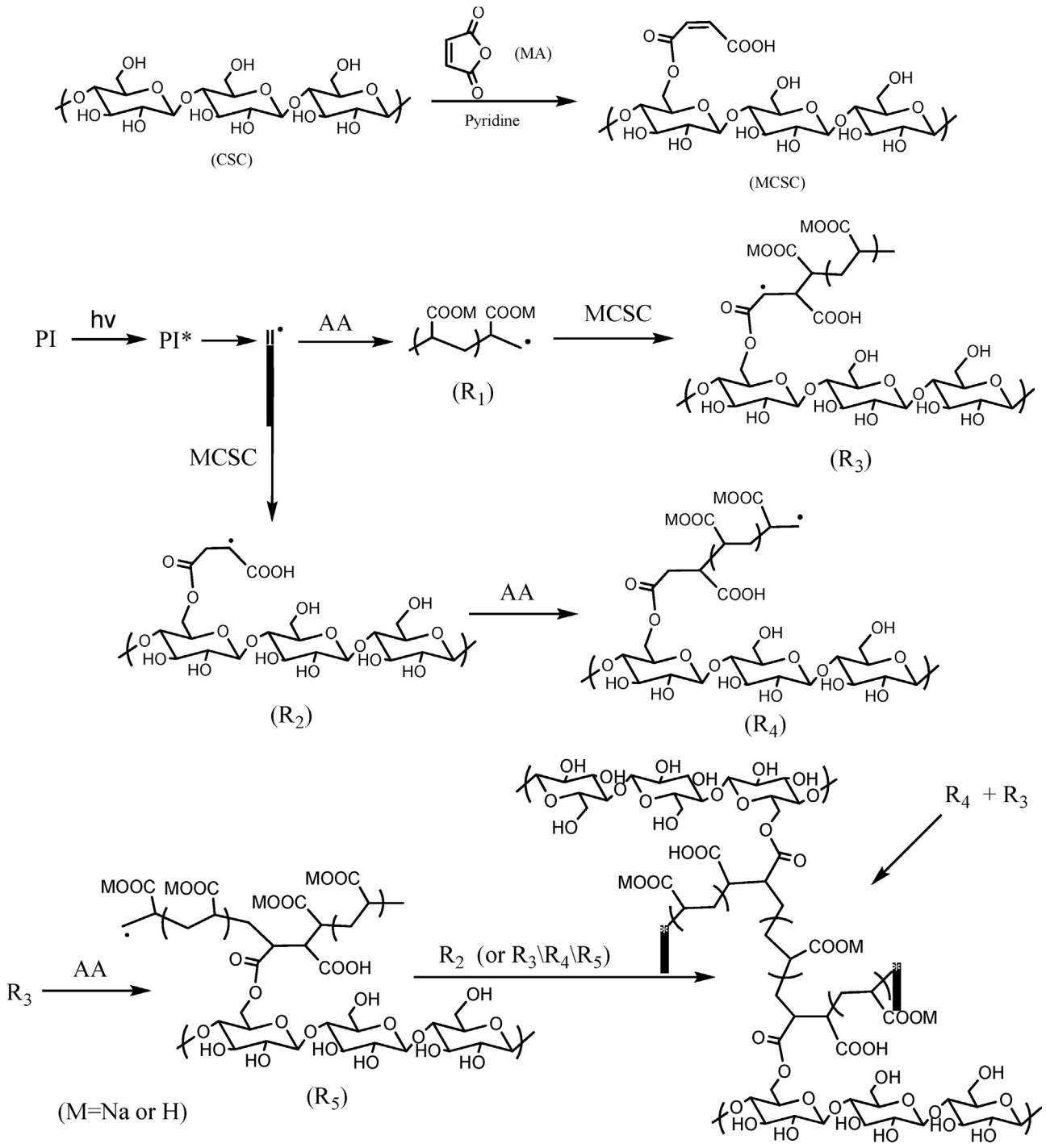

Fig. 1. Proposed mechanistic pathway for synthesis of MCSC-g-PAA superabsorbent.

(Fig. 3) showed proton peaks at the interval of δ 3.58–4.27 ppm corresponding to the protons of C2, C3, C5, C6, C4 and δ 5.28 corresponding to the proton of C1 in pyranose ring, these peaks manifested the existence of cellulose in the polymer. As depicted in the spectrum (Fig. 3) of MCSC-g-PAA, there were broad proton peaks at a range of δ 1.32–2.47 ppm corresponding to the protons of polyacrylic chains. The proton peaks appeared in the region of δ 2.70 corresponding to the protons (H^*) of —(—CO)CH^*—CH^*(COOH)— which is a bridge between polyacrylic chains and cellulose (Fig. 3). Based on the assignment of ^{1}H NMR spectra of MCSC-g-PAA, it can be concluded that AA was grafted to the cotton stalk cellulose.

3.2.3. Morphological analyses (SEM)

Fig. 4 is a SEM micrograph of CSC, MCSC and freeze dried MCSC-g-PAA superabsorbent after absorbing water. As can be seen, the surface of CSC is smooth and clean in Fig. 4a, the surface of MCSC is more irregular and rough than that of CSC as seen from Fig. 4b, which was due to the modification of cellulose with maleic anhydride. The SEM images (Fig. 4c) for the superabsorbent shows multi-layer network structure and highly porous morphology. The multi-layered gel contains many interconnected pores with irregular large size distributed in the gel, which caused the high water absorbency and swelling rate of the superabsorbent. This porous microstructure brings about an increased surface area

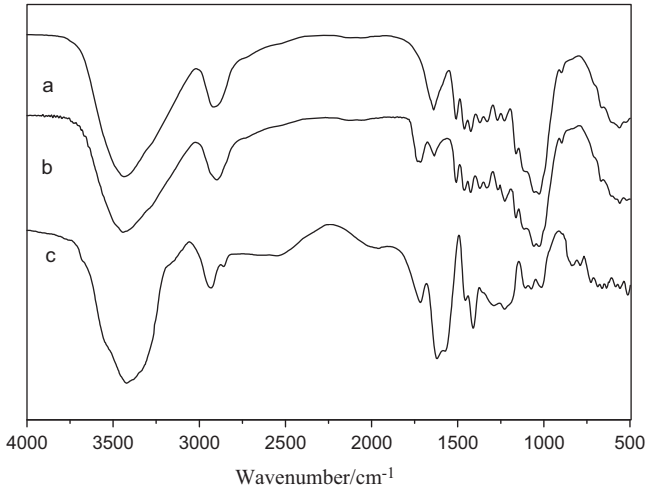

Fig. 2. FTIR spectra of (a) CSC, (b) MCSC and (c) MCSC-g-PAA.

and capillary effect which makes possible to transport the water into and through the superabsorbent polymers. The open pores in superabsorbent polymers can be small reservoirs for water storage when there is a means to transport the water into the open pores. The presence of cellulose into the gel matrix increases the amount of hydrophilic groups, which make diffusion of liquids inward the matrix easier and faster.

3.2.4. TGA analysis

The thermogravimetric analysis (TGA) of CSC, PAA and MCSC-g-PAA superabsorbent were shown in Fig. 5. It can be seen that the weight-loss rate CSC of is obviously faster than MCSC-g-PAA and PAA. At the initial stage, the weight loss about 7 wt% below 262 °C for CSC was ascribed to the loss of water, the weight loss about 5 wt% below 281 °C for PAA was ascribed to the loss of moisture present in the sample. The weight loss about 6 wt% below 273 °C for MCSC-g-PAA was ascribed to the removal of water absorbed. The rapid weight loss for CSC, from 262 to 416, reflects major thermal degradation, which is attributed to the thermal cleavage of the glucosidic units and scission of the C—O bonds. The weight loss about 9 wt% from 281 to 407 °C for PAA was attributed to the elimination of the water molecule from the two neighboring carboxylic groups of the polymer chains due to the formation of anhydride (Wang & Wang, 2010). The weight loss about 11 wt% from 273 to 396 °C for MCSC-g-PAA, was attributed to the elimination of the water molecule from the two neighboring carboxylic groups and the dehydration of saccharide rings and the breaking of C—O—C bonds in the chain of cellulose (Liu et al., 2009). The weight losses about 34 wt% from 401 to 511 °C for PAA and about 39 wt% from 396 to 518 °C for MCSC-g-PAA were due to the breakage of PAA chains and the destruction of crosslinked network structure (Liu et al., 2007). It can be concluded from the data that the total percentage weight loss of MCSC-g-PAA superabsorbent was higher than that of PAA, therefore the thermal stability of the MCSC-g-PAA superabsorbent was lower than that of PAA.

3.3. Effects of the synthesis conditions on the water absorbency and the monomer conversion in grafts

It was reported that subtle changes to the experimental conditions applied to synthesize superabsorbent polymers resulted with significant changes in the structures and the swelling properties of the materials obtained (Chen, Liu, Tan, & Jiang, 2009; Yu, Yun-fei, Huan-lin, & Hui-min, 2010). In this paper, the effects of the synthesizing conditions on the water absorption capacities of the superabsorbent polymer and the monomer conversion in grafts were investigated.

3.3.1. Influence of modification degree (or DS) of MCSC on water absorbency and the monomer conversion in grafts

Chemical modification of cotton stalk cellulose is one of the convenient ways to perform graft copolymerization by incorporating vinyl monomers onto the cellulose chain. Furthermore, the crosslinked network is essential to prepare a high performance superabsorbent polymer. Therefore, the maleyl group on the cellulose backbone lead to the crosslinking of polymer chains during UV induced graft polymerization process. In a word, MCSC plays as a crosslinker in this reaction, so both the modified degree and the amount of MCSC influence the crosslinking density and swelling properties of the superabsorbent.

The effects of DS of MCSC on the water absorbency of MCSC-g-PAA superabsorbent and the monomer conversion in grafts were summarized in Fig. 6. When CSC was used without modification (DS = 0), the gelation was mainly attributed to the UV-induced photo-crosslinking of monomer and CSC, but the crosslinking density of the polymer was insufficient to hold large amount of water, and resulting products were almost soluble homopolymer. Thereby both the water absorbency of the superabsorbent and the monomer conversion in grafts were the lowest. The maximum water absorbency (1125 g/g) was achieved at 0.067 of DS. At the lower value than this, the formation of very loosely cross

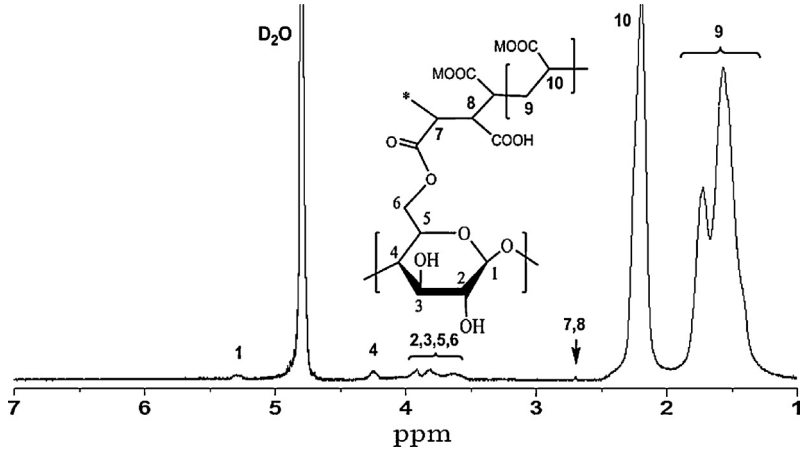

Fig. 3. ^{1}H NMR spectrum of MCSC-g-PAA.

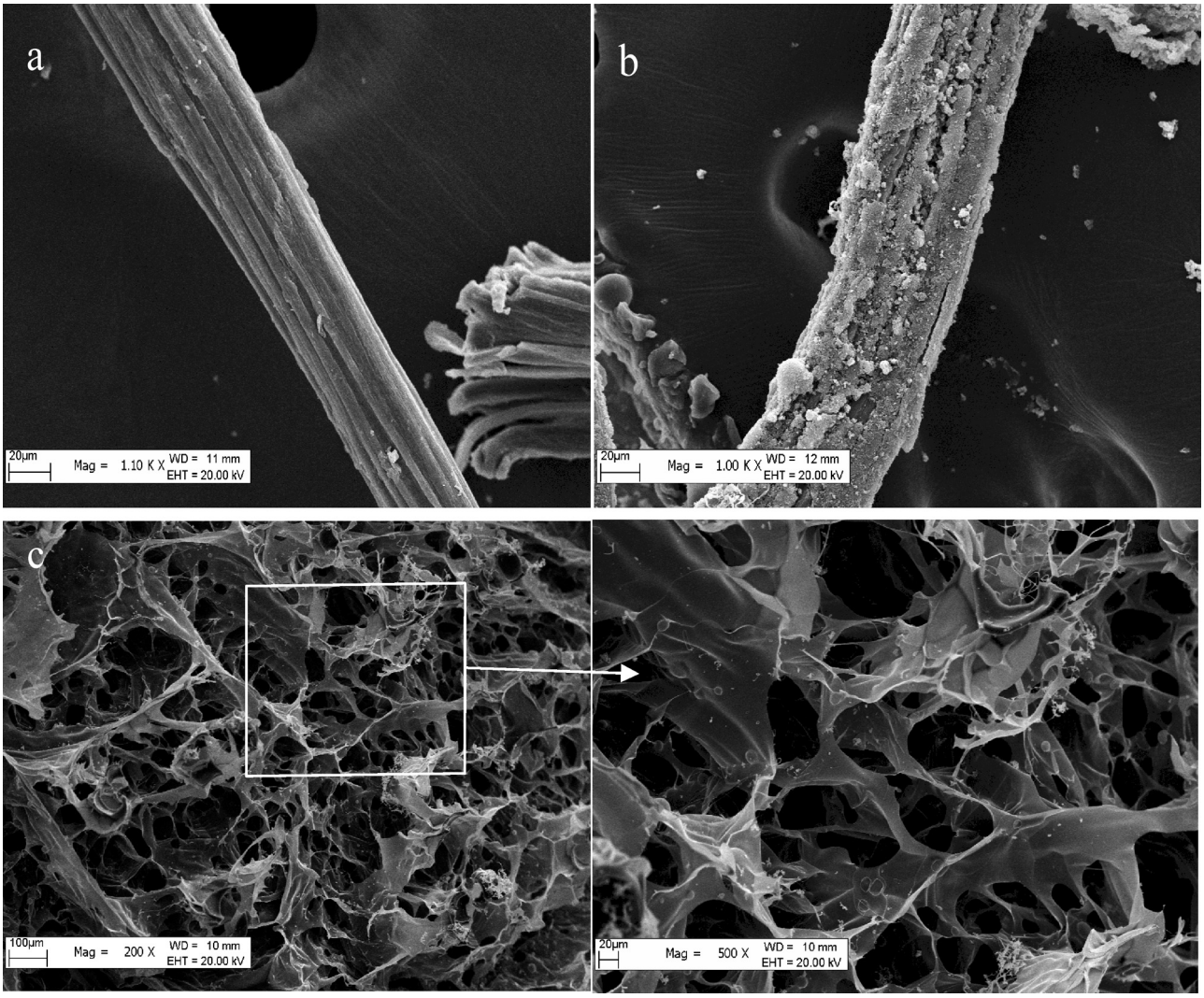

Fig. 4. SEM images of CSC, MCSC and MCSC-g-PAA superabsorbent (swollen in distilled water, then frozen in liquid nitrogen and lyophilized).

linked networks, results in poor swelling superabsorbent. Higher DS produces more cross linked points in polymeric chains and increases the extent of cross linking of the polymer network, which results in a rigid structure that cannot be expanded to hold a large quantity of water. Similar observations have been reported in the literature (Pourjavadi, Farhadpour, & Seidi, 2009). However, the monomer conversion in grafts increased gradually due to producing over crosslinked polymer.

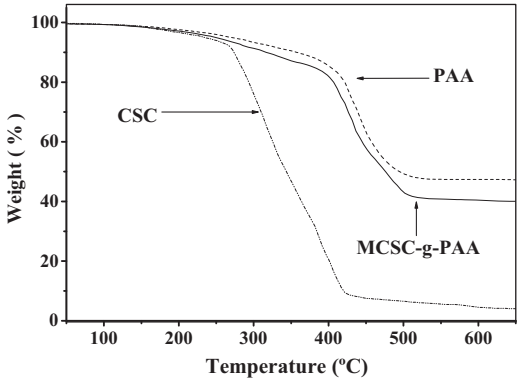

Fig. 5. Thermogravimetric analysis of CSC, PAA and MCSC-g-PAA superabsorbent.

3.3.2. *Effects of MCSC amount on water absorbency and the monomer conversion in grafts*

The effects of MCSC amount on the water absorbency of superabsorbent and the monomer conversion in grafts were studied by varying the MCSC amount from 3% to 18% (Fig. 7(a)). Fig. 7(a) shows

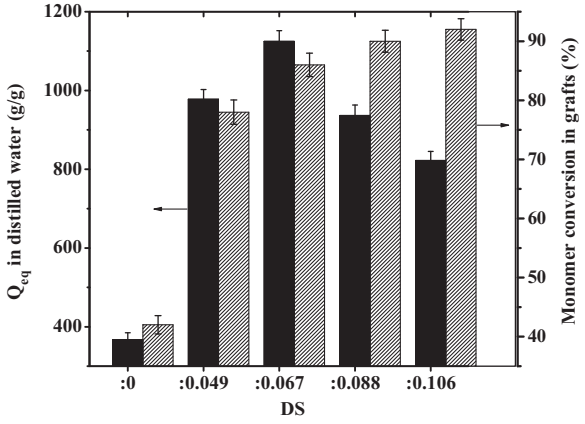

Fig. 6. Effects of modification degree of MCSC on the water absorbency of superabsorbent and the monomer conversion in grafts.

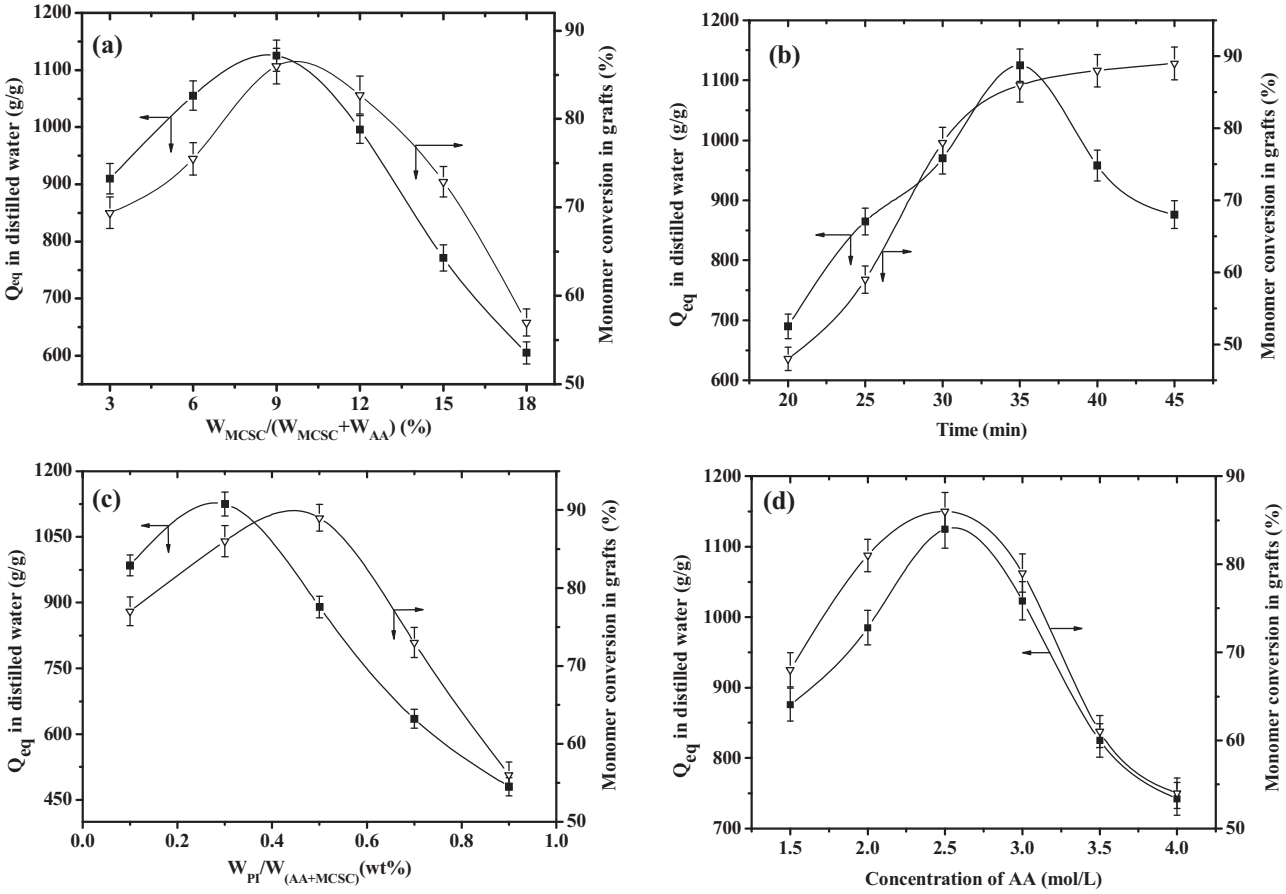

Fig. 7. Effects of (a) MCSC amount, (b) exposure time, (c) PI content and (d) monomer concentration on the water absorbency of superabsorbent and the monomer conversion in grafts.

that water absorbency of superabsorbent and the monomer conversion in grafts were increased by increasing MCSC amount up to 9% then decreased with further increase. The enhanced MCSC amount contributes to increasing of maleyl group in the mixture feed, which can react easily with monomers and induces crosslinking of the polymer chains. It can be observed that increasing MCSC amount more than 9%, the reaction medium gradually turned cloudy due to increasing of the partially insoluble agent and the penetration of the UV radiation into the layers was strongly impeded, which led to a slower graft polymerization. Consequently, both the water absorbency of superabsorbent and the monomer conversion in grafts were decreased gradually.

3.3.3. *Effect of exposure time on water absorbency*

The effects of exposure time on the monomer conversion in grafts and the water absorbency of MCSC-g-PAA superabsorbent were shown in Fig. 7(b). As can be seen, the monomer conversion in grafts increased rapidly during the early (30 min) reaction process and then increased very slowly. In contrast, the water absorbency of the superabsorbent was increased first with the exposure time, reached a maximum value at about 35 min, and then decreased at longer exposure times. When the exposure time increased, the free radicals were continuously produced, which accelerate the propagation reactions and form more three-dimensional network structure. This caused a steady rise of monomer conversion and increased the water absorbency of the polymer gradually. However, the excessive exposure time led to a increasing of crosslinking density of resultant polymer, it account for the fact that decrease of swelling capacity of the polymer with higher monomer conversion in grafts.

3.3.4. *Effect of the initiator amount on water absorbency and gel content*

The effects of the PI content on water absorbency of the superabsorbent and monomer conversion in grafts were shown in Fig. 7(c). Both the water absorbency and monomer conversion in grafts initially increased and reached the maximum at the PI contents of 0.3% and 0.5%, respectively. When PI content changed from 0.1 to 0.3%, the increase of the water absorbency and the monomer conversion in grafts attributed to the increased amount of macroradicals which accelerated consumption of monomer and formed appropriate crosslinking network structure. When PI content was 0.5%, the water absorbency of the polymer began to decrease due to excessive crosslinking but the monomer conversion in grafts reached its highest value. However, with the further increase of PI content, both of them decreased. This is because the excess PI generated more free radicals, to accelerate the chain termination reaction and led to initiate homopolymerization rather than grafting reaction.

3.3.5. *Effect of the monomer concentration on water absorbency*

The effects of monomer concentration on the monomer conversion in grafts and the water absorption capacities of MCSC-g-PAA superabsorbent were shown in Fig. 7(d). As can be seen, the monomer conversion in grafts and the water absorbency initially increased, and reached the maximum value when the monomer concentration was 2.5 mol L^{-1}. Apparently, the increased monomer concentration promoted the propagation step, and thus

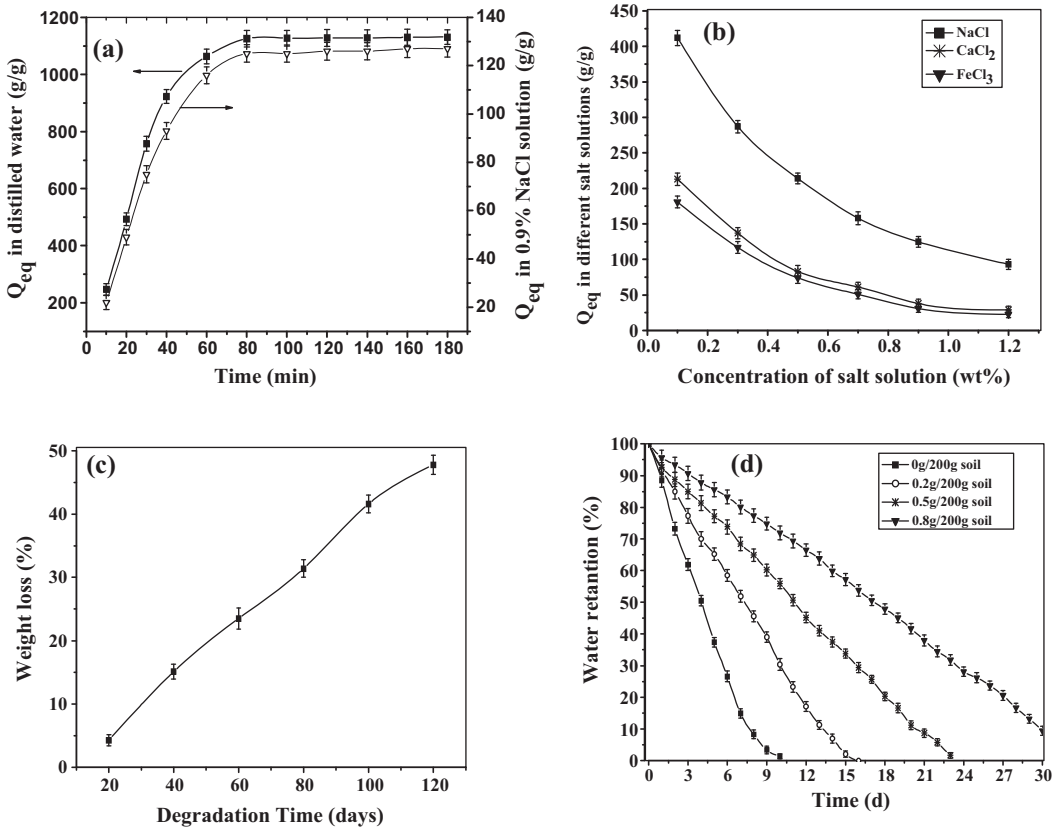

Fig. 8. Properties of the superabsorbent polymer (a) swelling kinetics in distilled water and 0.9% NaCl solution, (b) water absorbency in different salt solutions, (c) soil burial degradation, (d) water retention capacity in soil.

the monomer conversions in grafts, which contribute to the higher swelling property of the polymer. However, the monomer conversions and the water absorbency considerably decreased with the further increased monomer concentration. This result is ascribed to preferential homopolymerization rather than graft copolymerization, and to the enhanced chance of chain transfer to the monomer molecules (Pourjavadi, Soleyman, & Barajee, 2008). Another explanation is that the viscosity of the reaction medium not only increased with increasing monomer concentration, but also increased during the polymerization process. The increasing viscosity probably affected the mobility of the copolymer–monomer mixture which leading to a prematurely end of the radical growing polymerization.

3.4. Swelling properties of the superabsorbent polymer

3.4.1. Swelling kinetics of the superabsorbent

Fig. 8(a) represented absorption kinetics in distilled water and 0.9% NaCl solution for MCSC-PAA superabsorbent. Initially, the swelling rate sharply increased and then begins to level off. The equilibrium swelling was achieved after 30 min. There was a quick increase in the swelling rate during the first 1 h of immersion, reaching about 95% of the equilibrium value in this time range, followed by a slower process until the equilibrium was approximately reached at around 80 min. The same trend displayed in 0.9 wt% NaCl solution. The equilibrium water absorbency of the obtained sample was 1125 g/g in distilled water and 126 g/g in 0.9 wt% NaCl solution, respectively.

3.4.2. Water absorbency in different salt solutions

The characteristics of external solution such as salt concentration, cation type and charge valencies greatly influence the swelling behavior of the superabsorbent. The effects of salt solution concentration and cation type (cations with different charge) on swelling behavior of the polymer were shown in Fig. 8(b). With the increase of saline solution concentration, the water absorbency of the superabsorbent was significantly decreased. This result is ascribed to the reduced osmotic pressure difference between polymeric network and external saline solution decreased. In the case of salt solutions with multivalent cations, water absorbency of the samples decreased with the increased cationic charge (univalent > divalent > trivalent) at the same salt solution concentration. This finding may be attributed to the divalent and trivalent ions could form complexes (produce ionic crosslinking) with carboxylate groups on the polymer chains. Consequently, the network crosslink density is enhanced. With increasing the charge of these cations, the degree of crosslinking is increased. As a result, swelling capacity is decreased considerably ($NaCl > CaCl_2 > FeCl_3$).

3.4.3. Soil burial degradation

The biodegradability of MCSC-PAA superabsorbent for different time period was shown in Fig. 8(c). As can be seen, the weight loss of the sample increased with the increasing of degradation time and then the weight loss of the sample in soil was 46.7% after 150 days. As a result, the superabsorbent polymer prepared in this work proved to have good biodegradability.

3.4.4. Water retention in soil

Superabsorbent have effectively been used as a soil amendment in agricultural and horticultural applications to improve the physical properties of soil in view of increasing their water-holding capacity of soil (Zohuriaan-Mehr et al., 2010). It can increase seedling survival rates and accelerate plant growth. The water

retention capacity of the superabsorbent in soil at different dosages was shown in Fig. 8(d). The water reduction rate of the soil mixed with the MCSC-g-PAA superabsorbent is obviously slower compared with that without the superabsorbent. The soil without the superabsorbent loses all of the absorbed water after 11 days, whereas the water retention rate of the soil dosed with 0.2, 0.5, 0.8 g superabsorbent per 200 g soil were 23.3 wt%, 50.7 wt%, and 69.4 wt%, and the water retention period of these samples can be prolonged to 16, 24 and 30 days, respectively. When 0.8 g of superabsorbent per 200 g soil was utilized, 9.5% of the initial absorbed water can still remain after 30 days. Therefore, the use of MCSC-g-PAA in soil obviously improves its water retention capability.

4. Conclusions

A novel biodegradable MCSC-g-PAA superabsorbent polymer has been successfully synthesized by means of UV photopolymerization as a clean and environment friendly source of initiation, and using biodegradable MCSC as crosslinker. The optimal synthesis parameters were 0.067 DS, 9%wt MCSC, 0.3% initiator to (AA + MCSC) mass ratio, 2.5 mol L^{-1} monomer concentration, and 35 min expose time. The maximum water absorbency was 1125 g/g distilled water and 126 g/g 0.9 wt% aqueous NaCl solution with 86% of monomer conversion in grafts. Owing to the considerable water absorbency, salt resistance, biodegradability and water retention capacity of the prepared novel superabsorbent, it might be considered as an excellent candidate for agricultural field.

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