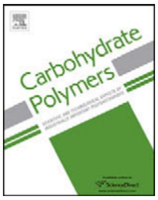
Carbohydrate Polymers 88 (2012) 589–595

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Swelling behaviors of organic/inorganic composites based on various cellulose derivatives and inorganic particles

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ARTICLE INFO

Article history:
Received 14 November 2011
Received in revised form
25 December 2011
Accepted 1 January 2012
Available online 8 January 2012

Keywords:
Superabsorbent composites
Cellulose derivatives
Various inorganic particles
Water absorbency
Swelling rate

ABSTRACT

A series of cellulose/acrylic polymer/inorganic particle superabsorbent composites were prepared by graft copolymerization of acrylic monomer onto various cellulose derivatives and inorganic particles. The effects of cellulose derivatives and inorganic particles on equilibrium water absorbency and swelling rate of these superabsorbent composites were investigated. For the composites incorporated with different cellulose derivatives, equilibrium water absorbency and the swelling rate in distilled water and saline solution are always in the order carboxymethyl cellulose > without cellulose > hydroxypropyl methyl cellulose > methyl cellulose > hydroxyethyl cellulose. Silicon dioxide (SiO_2) and titanium dioxide (TiO_2) based superabsorbent composites acquired the equilibrium water absorbency in distilled water as good as that of montmorillonite (MMT) based one and prior to that without inorganic particle. However, the equilibrium water absorbency of SiO_2 and TiO_2 based superabsorbent composites in saline solution are similar to that of zinc oxide (ZnO) and aluminum oxide (Al_2O_3) based ones.

1. Introduction

Superabsorbents are moderately crosslinked hydrophilic polymer networks that can absorb and retain large quantities of aqueous fluids even under certain pressure (Chen, Liu, Tang, & Tan, 2010; Gao et al., 2008; Kuang, Yuk, & Huh, 2011). Due to their excellent properties, superabsorbents are used for many applications including agriculture (Liang, Liu, & Wu, 2007; Liang, Yuan, Xi, & Zhou, 2009; Zhang, Li, & Wang, 2006), horticulture, hygienic products (Kosemund et al., 2009), wastewater treatment (Kasgoz, Durmus, & Kasgoz, 2008; Kundakci, Uzum, & Karadag, 2008; Wang, Zhang, & Wang, 2008) and drug delivery (Wang, Zhang, & Wang, 2009; Wu et al., 2008), etc. However, commercial superabsorbents are almost confined to crosslinked poly(acrylic acid) with high production cost and serious environment impact (Sinan, Baris Er Goknur, Serkan, Yusuf, & Niyazi, 2009; Wang & Wang, 2010).

Cellulose is a most abundant natural polymer, exhibiting several favorable properties, including good biodegradability, biocompatibility, low cost and low toxicity. Hence, it is an important raw material for many industries (Abd El-Mohdy, 2007; Chang & Zhang, 2011). Cellulose derivatives have many different functional groups and higher solubility in water. The biodegradability and swelling properties of superabsorbent may be improved if cellulose derivatives are introduced. So the application of cellulose derivatives in superabsorbent fields becomes attractive and promising.

In recent years, polymeric–inorganic hybrid materials have attracted increasing attention due to potential applications in electric, optical, magnetic, and biological, etc. fields. Introduction of inorganic into superabsorbent polymer networks is an effective way to develop materials with good functions. In many previous studies, montmorillonite (Mansoori, Atghia, Zamanloo, Imanzadeh, & Sirousazar, 2010), kaolin (Pourjavadi, Ayyari, & Amini-Fazl, 2008), attapulgite (Zhang, Wang, & Wang, 2007), and vermiculite (Zheng, Li, Zhang, & Wang, 2007) have all been used to fabricate superabsorbent composites. The incorporation of these mineral powders can not only reduce production cost, but also improve swelling ability, gel strength, mechanical, and thermal stability of corresponding superabsorbent composites.

The organic–inorganic superabosorbent composites with cellulose derivatives and inorganic undoubtedly become promising materials because they showed both excellent performance and environmental friendly characteristics. However, most of the literatures about this research report on carboxymethyl cellulose based superabsorbent and polymer-clays superabsorbent. Little information can be found about other cellulose derivative and inorganic particle until now.

The present work aims to develop different cellulose/acrylic polymer/inorganic particle superabsorbent composites by varying cellulose derivatives and inorganic particles for obtaining higher

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doi:10.1016/j.carbpol.2012.01.003

swelling properties and to study the effects of cellulose derivatives and inorganic particles on equilibrium water absorbency and swelling rate.

2. Experimental

2.1. Materials

Acrylic acid (AA), acrylamide (AM), potassium persulfate (KPS), carboxymethyl cellulose, hydroxypropyl methyl cellulose, methyl cellulose and hydroxyethyl cellulose were purchased from Tianjin Chemicals. 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) supplied by Allplus Chemicals Limited, Nanjing. *N*,*N*′-methylenebisacrylamide (MBA) was bought from Aoran Chemicals, Tianjin. Montmorillonite (MMT) was provided by Qing-he Chemical Factory, Zhangjiakou. Silicon dioxide (SiO_2), titanium dioxide (TiO_2), zinc oxide (ZnO) and aluminum oxide (Al_2O_3) were supplied by Taijihuan Nano Products Limited, Qinhuangdao.

2.2. Preparation of cellulose/acrylic polymer/inorganic particle superabsorbent composites

Cellulose solution has been prepared by slow addition of 1 g cellulose powder to 80 mL distilled water in a 250-mL three-necked flask equipped with a mechanical stirrer, a reflux condenser and a thermometer. Then 0.45 g inorganic particle was added under continuous stirring to form a uniform sticky solution. The solution was heated to 60 °C. The initiator KPS (0.16 g) was added and kept at 60 °C for 10 min to generate radicals. After cooling the reactants to 40 °C, the mixture of 1.17 g AA, 3.46 g AM, 3.37 g AMPS and 0.04 g MBA was added to the flask. The pH was adjusted by NaOH solution. The temperature was risen to 70 °C and maintained for 2 h to complete reaction. The obtained products have been precipitated by pouring it into the water/methanol mixture (ratio 1:5). The precipitate of graft copolymer has been separated, dried and weighed.

2.3. Measurement of equilibrium water absorbency and swelling rate

The pre weighted dry superabsorbent composite was immersed in excessive distilled water or saline solution (0.9 wt% NaCl solution) and kept undisturbed for 10 h at room temperature until equilibrium swelling was reached. The swollen superabsorbent composite was filtered using a 100-mesh sieve and drained for 20 min until no free water remained. After weighing the swollen superabsorbent composite, the equilibrium water absorption can be calculated using the following equation:

$$Q_{eq} = \frac{w_2 - w_1}{w_1} \qquad (1)$$

where Q_{eq} is the equilibrium water absorption defined as grams of water per gram of sample; w_1 and w_2 are the mass of sample before and after swelling, respectively.

Swelling rate of the superabsorbent composite was measured according to the following process. The pre weighted superabsorbent composite was poured into excessive distilled water or saline solution (0.9 wt% NaCl solution) at room temperature. At certain time intervals, the water absorbency of the superabsorbent composite was measured according to Eq. (1). The measurement condition is the same as that for equilibrium water absorbency.

3. Results and discussion

3.1. Effects of cellulose on equilibrium water absorbency

Superabsorbent is three-dimensional networks of hydrophilic polymers connected by chemical and/or physical crosslinking. Superabsorbent can be prepared with different functional groups such as carboxylic acid, amine, hydroxyl, amide and sulfonic acid groups (Bao, Ma, & Li, 2011; Zheng, Hua, & Wang, 2010). When a superabsorbent is placed in water, the water diffuses into the polymer matrix, thus causing it to swell. This diffusion process involves migration of water into pre-existing or dynamically formed spaces between macromolecular chains. The functional groups attached along the macromolecular chains ionize completely to give fixed charges along the polymeric chains and free counter ions within the gel phase. The free counter ions remain inside the gel to neutralize the fixed charges on the network chains. So, the presence of charges in the superabsorbent structure causes an osmotic pressure difference between the gel and the water phase. This pressure difference produces a strong driving force to diffuse water to the gel phase. The diffusion process continues until the osmotic pressure difference becomes zero (Pourjavadi et al., 2008). The higher concentration of free counter ions within the gel makes the osmotic swelling pressure appreciably high, thus resulting in a very high degree of swelling of superabsorbent. In addition to this, the electrostatic repulsion among similarly charged groups fixed along the polymeric chains also causes an extensive chain relaxation process within the network. Hence, superabsorbent can incorporate and retain large amounts of water. According to the water absorbing mechanism of superabsorbent, the absorbency is closely related to the functional groups in superabsorbent chains.

Fig. 1 presents the variation of equilibrium water absorbency for cellulose/acrylic polymer/inorganic particle superabsorbent composites incorporated with the same content of different cellulose derivatives in distilled water and saline solution. The inorganic particle used in these experiments is MMT. It can be seen that equilibrium water absorbency in distilled water and saline solution are always in the order carboxymethyl cellulose > without cellulose > hydroxypropyl methyl cellulose > methyl cellulose > hydroxyethyl cellulose (the structures of different cellulose derivatives are seen in Fig. 2). This may be because carboxyl group is anion hydrophilic group which can be ionized. The polymeric network tends to swell and the space for absorbing and holding water increases due to anion–anion electrostatic repulsion. Hence, the equilibrium water absorbency of superabsorbent composite incorporated with carboxymethyl cellulose is the biggest. Hydroxyl group is also hydrophilic group, but its hydrophilicity is smaller than carboxyl group. On the other hand, hydroxyl group cannot be ionized. So the electrostatic repulsion of polymeric chains is smaller. The polymeric network is less influenced. The equilibrium water absorbency of superabsorbent composite incorporated with cellulose containing hydroxyl group is smaller than that incorporated with carboxymethyl cellulose. The rigidity of methyl group has stereo-hindrance effect for free rotation of polymeric chains and makes the structure of polymeric network to fix. The extra intermolecular hydrophobic interaction of the methyl can further strengthen the polymeric network, inducing formation of more stable superabsorbent composite (Li et al., 2006; Li, Li, Zhou, Ni, & Leong, 2001). From the testing result, it is concluded that the influence of methyl group on the water absorbency of superabsorbent composite is more than hydroxyl group. Because cellulose is introduced in the initial polymerization, the radicals supplied by decomposition of initiator can extract hydrogen from the hydroxyl group of cellulose to form alkoxy radicals on the substrate. The monomer molecules, which are in close vicinity of the reaction sites, become acceptor of cellulose radicals resulting in chain initiation and

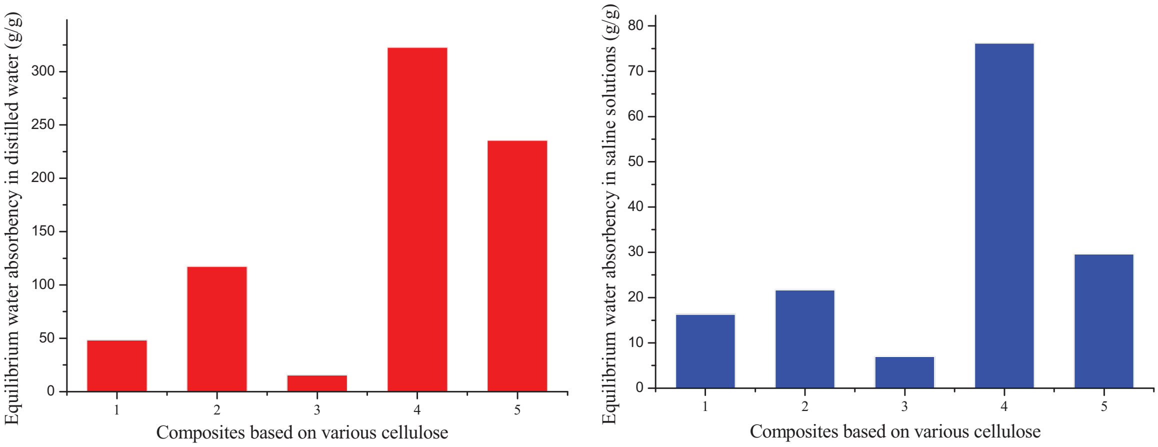


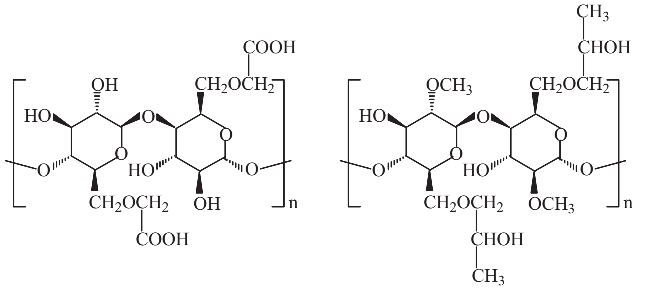
Fig. 1. The equilibrium water absorbency of superabsorbent composites based on MMT and various cellulose derivatives in distilled water and saline solution (1 – methyl cellulose, 2 – hydroxypropyl methyl cellulose, 3 – hydroxyethyl cellulose, 4 – carboxymethyl cellulose, 5 – without cellulose).

thereafter themselves become free radical donor to neighboring molecules. In this way grafted chain grows on the cellulose. Hence, cellulose plays the crosslinker role in the polymerization system of superabsorbent composites. According to the literature (Chen, Liu, Tan, & Jiang, 2009), when the crosslinking density is high, the equilibrium swelling ratio is decreased. This explains why the equilibrium water absorbency of superabsorbent composite without cellulose is bigger than those incorporated with hydroxypropyl methyl cellulose, methyl cellulose and hydroxyethyl cellulose.

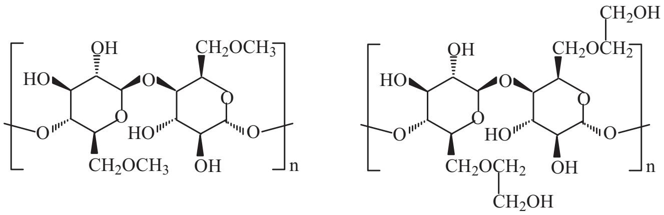
It can also be seen from Fig. 1 that the absorbency for these superabsorbent composites in saline solution are less than in distilled water. The reason for this phenomenon is the osmotic pressure difference is reduced in salt solutions, which leads to less swelling in comparison with distilled water.

3.2. *Effects of cellulose on swelling rate*

In practical applications, not only is a higher swelling capacity required, but also a higher swelling rate is needed. Swelling rate of superabsorbent is mainly determined by factors such as swelling ability, surface area, particle size and composition of the polymer (Pourjavadi & Salimi, 2008; Zhang & Wang, 2007). Fig. 3 shows swelling rate of the cellulose/acrylic polymer/inorganic particle superabsorbent composites doped with different types of cellulose derivatives in distilled water and saline solution. The swelling increases with time, but with further increase in time reaches a limiting value which is the equilibrium value. It was found that superabsorbent composites containing methyl cellulose, hydroxypropyl methyl cellulose and hydroxyethyl cellulose need about 300 min and 150 min to reach equilibrium water absorbency in distilled water and saline solution, respectively, which is similar to the swelling tendency of superabsorbent composite without cellulose. However, the superabsorbent composite incorporated with carboxymethyl cellulose need 400 min and 100 min to reach equilibrium water absorbency in distilled water and saline solution, respectively. The swelling rate increases in the order carboxymethyl cellulose > without cellulose > hydroxypropyl methyl cellulose > methyl cellulose > hydroxyethyl cellulose. The phenomena above may be attributed to the higher osmotic swelling pressure and chain relaxation process of carboxymethyl cellulose than other cellulose. Compared with superabsorbent composite without cellulose, the crosslinking density of superabsorbent composite containing cellulose has slightly increase due to a little dosage of cellulose. But the influence of osmotic swelling pressure on swelling capacity is significant. Hence, the swelling rate of superabsorbent composite incorporated with carboxymethyl cellulose is bigger than that without cellulose. It can also be seen that the superabsorbent composites swell faster at the first, and then the swelling rate decreases. When $Q_t/Q_{eq} < 0.60$, osmotic pressure and chain relaxation are responsible for the higher swelling rate, however, the swelling of the superabsorbent composites is only dominated by relaxation of the polymer chains when $Q_t/Q_{eq} > 0.60$, and then the swelling rate decreases. This result is in accord with Bajpai's study in the poly(acrylamide-co-sodium acrylate) system (Bajpai & Johnson, 2005).



Carboxymethyl cellulose Hydroxypropyl methyl cellulose



Methyl cellulose Hydroxyethyl cellulose

Fig. 2. The structures of cellulose derivatives.

3.3. *Effects of inorganic particle on equilibrium water absorbency*

Inorganic particle plays an important part in influencing properties of superabsorbent composite, since it is the reaction between inorganic particle and monomer that forms superabsorbent composite polymeric network. In this section, five kinds of inorganic particles are introduced into the polymeric network, respectively, to investigate the effect of inorganic particles type on equilibrium water absorbency of the superabsorbent composites. The cellulose derivative used in these experiments is carboxymethyl cellulose. Fig. 4 presents the variation of equilibrium water absorbency for

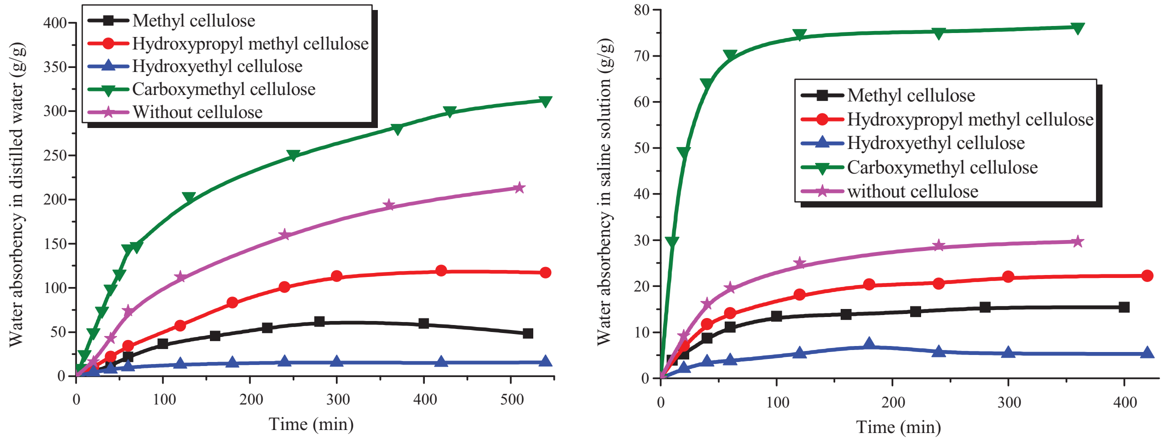


Fig. 3. The swelling rate of superabsorbent composites based on MMT and various cellulose derivatives in distilled water and saline solution.

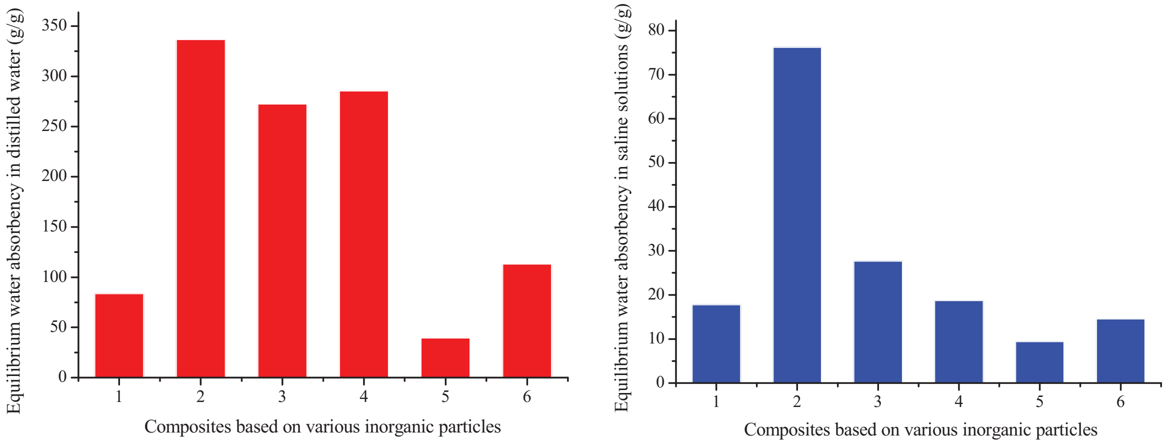


Fig. 4. The equilibrium water absorbency of superabsorbent composites based on carboxymethyl cellulose and various inorganic particles in distilled water and saline solution (1 – Al_2O_3, 2 – MMT, 3 – SiO_2, 4 – TiO_2, 5 – ZnO, 6 – without inorganic particle).

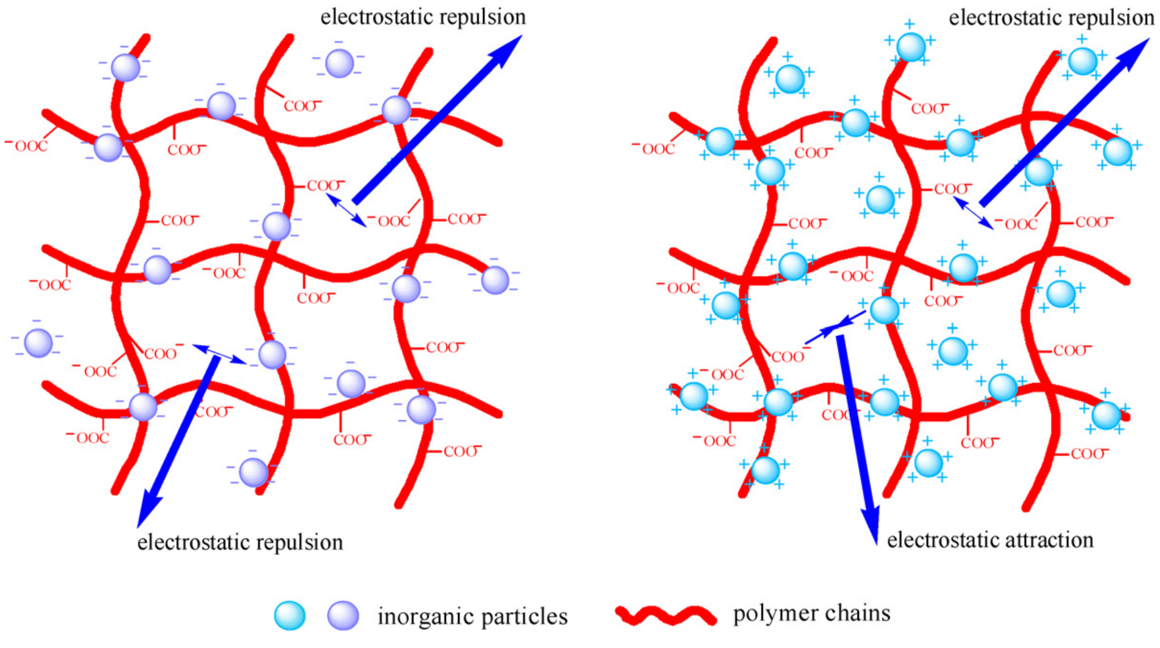


Fig. 5. The diagram of charging effect in superabsorbent composite.

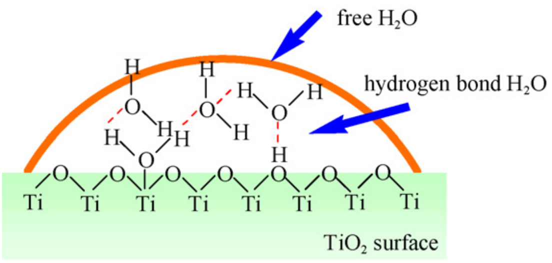


Fig. 6. Structural model of H_2O cluster adsorbed on the inorganic particles surface (taking TiO_2 as an example).

the superabsorbent composites in distilled water and saline solution with inorganic particles type. Equilibrium water absorbency in distilled water for superabsorbent composites is in the order MMT > TiO_2 > SiO_2 > without inorganic particle > Al_2O_3 > ZnO. But equilibrium water absorbency in saline solution for superabsorbent composites is in the order MMT > SiO_2 > TiO_2 > without inorganic particle ≈ Al_2O_3 > ZnO.

Among the inorganic particles selected in this study, montmorillonite belongs to the family of 2:1 layered silicate (Suprakas & Masami, 2003). Their crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+}, or Mg^{2+} replaced by Li^{1+}) generates negative charges that are counterbalanced by alkali and alkaline earth cations situated inside the galleries. As a result, montmorillonite has the high osmotic swelling pressure and chain relaxation process in water. It exhibits good hydration and distension. According to the literatures, the isoelectric points (IEP) of SiO_2 and TiO_2 are 2.5 (Lee, Kong, Kim, & Kim, 2007; Mohan et al., 2007) and 5.6–6.4 (Lenka et al., 2008; Zhang, Shi, Yuan, Zhao, & Fang, 2009), respectively. So the surface of SiO_2 and TiO_2 are negatively charged. The electronegativity of superabsorbent composite was strengthened and the electrostatic repulsion of polymeric chains was increased when SiO_2 and TiO_2 were introduced, respectively, into the polymer matrix. However, the IEP of ZnO and Al_2O_3 are 8.95 (Zygmunt & Izabela, 2004) and 8.5 (Mohan et al., 2007), respectively. ZnO and Al_2O_3 are positively charged. The electronegativity of superabsorbent composite was weaken after introducing ZnO and Al_2O_3 leading to the electrostatic repulsion of polymeric chains decreasing (seen in Fig. 5). Therefore, the water absorbency of superabsorbent composites containing SiO_2 and TiO_2 were bigger than that without inorganic particle, but those containing ZnO and Al_2O_3 were smaller.

It is reported that the structural model of H_2O cluster adsorbed on the inorganic particles surface is seen in Fig. 6 (Takeuchi, Martra, Coluccia, & Anpo, 2005). The H_2O molecules, which directly interact with surface cations or surface hydroxyls of the inorganic particles, form a monolayer as chemisorbed H_2O molecules and then the hydrogen-bonded H_2O molecules form multilayers as physisorbed H_2O molecules. Finally, H_2O molecules without active hydrogen bonds cover the polymeric chained H_2O molecules to form the outermost shell of the H_2O cluster. These polymeric chained H_2O molecules are called “hydrogen-bonded water”, while on the other hand, the hydrogen-bond-free H_2O molecules in the outermost shell are called “free water”. The number of surface cations and surface hydroxyls vary with different inorganic particles. Therefore, this is also one of the reasons for water absorbency differences of superabsorbent composites containing various inorganic particles.

The water absorbency in distilled water of superabsorbent composite containing TiO_2 was bigger than SiO_2. This may be because the number of surface cations and surface hydroxyls on TiO_2 is much more than SiO_2. The influence of inorganic particles adsorbed water on the water absorbency of superabsorbent composite plays a dominant role, compared with the influence of IEP. However, the most surface cations on TiO_2 are masked by chloride ions in saline solution. The surface adsorbed water on TiO_2 reduced. As a result, the water absorbency in saline solution for superabsorbent composite containing TiO_2 was smaller than SiO_2.

3.4. *Effects of inorganic particle on swelling rate*

The swelling kinetics of superabsorbent composites with different inorganic particles in distilled water and saline solution were also investigated (Fig. 7). It can be seen that the swelling rate of superabsorbent composites sharply increases and then begins to level off. Additionally, the swelling rate in distilled water increases in the order MMT > TiO_2 > SiO_2 > without inorganic particle > Al_2O_3 > ZnO. However, the swelling rate in saline solution increases in the order MMT > SiO_2 > TiO_2 ≈ without inorganic particle ≈ Al_2O_3 > ZnO. These behaviors are because the IEP and the number of surface hydroxyls vary with different inorganic particles, which allow the osmotic swelling pressure and chain relaxation of superabsorbent composites to change in different degree. These results indicated that the type of inorganic particles introduced has some influence on swelling kinetics of corresponding superabsorbent composite.

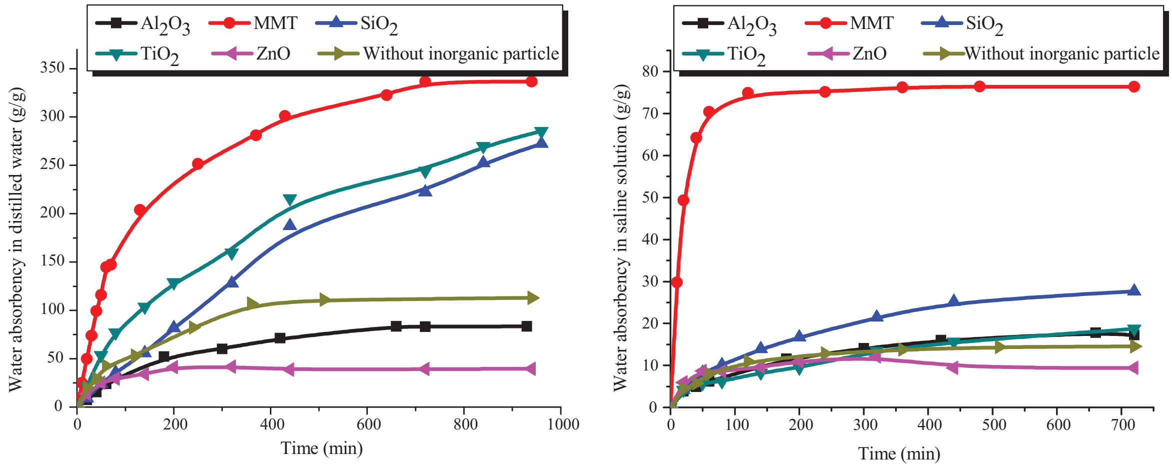


Fig. 7. The swelling rate of superabsorbent composites based on carboxymethyl cellulose and various inorganic particles in distilled water and saline solution.

4. Conclusions

Cellulose/acrylic polymer/inorganic particle superabsorbent composites were synthesized by free-radical graft copolymerization. The effects of cellulose derivates and inorganic particles on swelling properties of the cellulose/acrylic polymer/inorganic particle superabsorbent composites were investigated. For the superabsorbent composites incorporated with different cellulose, equilibrium water absorbency and the swelling rate in distilled water and saline solution are always in the order carboxymethyl cellulose > without cellulose > hydroxypropyl methyl cellulose > methyl cellulose > hydroxyethyl cellulose. It reveals that the influence of functional group on swelling properties is great. The swelling properties of superabsorbent composites are related to not only the hydrophilicity of functional group but also the rigidity of functional group. The type of inorganic particles also has great effect on equilibrium water absorbency and swelling rate, which may be related to the IEP and the number of surface hydroxyls of inorganic particle incorporated. In addition, the superabsorbent composites incorporated with different inorganic particles exhibit their own advantages. For example, SiO_2 and TiO_2 based superabsorbent composites acquired the equilibrium water absorbency in distilled water as good as that of MMT based one. However, the equilibrium water absorbency of SiO_2 and TiO_2 based superabsorbent composites in saline solution are similar to that of ZnO and Al_2O_3 based ones. There are synergetic effect between cellulose derivatives and inorganic particles in superabsorbent composites. The cellulose/acrylic polymer/inorganic particle superabsorbent composites can meet practical applications by adjusting the type of cellulose derivatives and inorganic particles. If we want to obtain a superabsorbent composite with low water absorbency, inorganic particle with high IEP (such as ZnO or Al_2O_3) and cellulose derivative with hydroxyl group (such as hydroxyethyl cellulose) can be selected in designing superabsorbent composites. However, inorganic particle with low IEP (MMT, SiO_2 or TiO_2) and cellulose derivative with carboxyl group (carboxymethyl cellulose) can be used, when we expect to get a superabsorbent composite with high water absorbency. Moreover, the cellulose/acrylic polymer/inorganic particle superabsorbent composites can reduce the excessive consumption of petroleum resource and minimize the pollution resulting from the industrial polymers. This study may provide some suggestions for the superabsorbent composites field.

Acknowledgements

Thanks for the supports from National Nature Science Foundation of China (Nos.: 21006061, 51073091), 973 Program (No.: 2011CB612309), Scientific Research Plan of Shaanxi Province (No.: 2011kjxx01), Key Academic Incubation Program of Shaanxi University of Science and Technology (No.: XSG2010007) and Scientific Research Group of Shaanxi University of Science and Technology (No.: TD09-03).

References

Abd El-Mohdy, H. L. (2007). Water sorption behavior of CMC/PAM hydrogels prepared by γ-irradiation and release of potassium nitrate as agrochemical. *Reactive & Functional Polymers*, *67*, 1094–1102.

Bajpai, S. K., & Johnson, S. (2005). Superabsorbent hydrogels for removal of divalent toxic ions. Part I: Synthesis and swelling characterization. *Reactive & Functional Polymers*, *62*, 271–283.

Bao, Y., Ma, J. Z., & Li, N. (2011). Synthesis and swelling behaviors of sodium carboxymethyl cellulose-g-poly (AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel. *Carbohydrate Polymers*, *84*, 76–82.

Chang, C. Y., & Zhang, L. N. (2011). Cellulose-based hydrogels: Present status and application prospects. *Carbohydrate Polymers*, *84*, 40–53.

Chen, Y., Liu, Y. F., Tan, H. M., & Jiang, J. X. (2009). Synthesis and characterization of a novel superabsorbent polymer of *N*,*O*-carboxymethyl chitosan graft copolymerized with vinyl monomers. *Carbohydrate Polymers*, *75*, 287–292.

Chen, Y., Liu, Y. F., Tang, H. L., & Tan, H. M. (2010). Study of carboxymethyl chitosan based polyampholyte superabsorbent polymer I: Optimization of synthesis conditions and pH sensitive property study of carboxymethyl chitosan-*g*-poly(acrylic acid-co-dimethyldiallylammonium chloride) superabsorbent polymer. *Carbohydrate Polymers*, *81*, 365–371.

Gao, J. Z., Wang, A. X., Li, Y., Fu, Y., Wu, J. L., Wang, Y. D., et al. (2008). Synthesis and characterization of superabsorbent composite by using glow discharge electrolysis plasma. *Reactive & Functional Polymers*, *68*, 1377–1383.

Kasgoz, H., Durmus, A., & Kasgoz, A. (2008). Enhanced swelling and adsorption properties of AAm-AMPSNa/clay hydrogel nanocomposites for heavy metal ion removal. *Polymers for Advanced Technologies*, *19*, 213–220.

Kosemund, K., Schlatter, H., Ochsenhirt, J. L., Krause, E. L., Marsman, D. S., & Erasala, G. N. (2009). Safety evaluation of superabsorbent baby diapers. *Regulatory Toxicology and Pharmacology*, *53*, 81–89.

Kuang, J., Yuk, K. Y., & Huh, K. M. (2011). Polysaccharide-based superporous hydrogels with fast swelling and superabsorbent properties. *Carbohydrate Polymers*, *83*, 284–290.

Kundakci, S., Uzum, O. B., & Karadag, E. (2008). Swelling and dye sorption studies of acrylamide/2-acrylamido-2-methyl-1-propanesulfonic acid/bentonite highly swollen composite hydrogels. *Reactive & Functional Polymers*, *68*, 458–473.

Lee, J. W., Kong, S., Kim, W. S., & Kim, J. (2007). Preparation and characterization of SiO_2/TiO_2 core–shell particles with controlled shell thickness. *Materials Chemistry and Physics*, *106*, 39–44.

Lenka, S. S. C., Catherine, S., Simonnot, M. O., Michel, S., Manuel, D., & Florence, M. B. (2008). Comparison between batch and column experiments to determine the surface charge properties of rutile TiO_2 powder. *Journal of Colloid and Interface Science*, *325*, 363–370.

Li, J., Li, X., Ni, X. P., Wang, X., Li, H. Z., & Leong, K. W. (2006). Self-assembled supramolecular hydrogels formed by biodegradable PEO–PHB–PEO triblock copolymers and α-cyclodextrin for controlled drug delivery. *Biomaterials*, *27*, 4132–4140.

Li, J., Li, X., Zhou, Z. H., Ni, X. P., & Leong, K. W. (2001). Formation of supramolecular hydrogels induced by inclusion complexation between pluronics and α-cyclodextrin. *Macromolecules*, *34*, 7236–7237.

Liang, R., Liu, M. Z., & Wu, L. (2007). Controlled release NPK compound fertilizer with the function of water retention. *Reactive & Functional Polymers*, *67*, 769–779.

Liang, R., Yuan, H. B., Xi, G. X., & Zhou, Q. X. (2009). Synthesis of wheat straw-*g*-poly(acrylic acid) superabsorbent composites and release of urea from it. *Carbohydrate Polymers*, *77*, 181–187.

Mansoori, Y., Atghia, S. V., Zamanloo, M. R., Imanzadeh, G., & Sirousazar, M. (2010). Polymer–clay nanocomposites: Free-radical grafting of polyacrylamide onto organophilic montmorillonite. *European Polymer Journal*, *46*, 1844–1853.

Mohan, S. R., Jorge, R., Aída, G. A., Jorge, A., Luis, C., & Maity, S. K. (2007). Support effects in CoMo hydrodesulfurization catalysts prepared with EDTA as a chelating agent. *Journal of Catalysis*, *246*, 100–108.

Pourjavadi, A., Ayyari, M., & Amini-Fazl, M. S. (2008). Taguchi optimized synthesis of collagen-*g*-poly(acrylic acid)/kaolin composite superabsorbent hydrogel. *European Polymer Journal*, *44*, 1209–1216.

Pourjavadi, A., & Salimi, H. (2008). New protein-based hydrogel with superabsorbing properties: Effect of monomer ratio on swelling behavior and kinetics. *Industrial & Engineering Chemistry Research*, *47*, 9206–9213.

Sinan, K., Baris Er Goknur, B., Serkan, O., Yusuf, U., & Niyazi, B. (2009). Crosslinked DADMAC polymers as cationic super absorbents. *Reactive & Functional Polymers*, *69*, 660–665.

Suprakas, S. R., & Masami, O. (2003). Polymer/layered silicate nanocomposites: A review from preparation to processing. *Progress in Polymer Science*, *28*, 1539–1641.

Takeuchi, M., Martra, G., Coluccia, S., & Anpo, M. (2005). Investigations of the structure of H_2O clusters adsorbed on TiO_2 surfaces by near-infrared absorption spectroscopy. *The Journal of Physical Chemistry B*, *109*, 7387–7391.

Wang, L., Zhang, J. P., & Wang, A. Q. (2008). Removal of methylene blue from aqueous solution using chitosan-*g*-poly(acrylic acid)/montmorillonite superadsorbent nanocomposite. *Colloid Surface A*, *322*, 47–53.

Wang, Q., Zhang, J. P., & Wang, A. Q. (2009). Preparation and characterization of a novel pH-sensitive chitosan-*g*-poly(acrylic acid)/attapulgite/sodium alginate composite hydrogel bead for controlled release of diclofenac sodium. *Carbohydrate Polymers*, *78*, 731–737.

Wang, W. B., & Wang, A. Q. (2010). Nanocomposite of carboxymethyl cellulose and attapulgite as a novel pH-sensitive superabsorbent: Synthesis, characterization and properties. *Carbohydrate Polymers*, *82*, 83–91.

Wu, D., Wang, T., Lu, B., Xu, X., Cheng, S., & Jiang, X. (2008). Fabrication of supramolecular hydrogels for drug delivery and stem cell encapsulation. *Langmuir*, *24*, 103–106.

Zhang, J. P., Li, A., & Wang, A. Q. (2006). Synthesis and characterization of multifunctional poly(acrylic acid-co-acrylamide)/sodium humate superabsorbent composite. *Reactive & Functional Polymers*, *66*, 747–756.

Zhang, M. H., Shi, L. Y., Yuan, S., Zhao, Y., & Fang, J. H. (2009). Synthesis and photocatalytic properties of highly stable and neutral TiO_2/SiO_2 hydrosol. *Journal of Colloid and Interface Science*, *330*, 113–118.

Zhang, J. P., & Wang, A. Q. (2007). Study on superabsorbent composites. IX: Synthesis, characterization and swelling behaviors of polyacrylamide/clay composites based on various clays. *Reactive & Functional Polymers*, *67*, 737–745.

Zhang, J. P., Wang, Q., & Wang, A. Q. (2007). Synthesis and characterization of chitosan-*g*-poly(acrylic acid)/attapulgite superabsorbent composites. *Carbohydrate Polymers*, *68*, 367–374.

Zheng, Y., Hua, S. B., & Wang, A. Q. (2010). Adsorption behavior of Cu^{2+} from aqueous solutions onto starch-*g*-poly(acrylic acid)/sodium humate hydrogels. *Desalination*, *263*, 170–175.

Zheng, Y., Li, P., Zhang, J. P., & Wang, A. Q. (2007). Study on superabsorbent composite XVI. Synthesis, characterization and swelling behaviors of poly(sodium acrylate)/vermiculite superabsorbent composites. *European Polymer Journal*, *43*, 1691–1698.

Zygmunt, S., & Izabela, P. (2004). Agglomerate flotation of fine oxide particles. *International Journal of Mineral Processing*, *74*, 85–90.