Carbohydrate Polymers 90 (2012) 165–173

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Superabsorbent nanocomposite (alginate-g-PAMPS/MMT): Synthesis, characterization and swelling behavior

Mithilesh Yadav, Kyong Yop Rhee*

Industrial Liaison Research Institute, Department of Mechanical Engineering, College of Engineering, Kyung Hee University, 446-701 Yongin, Republic of Korea

ARTICLE INFO

Article history:
Received 20 March 2012
Received in revised form 27 April 2012
Accepted 4 May 2012
Available online 11 May 2012

Keywords:
Sodium alginate
2-Acrylamido-2-methyl-1-propanesulfonic acid
Montmorillonite
Swelling ratio
N,N′-methylenebisacrylamide

ABSTRACT

A superabsorbent composite (alginate-g-PAMPS/MMT) was prepared by graft copolymerization from alginate, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and Na+ montmorillonite (MMT) in an inert atmosphere. Effects of polymerization variables on water absorbency, including the content of Na+ montmorillonite, sodium alginate, N,N′-methylenebisacrylamide and AMPS, were studied. The introduced montmorillonite formed a loose and porous surface and improved the water absorbency of the alginate-g-PAMPS/MMT superabsorbent composite. Swelling behaviors of the superabsorbent composites in various cationic salt solutions (NaCl, $CaCl_2$ and $FeCl_3$) and anionic salt solutions (NaCl and Na_2SO_4) were also systematically investigated. The superabsorbent composite was further characterized using Fourier transform infrared spectroscopy (FTIR), rheology, thermogravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscopy (SEM) taking alginate-g-PAMPS as a reference.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

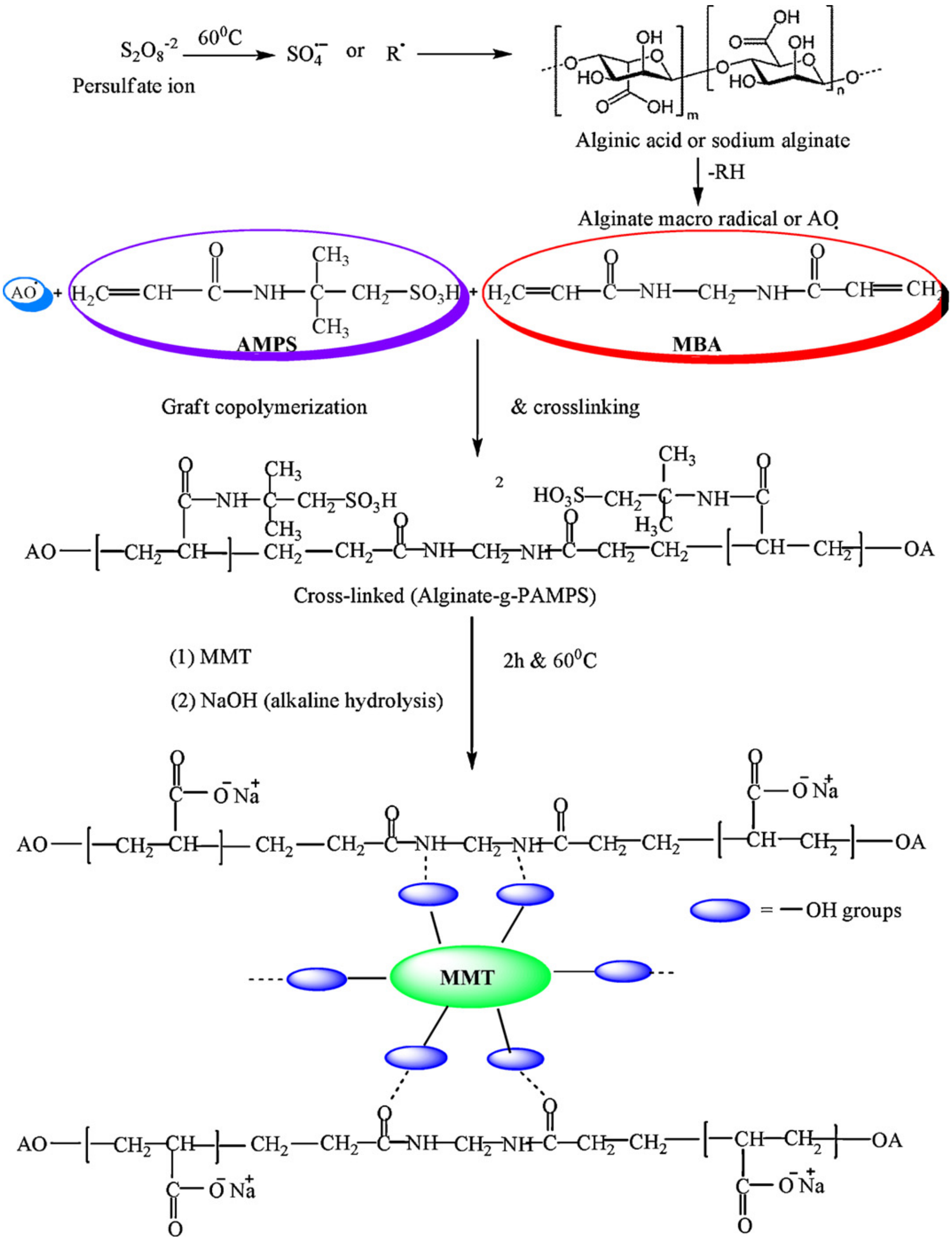
Superabsorbent hydrogels are mainly hydrophilic polymer networks that swell to a high degree in water or biological fluids due to an extremely high affinity to water (Fujioka, Tanaka, & Yoshimura, 2009; Harandi, Zohuriaan-Mehr, Yousefi, Ershad-Langroudi, & Kabiri, 2006; Wang & Wang, 2009). Superabsorbents can absorb a large amount of water compared with general water absorbing materials in which the absorbed water is hardly removable even under some pressure. Because of their excellent characteristics, superabsorbents are widely used in health, agriculture and horticulture applications, which has resulted in considerable interest and research in this field (Sakiyama, Chu, Fujii, & Yano, 1993; Shiga, Hirose, Okada, & Kurauchi, 1992; Shiga, Hirose, Okada, & Kurauchi, 1993; Yoshida, Asano, & Kumakura, 1989) since the first superabsorbent polymer was reported by the U.S. Department of Agriculture in 1976 (Fanta & Doane, 1976). Hydrogels that respond to external stimuli such as heat, pH, electric fields and chemical environments are often referred to as “intelligent” or “smart” hydrogels (Amalia, Rivas, & Riquelme, 2007; Peppas, 1986; Takashi, Atsushi, Katsuhiko, & Allan, 2004). These responsive hydrogels have become an important area of research and development in the fields of medicine, pharmacy, and biotechnology (Andrade, 1976; Galaev & Mattiasson, 1993; Schacht, 2004). Most hydrogels are formed by copolymerization of different vinyl monomers containing hydrophilic side groups with natural polysaccharides as well as their derivatives (Pourjavadi, Bardajee, & Soleyman, 2009; Pourjavadi, Samadi & Ghasemzadeh, 2008; Pourjavadi, Kurdtabar, Mahdavinia, & Hosseinzadeh, 2006). Because of their exceptional properties, i.e. biocompatibility, biodegradability, renewability, and non-toxicity, polysaccharides form the main part of the natural-based superabsorbent hydrogels. The higher production cast and low gel strength of these superabsorbents, however, severely restrict their application.

To overcome these limitations, low cost inorganic compounds can be used. The introduction of inorganic fillers to a polymer matrix increases its strength and stiffness. Among inorganic compounds, special attention has been paid to clay minerals for use in nanocomposites because of their small particle size and intercalation properties. Nanocomposites exhibit improved or even novel properties when compared to micro- and macro-composites. Strong interfacial interactions between the dispersed clay layers and the polymer matrix lead to enhanced mechanical, thermal and barrier properties over the virgin polymer. Montmorillonite (MMT) is a layered aluminum silicate with exchangeable cations and reactive —OH groups on the surface. It is one of the most widely used layered silicates because its lamellar elements display high in plane strength, stiffness, and high aspect ratio (Mansoori, Atghia, Zamanloo, Imanzadeh, & Sirousazar, 2010). Alginate[degree of substitution (DS) = 0.5], also called algin or alginic acid, is a naturally occurring colloidal hydrophilic polysaccharide (Bhat & Aminabhavi,

---

* Corresponding author. Tel.: +82 31 201 2565; fax: +82 31 202 6693.
E-mail address: rheeky@khu.ac.kr (K.Y. Rhee).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.05.010



Scheme 1. Proposed mechanistic pathway for synthesis of alginate-g-PAMPS/MMT superabsorbent nanocomposite gel.

2007) obtained from various species of brown seaweed (phaeophyceae) (Kulkarni, Soppimath, Aminabhavi, & Rudzinski, 2001; Lim, Kawai, Hori, & Osawa, 1986; Medlin, Kooistra, Potter, Saunders, & Andersen, 1997; Toti & Aminabhavi, 2002; Toti, Kariduraganavar, & Soppimath, 2002). It is a linear copolymer consisting mainly of a residue of β-1,4-linked D-mannuronic acid and α-1,4-linked l-guluronic, as shown in Scheme 1 (Painter & Aspinall, 1983; Rinaudo & Kamerling, 2007; Santacruz, Gutiĕırrez, Nieto, & Moreno, 2002). It has a broad range of applications in pharmaceutical (Badwan, Abumalooh, Sallam, Abuhalaf, & Jawan, 1985; Renken & Hunkeler, 2007), biomedical (Yoshioka, Tsuru, Hayakawa, & Osaka, 2003) and agricultural areas (Lohmann, 1992; Tsuji, 1995). It also plays an important role as an adduct product (Martinsen, Skjak-Braek, & Smidsrod, 1989) in food due to its ability to form a highly viscous solution. Some workers reported that alginate can easily form a gel (Draget, Oestgaard, & Smidsrod, 1989; Rhim, 2004) in the presence of a divalent cation as the calcium ion. Graft copolymerization of hydrophilic vinyl monomers onto alginate using efficient redox initiators is one of the best and most convenient methods of synthesizing these materials (Yadav, Mishra, Sand, & Behari, 2011) among many diverse approaches including the use of a catalyst such as AIBN (Abdel-Razik, 1997; Egboh, George, & Barrie, 1984). Further, high energy radiation (Cardona & George, 2002; Dargaville, George, Hill, & Whittaker, 2003; Kabanov & Kudryavtsev, 2003) such as X-ray or gamma-ray is used for modifying the natural polysaccharides to impart desirable properties like swelling according to the needs of the particular final applications. Superabsorbents based on alginate and its graft copolymerization with methacrylamide have been reported (Pourjavadi, Amini-Fazl, & Hosseinzadeh, 2005). Further, 2-acrylamido-2-methylpropanoesulfonic acid (AMPS) is a hydrophilic vinyl monomer containing nonionic and anionic groups. Increasing the number of ionic groups in the superabsorbent is known to increase the swelling capacity, while the nonionic groups can improve the salt tolerance of the material. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) is also used in hydrogel preparation (Durmaz & Okay, 2000; Ozmen & Okay, 2005). AMPS-based hydrogels exhibit electroresponsive properties and can be used in electronics applications (Sayil & Okay, 2002; Zhang & Easteal, 2003). They can also be used, for example, in biochemistry applications for skin contact electrodes (Kim, Lee, & Kim, 2004) and as muscle actuators (gel robots) (El-Hag Ali, Abd El Rehim, Hegazy, & Ghobashy, 2006). The incorporation of MMT can not only reduce production cost, but also improve the properties (such as swelling ability, gel strength, mechanical and thermal stability) of superabsorbents. In this paper, we report the preparation of a superabsorbent by graft copolymerization of vinyl monomers along the chains of alginate in the presence of MMT.

2. Experimental

2.1. Materials

The polysaccharide sodium alginate (NaAlg, chemical grade, MW 14,000 to 132,000) was purchased from Sigma Aldrich Chemical Co. (South Korea). 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS, Sigma Aldrich), ammonium persulfate (APS, Sigma Aldrich), Na^+Montmorillonite (MMT, Sigma Aldrich), N,N′-methylenebisacrylamide (MBA, Sigma Aldrich),calcium chloride(Sigma–Aldrich), iron chloride(Sigma–Aldrich) and sodium sulfate (Sigma Aldrich) were of analytical grade and were used as received. Methanol was provided by Daejung reagent chemicals Co. Ltd (South Korea). Deionized water was used for the hydrogel preparation and swelling measurements.

2.2. Preparation of alginate-g-PAMPS/MMT superabsorbent nanocomposites

Scheme 1 represents the general procedure for the preparation of superabsorbent composites. An alginate solution was prepared by slow addition of a pre-weighed amount (0.20–1.00 g) of Alginate powder to 100 mL of deionized water in a 250-mL three-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a nitrogen line. After purging with nitrogen for 30 min to remove the oxygen dissolved in the system, the solution was heated to 60 °C, and then an appropriate amount of APS was introduced into the alginate to generate radicals. Ten minutes later, the mixture solution of AMPS (4.42–24.15 mol/L), MBA (0.973–4.54 mol/L), and a certain amount of MMT (1–8.5 g) was added to the flask. The water bath was kept at 60 °C for 2 h to complete the reaction. The pH was adjusted by means of a NaOH solution (Zhang, Wang, & Wang, 2007). The resulting product was transferred into a sodium hydroxide aqueous solution (1 M) to be neutralized to pH 7 and then was precipitated by pouring it into a water/methanol mixture (ratio 1:5). After excessive methanol was wiped off of the surface using filter paper, the samples were dried in an oven at 60 °C to a constant weight. The product was milled, and all of the samples used for the test had a similar particle size.

2.3. Method of characterization

Wide angle X-ray diffraction patterns of alginate, alginate-g-PAMPS, alginate-g-PAMPS/MMT and MMT were recorded using a Rigaku Rotalflex (RU-200B) X-ray diffractometer employing Cu KR radiation with a Ni filter. The tube current was 300 mA with a tube voltage of 40 kV. The 2θ angular regions between 5 and 80° were explored. FTIR spectra of the MMT, alginate, alginate-*g*-PAMPS, and alginate-*g*-PAMPS/MMT nanocomposites were measured using a JASCO FT-IR spectrometer with KBr pellets from 450 to 4000 cm^{-1}. Surface morphology of the alginate-*g*-PAMPS and alginate-*g*-PAMPS/MMT nanocomposites were studied by means of a field emission scanning electron microscope (FE-SEM) (LEO SUPRA 55, Carl Zeiss, Germany) at an acceleration voltage of 20 kV. Thermal stability of the alginate-*g*-PAMPS and alginate-*g*-PAMPS/MMT were investigated using a TA instrument (SDT Q600 V20.5 Build 15) from 50 °C to 900 °C under a nitrogen atmosphere at a heating rate of 10 °C. Rheological measurements were performed using a HAKKE MARS (Thermo Electron Gmbh, Korea Polymer Testing & Research Institute) at 25 °C.

2.4. Property investigation

2.4.1. Study of water absorbency of superabsorbent nanocomposite (alginate-g-PAMPS/MMT) gels

Here we study the water absorbency of superabsorbent nanocomposite in terms of swelling ratio and percentage swelling. The swelling of synthesized superabsorbent nanocomposite gels (Alginate-g- PAMPS/MMT) was carried out in deionized water or in a salt solution. Accurately pre-weighed powder samples (0.1 g) of each were immersed into a home-made tea bag containing 20 mL of deionized water or the desired salt solution (100 mL) and kept undisturbed for 20 h at room temperature until equilibrium swelling was reached. After swelling, tea bags were suspended to remove excessive fluid, and then the whole gel was weighed. The swelling ratio (S_r) and percent swelling (P_s) were calculated by using the following expressions (EL-Rehim, Hegazy, & Ali, 2000).

$$S_r = \frac{W_2 - W_1}{W_1} \tag{1}$$

$$\text{Percent swelling } (P_s) = \text{Swelling ratio } (S_r) \times 100 \tag{2}$$

where W_1 and W_2 are the mass of sample (g) before and after swelling, respectively.

2.4.2. Swelling in salt solutions

Water absorbent capacity of superabsorbent nanocomposite gels was determined in various saline solutions (NaCl, $CaCl_2$, $FeCl_3$ and Na_2SO_4) with different concentrations according to the method described above in Section 2.4.1.

2.4.3. Determination of swelling kinetics

A series of weighed dried samples (0.1 g) were placed in excess distilled water. The superabsorbents were then separated from unabsorbed water and weighed at set intervals. This process was repeated until the weight of the superabsorbents remained constant. The water absorbency at different times was then calculated according to Eq. (1).

3. Results and discussion

3.1. Determination of optimum reaction conditions

The copolymerization reaction for superabsorbent nanocomposite gels (alginate-g-PAMPS/MMT) has been carried out at different concentrations of precursors in order to study their effect on water absorbency. These precursors are Na^+ Montmorillonite (MMT), sodium alginate (NaAlg), N, N′-methylenebisacrylamide (MBA) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS). Time and temperature were kept constant during the reaction.

3.2. Effect of MMT, sodium-alginate, MBA and AMPS concentration on water absorbency

The effect of MMT concentration on percentage swelling has been studied by varying MMT content from 1 g to 8.5 g. Swelling percentage decreases (from 2656 to 1600 g/g) on increasing concentration of MMT from 1 g to 8.5 g, which might be attributed to the following facts. The interactions between MMT, alginate, and AMPS became gradually more intense with increasing MMT content. Consequently, more chemical and physical cross-linkages were formed in the polymeric network, causing the elasticity of the polymer chains to decrease, which decreased the water absorbency of the superabsorbent nanocomposite. Additionally, the hydrophilicity of MMT is lower than that of AMPS. As such, the hydrophilicity of the nanocomposite decreases with higher MMT content, which also restricts swelling.

To examine the effect of alginate weight on hydrogel swelling, the reaction was carried out at different weights of alginate. As shown, the percentage swelling increased (from 2149 to 2656 g/g) by increasing the Na-Alg weight from 0.20 to 0.60 g. As the Na-Alg weight was increased in the polymerization feed, the active sites can more easily react with monomers. Increasing Na-Alg content more than 0.60 g results in a high viscosity of the medium and a decrease in the diffusion of monomers to active sites to produce crosslinked hydrogels (Pourjavadi, Zeidabadi, & Barzegar, 2010).

The variation of MBA concentration of Alg-g-PAMPS/MMT composites from 0.97 to 4.54 mol/L reveals that the percentage swelling increases (from 1913 to 2656 g/g) on increasing the MBA concentration from 0.97 to 2.27 mol/L. This behavior was similar to that found for some reported works (Jianming, Jihuai, Zhengfang, & Minli, 2001; Jihuai, Jianming, Meng, & Congrong, 2000). However, on further increasing the concentration of MBA from 2.27 to 4.54 mol/L, a decrease in water absorbency (from 2656 to 1960 g/g) was observed, which is probably due to a decrease in the space between the polymer chains as the crosslinker concentration is increased.

The effect of AMPS (mol/L) on the percentage swelling of the hydrogel was studied by varying the AMPS from 4.83 to 24.15 mol/L. Maximum swelling (3465 g/g) was obtained at an AMPS concentration of 24.15 mol/L. According to experimental results, increasing the AMPS concentration at a specific monomer feed composition increased the percentage swelling. This is because AMPS has polar groups like —CONH and $—SO^{-}{}_{3}$, so swelling increases according to Eq. (3) (Flory, 1953),

$$q_m^{5/3} = \frac{\left[\left(i/2\nu_u S*^{1/2}\right)^2 + (1/2 - X_1)/\nu_1\right]}{\nu_e/V_0} \tag{3}$$

where q_m is the swelling ratio, i/ν_u is the concentration of the fixed charge of the unswelling networks, $S^{*1/2}$ is the ionic strength of the swollen solution, and ν_e/V_0 is the crosslinking density that refers to the number of effectively crosslinked chains per unit volume. The expression $(1/2 - X_1)/\nu_1$ represents the network-medium affinity, and swelling capacity will also be increased by increasing the network medium affinity.

3.3. FTIR spectra analysis

3.3.1. FTIR spectra analysis of alginate-g-PAMPS, and alginate-g-PAMPS/MMT

Infrared spectrum of alginate showed strong peaks at 3426.19 cm^{-1} due to OH stretching vibrations. On comparing the FTIR spectra of alginate (presented in Fig. 1), alginate-*g*-PAMPS, and alginate-*g*-PAMPS/MMT showed variations in intensity and shifting of the OH stretching peak from 3426.19 cm^{-1} to 3347.57 and 3438.01 cm^{-1}, indicating the participation of hydroxyl groups in the chemical reaction. In addition to this, the grafting of the monomer was further confirmed by characteristic absorption bands at 1609.99, 1418.96, 1028.94, and 627.37 cm^{-1}, which are attributed to the C═O stretching vibration of the amide, C—N stretching vibration of the amide, S—O stretching vibration of —SO$_3$H and C—S stretching vibration, respectively; these bands indicate the existence of PAMPS chains. Absorption bands at 3386.87 and 3204.76 cm^{-1} ascribed to —OH of MMT disappeared in the spectrum of alginate-*g*-PAMPS/MMT as compared to that of MMT. Also, the broad absorption band at 1046.27 cm^{-1} ascribed to the Si—OH of MMT shifted to a sharp absorption band at 1044.38 cm^{-1}, and the intensity decreased. These results indicate the participation of the —OH group of MMT in the formation of the nanocomposite. After alkaline hydrolysis, the new absorption modes observed at 1458.34 and 1550.74 cm^{-1} can be attributed to symmetric and asymmetric stretching modes of carboxylate groups, respectively. Finally, it can be concluded from the figure that graft-copolymerization has taken place among alginate, AMPS, and MMT.

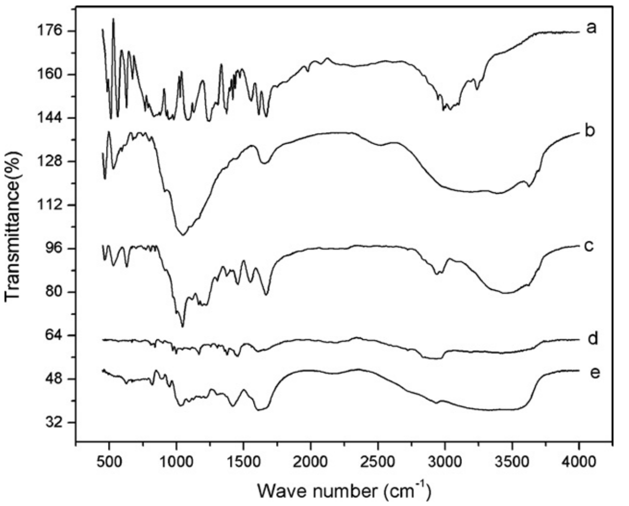


Fig. 1. FTIR of (a) AMPS, (b) MMT, (c) alginate-g-PAMPS/MMT, (d) Alginate and (e) alginate-g-PAMPS.

3.3.2. Morphology analysis

Scanning electron micrographs of crosslinked alginate-*g*-PAMPS composites containing 0 g MMT, 1.0 g MMT, 4.5 g MMT and 8.5 g MMT are depicted in Fig. 2a–d, respectively. Obviously, the surface morphology of the alginate-*g*-PAMPS/MMT nanocomposite is different from that of alginate-*g*-PAMPS. It can be observed that crosslinked alginate-*g*-PAMPS (Fig. 2a) displays a smooth and tight surface. However, composites containing MMT (Fig. 2b and c) present a loose and porous surface, facilitating the permeation of water into the polymeric network. These SEM results also confirm that the MMT powders are more finely dispersed in the polymer matrix (Liang, Yuan, Xi, & Zhou, 2009; Bao, Jianzhong, & Li, 2011).

3.3.3. XRD patterns of superabsorbent nanocomposite (alginate-g-PAMPS and alginate-g-PAMPS/MMT = 1.0, 2.5, 4.5, and 8.5)

Fig. 3 exhibits the XRD patterns of Na$^+$MMT, composites containing 0 g MMT, 1 g MMT, 2.5 g MMT, 4.5 g MMT and 8.5 g MMT, respectively. XRD patterns were collected from 5° to 80° (2θ). It can be observed that MMT shows some characteristic peaks at $2\theta = 9.09°$ (9.71 Å), 19.83° (4.47 Å), 27.94° (3.19 Å), 34.93° (2.57 Å), 43.13° (2.09 Å) and 62.00° (1.49 Å), respectively. The XRD pattern of pure UVMT shows a strong peak at $2\theta = 9.09$, which corresponds to a basal spacing of 9.71 Å. After reaction, this peak has almost

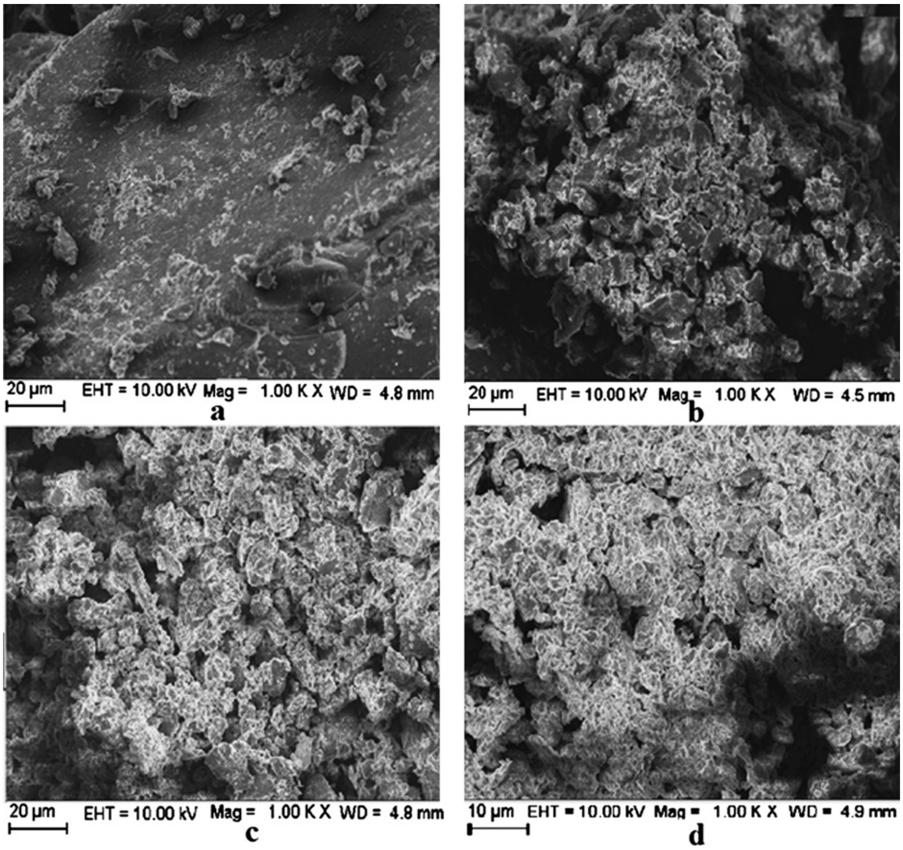


Fig. 2. SEM micrographs of (a) alginate-g-PAMPS/MMT = 0, (b) alginate-g-PAMPS/MMT = 1.0, (c) alginate-g-PAMPS/MMT = 4.5, (d) alginate-g-PAMPS/MMT = 8.5, MMT content in the feed is 0, 1.0, 4.5, and 8.5 g, in (a), (b), (c), (d), respectively.

disappeared, and other diffraction peaks are similar to those of pure MMT, and 2θ remains unchanged. In other words, we detected no peak for the composites prepared from MMT, which implies that they all possess exfoliated structures in the composite. Similar results are obtained in some reported papers (Luo, Zhang, Chen, Fang,2005; Zheng, Gao, & Wang, 2008). Results obtained indicate that MMT has been finely dispersed in the polymer matrix, and the copolymerization reaction is performed on the surface of MMT. This is consistent with the results achieved from SEM.

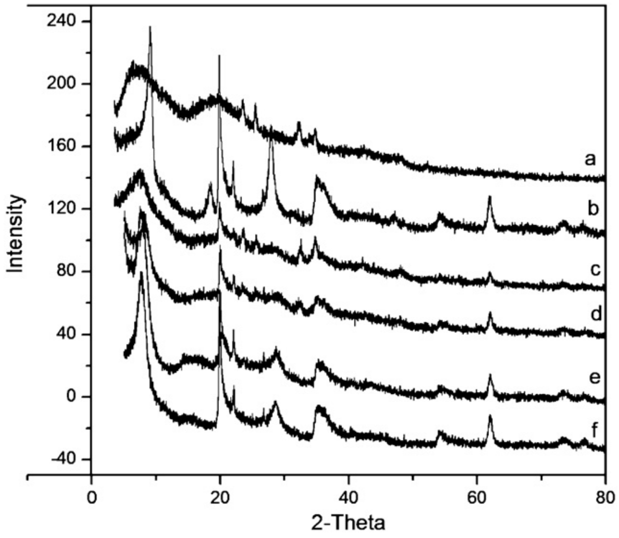


Fig. 3. XRD powder patterns of (a) alginate-g-PAMPS/MMT = 0, (b) MMT (c) alginate-g-PAMPS/MMT = 1 g, (d) alginate-g-PAMPS/MMT = 2.5 g, (e) alginate-g-PAMPS/MMT = 4.5 g and (f) alginate-g-PAMPS/MMT = 8.5 g.

3.3.4. *Thermogravimetric analysis*

Thermal stability improvement for a polymer clay composite or superabsorbent composite has been reported in a number of works (Golebiewski & Galeski, 2007; Kabiri, Mirzadeh, & Zohuriaan- Mehr, 2010; Zheng, Li, Zhang, & Wang 2007). Thermogravimetric results, i.e., TGA curves of alginate-g-PAMPS and alginate-g-PAMPS/MMT are presented in Fig. 4(a) and (b), respectively, and show multi step degradation. The 3.5% weight loss at 122.22 °C might be due to loss of absorbed water, which begins at about 50.0 °C. The polymer decomposition temperature (PDT) was found to be 131.8 °C. Weight loss rate increases with increasing temperature from 200 °C to 400 °C and thereafter decreases and attains a maximum value about at 750 °C. The degradation of graft copolymer (alginate-g-PAMPS) occurs in more than one step, i.e., between 200–250, 280–400 and 600–750 °C, respectively. Three $T_{\max}$ 236.4, 349.2 and 701.4 °C have been found due to three step degradation. The integral procedural decomposition temperature accounts for the whole shape of the curve in a single number by measuring the area under the curve. Thus, thermal stability of pure alginate and its graft copolymers has also been determined by calculating IPDT values.

The integral procedure decomposition temperature (IPDT) proposed by Doyle (Doyle, 1961) has been correlated with the volatile parts of polymeric materials and is used for estimating the inherent thermal stability of polymeric materials (Vyazovkin & Sbirrazzuoli, 2006). IPDT was calculated from

$$\mathrm{IPDT}\,(^{\circ}\mathrm{C}) = A * K * (T_f - T_i) + T_i \qquad (4)$$

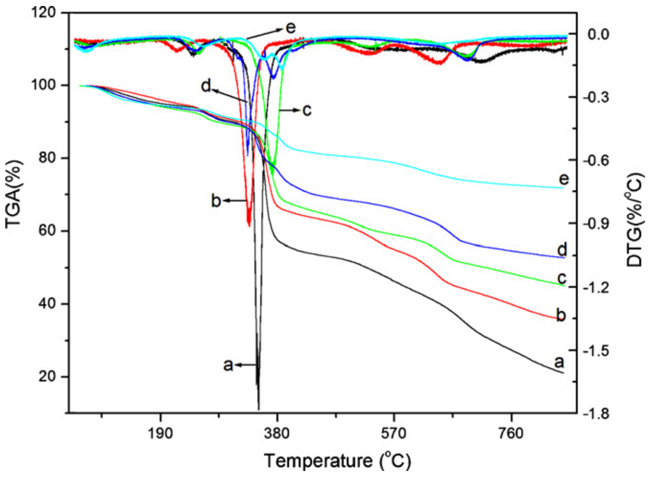


Fig. 4. Thermogravimetric analysis of (a) alginate-g-PAMPS/MMT = 0, (b) alginate-g-PAMPS/MMT = 1.0, (b) alginate-g-PAMPS/MMT = 2.5, (c) alginate-g-PAMPS/MMT = 4.5, (d) alginate-g-PAMPS/MMT = 8.5, MMT content in the feed is 0, 1.0, 2.5, 4.5, and 8.5 g, in (a), (b), (c), (d), (e), respectively.

$$A* = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \tag{5}$$

$$K* = \frac{S_1 + S_2}{S_1} \tag{6}$$

where A^* is the area ratio of the total experimental curve defined by the total TGA thermogram, T_i is the initial experimental temperature, and T_f is the final experimental temperature. A representation of S_1, S_2 and S_3 for calculating A^* and K^* are given in some reported works (Chiang, Chang, & Chiu, 2007). Integral procedural decomposition temperatures (IPDTs) and the final decomposition temperatures (FDTs) have been found at 835.69 0 °C and 750 °C, respectively. But, in the case of alginate-g-PAMPS/MMT, a weight loss of 1.82%, at about 50.0 °C might be due to loss of absorbed methanol. The polymer decomposition temperature (PDT) was found at 156.4 °C, however, the degradation of alginate-g-PAMPS/MMT starts at about 150.8 °C (Fig. 5). The rate of weight loss increases with increasing temperature from 200.4 °C to 338.89 °C and thereafter decreases and attains a maximum value of 64.15% at about 850 °C. The degradation of graft copolymer (alginate-g-PAMPS/MMT) occurs in more than one step, i.e., between 150–250, 250–400, 450–560 and 600–700 °C, respectively. Four T_{max} 150–250, 250–400, 450–560 and 600–700 °C have been found due to four step degradation. First T_{max} at 212.6 °C might be due to elimination of CO_2 from the polymeric backbone. Second T_{max} at 332.8 °C might be due to elimination of $\text{—NHC(CH}_3)_2\text{CH}_2\text{SO}_3$ group from pendent chain attached to the polymeric back bone. The third T_{max} 522.6 °C at might be due to elimination of CO molecule from pendent chain attached to the polymeric backbone. The fourth T_{max} 636.6 °C at might be due to elimination of CO_2 molecule superabsorbent composite. IPDT and FDT have been found at about 1276.37 °C and 850 °C, respectively. On comparing the thermograms of alginate-g-PAMPS and alginate-g-PAMPS/MMT, the FDT and IPDT have been found to be higher for alginate-g-PAMPS/MMT. This indicates that alginate-g-PAMPS/MMT is more thermally stable than a clay free composite. All experimental results of the degradation temperatures of the composites studied as a function of MMT are listed in Table 1. The curves presented in the figures contain the information necessary to evaluate the kinetics of degradation by Briodo's method (Broido, 1969). According to this method, the weight of the material, W, at any time, t, is related to the fraction of the number of initial molecules not yet decomposed, as in Eq. (7).

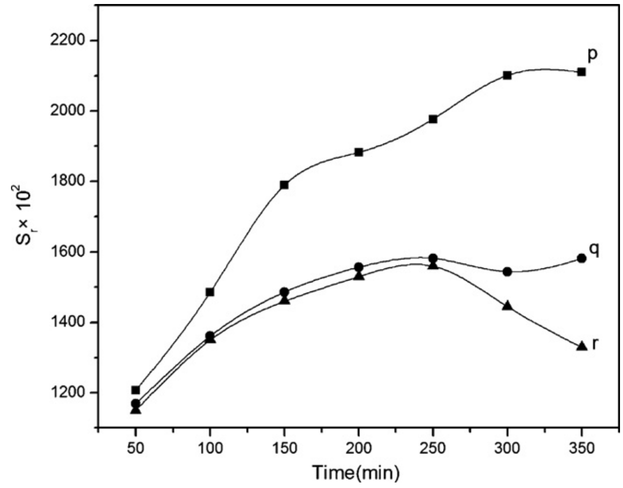


Fig. 5. The swelling kinetics of (p) alginate-g-PAMPS/MMT = 1.0, (q) alginate-g-PAMPS/MMT = 4.5, (r) alginate-g-PAMPS/MMT = 8.5, MMT content in the feed is 1.0, 4.5, and 8.5 g, in (p), (q), (r), respectively.

Table 1
Effect of MMT on the thermal stabilities of the composites studied.

MMT content (g)	PDT (°C)	T_{max} (°C)	A	K	IPDT (°C)
0	131.8	349.2	0.61	1.52	835.69
1.0	156.4	332.8	0.68	2.13	1276.37
2.5	165.3	369.7	0.71	2.76	1740.88
4.5	186.9	331.3	0.74	3.44	2251.38
8.5	217.3	386.5	0.83	6.94	5110.59

$$Y = \frac{W_t - W_\infty}{W_0 - W_\infty} \tag{7}$$

where W_0 is the initial weight of the material and W_∞ is the weight of the residue at the end of the degradation. Equation (8) is used to estimate E_a:

$$\ln\ \ln\left(\frac{1}{Y}\right) = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \text{constant} \tag{8}$$

where E_a is the energy of activation; R, the gas constant and T is the temperature in Kelvin. The energy of activation has been evaluated from Eq. (8) by plotting $\ln(1/Y)$ versus $1/T$ and the slope of the straight line gives the energy of activation. Values of E_a for alginate-g-PAMPS, alginate-g-PAMPS/MMT (1 g), alginate-g-PAMPS/MMT (2.5 g), alginate-g-PAMPS/MMT (4.5 g) and alginate-g-PAMPS/MMT (8.5 g) were found to be 21.73, 24, 25, 15 and 25.92 Kcal/mol, respectively.

Some reported works (Haraguchi, Li, Matsuda, Takeshia, Elliott, 2005; Kabiri & Zohuriaan-Mehr, 2003) give another reason for the higher thermal stability of the nanocomposite hydrogel in comparison with the clay free hydrogel, namely, that stability is attributed to crosslink formation between the clay and growing chains of the polymer.

3.3.5. Water absorbency in various saline solutions

Table 2 represents the swelling behaviors of the composites (Alg-g-PAMPS/MMT) in NaCl, $CaCl_2$, $FeCl_3$ and Na_2SO_4 solutions at different concentrations. Based on the experimental results, it can concluded that the absorbency of composites (Alg-g-PAMPS/MMT) is very high for distilled water at lower salt concentrations (0.1 wt.%). However, the swelling capacity of the composites was significantly decreased with increasing salt solution concentration. Water absorbency for the composites in the studied solutions is in the order of monovalent > divalent > trivalent cations, and the decreasing tendency of water absorbents with salt concentration is

Table 2
Swelling behavior of composite in different salt solutions.

Wt.% salt solution	Ionic strength (mol ion/dm^3)					Ps = Sr × 10^2		
	NaCl	$CaCl_2$	$FeCl_3$	Na_2SO_4	NaCl	$CaCl_2$	$FeCl_3$	Na_2SO_4
0.1	0.0171	0.0269	0.0369	0.0282	2587	2200	1630	2391
0.4	0.0684	0.1076	0.1476	0.1128	1896	2485	1314	1861
0.7	0.1197	0.1883	0.2583	0.1974	1649	1385	1280	1658
1.0	0.1710	0.2690	0.3690	0.2820	1631	1365	1266	1589
1.3	0.2223	0.3497	0.4797	0.3666	1625	1150	1259	1431
1.6	0.2736	0.4304	0.5904	0.4512	1615	1138	1135	1426
1.9	0.3249	0.5111	0.7011	0.5358	1544	1090	1121	1336

more obvious in a multivalent salt solution than in a monovalent salt solution. The salt type and concentration can be expressed in terms of ionic strength (Bao et al., 2011).

$$\text{Ionic strength}\,(I) = 0.5\ \Sigma(C_i Z^2 i) \tag{9}$$

where I, C_i, and Z_i are the ionic strength, the ionic concentration, and charge on each individual ion, respectively.

From Table 2, it can be seen that the order of ionic strength isotonic and non-isotonic salt solutions is $Fe^{3+} > Ca^{2+} > Na^+$ and ${SO_4}^{2-} > Cl^-$, respectively. The effect of the ionic strength on the water absorbency can be expressed by Flory's equation, provided above as Eq. (3). According to Eq. (2), when the ionic strength of a saline solution increases, the water absorbency decreases. Therefore, the experimental results abide by Flory's equation. The observed results can be explained as follows. In the case of multivalent cationic solutions, 'ionic crosslinking' in the superabsorbent network, derived from the complexation of hydrophilic groups with multi-valent cations, often cause an increase in the crosslinking density of the network, and so the swelling capacity consequently decreases (Shi, Wenbo Wang, & Aiqin Wang, 2011). The water absorbency in terms of percentage swelling decreased as the concentration of various salt solutions increased, which can also be explained on the basis of the 'charge screening effect' in salt solutions. Further, additional cations cause a non perfect anion–anion electrostatic repulsion, resulting in a decrease of osmotic pressure difference between gel network and the external solution, and so the swelling capacity is drastically reduced (Mohan, Keshava Murthy, & Mohana Raju, 2005). To investigate the effect of different anions on the water absorbency of the Alg-g-PAMPS/MMT superabsorbent composite, samples were prepared wherein the concentrations of NaCl and $1/2(Na_2SO_4)$ solutions are equal, i.e., the contribution of Na^+ to the whole ionic strength is equal regardless of the valence of the anions. Table 2 shows the effects of Cl^- and ${SO_4}^{2-}$ on the saturated water absorbency of the Alg-g-PAMPS composites. It can be seen from Table 2 that the valence of the anion has an effect on the water absorbency of the superabsorbent composite. Water absorbencies of the superabsorbent composite containing 1 g Na^+ MMT in various sodium salt solutions are in the order $Cl^- > {SO_4}^{2-}$. This result indicates that the water absorbency of the superabsorbent composite in a salt solution containing divalent anions (${SO_4}^{2-}$) is higher than that in salt solutions containing monovalent anions (Cl^-) at the same concentration.

3.3.6. Swelling kinetics of superabsorbent composite

Swelling kinetics were characterized by the Voigt-based viscoelastic model (Kabiri, Omidian, Hashemi, & Zohuriaan-Mehr, 2003; Omidian, Hashemi, Sammes, & Meldrum,1998)

$$S_t = P(1 - e^{-t/r}) \tag{10}$$

where S_t is the swelling capability at any moment (g/g), p is the power parameter (g/g), t is the time (min), and r is the rate parameter (time required to reach 63% of equilibrium swelling) (min). The data obtained from the equilibrium swelling and the swelling rate for each sample were fitted to the above equation to find the values of the rate and power parameters. The rate parameter, r, is a measure of the swelling rate of a superabsorbent sample so that a lower r-value is indicative of a higher swelling rate. The power parameter, p, reflects the water-holding capacity of an individual superabsorbent. Swelling kinetics of a superabsorbent composite are shown in Fig. 5. It can be seen that the swelling rate of the superabsorbent composite is highest within the first 200 min. Later, the swelling rate is reduced, and the curves of the swelling rate become flatter. The results indicated that the rate parameters for the MMT-1 g, MMT-4.5 g and MMT-8.5 g samples were found to be 78.89, 63.94 and 65.80 min, respectively. However, the p-value showed a different trend and was found to be 25.69, 21.53 and 21.60 g/g for MMT-1 g, MMT-4.5 g and MMT-8.5 g, respectively. Based on these results, it can be concluded that though the r-value for MMT-1 g is slightly higher than that of MMT-4.5 g and MMT-8.5 g, the p-value is much higher, suggesting that introduction of MMT into the sample can provide higher water absorbency.

3.4. Rheological studies

Rheological studies were carried out to follow gel strength of typical hydrogels swollen in water. The storage modulus may be taken as a measure of the mechanical strength of the hydrogel. It is inversely related to the average molecular weight between crosslinks (Mc) (Jiang, Su, Mathera, & Bunninga, 1999)

$$G' = \frac{\rho RT}{Mc} \tag{11}$$

where G' is the relaxed rubbery modulus, ρ the density, R the gas constant and T the temperature. Since Mc has an inverse relationship with the rubbery modulus, its increase (i.e. lower crosslink density) results in swelling enhancement. It is well known that the gel strength changes inversely with the swelling capacity, i.e. the higher the swelling capacity, the lower the gel strength will be.

Fig. 6 shows the storage modulus of the hydrogel nanocomposites (alginate-g-PAMPS/MMT) with various contents of MMT. The storage modulus increases maximum with the incorporated MMT content up to 1 g. After this, it greatly decreases with increasing MMT content. The decreasing trend of modulus is continued even below that of the clay-free sample.

In the results and discussion section it is clear that a large increase of clay content (more than 1 g) has an undesirable effect on the polymerization progress. Therefore, some part of the crosslinker cannot be utilized during polymerization which leads to an increase in soluble fraction (i.e. lower gel content) as well as

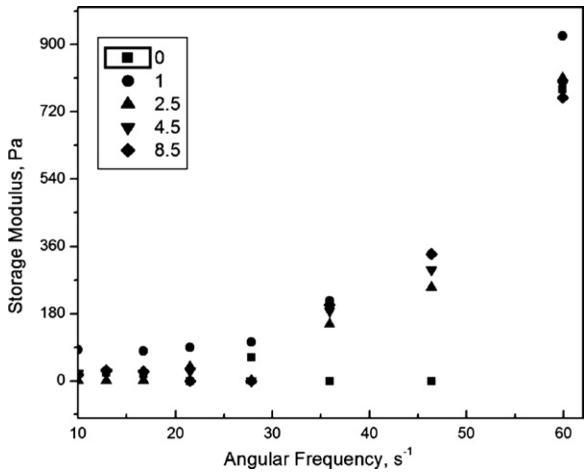


Fig. 6. Storage modulus versus angular frequency of (a) alginate-*g*-PAMPS = 0, (b) alginate-*g*-PAMPS/MMT = 1.0, (b) alginate-*g*-PAMPS/MMT = 2.5, (c) alginate-*g*-PAMPS/MMT = 4.5, (d) alginate-*g*-PAMPS/MMT = 8.5, MMT content in the feed is 0, 1.0, 2.5, 4.5, and 8.5 g, in (a), (b), (c), (d), (e), respectively.

swelling capacity enhancement. Since swelling capacity enchantment can be taken as a result of higher *M*c, the storage modulus decreases with increasing MMT content. Actually, incorporation of MMT higher than a certain amount (1 g) disfavors the crosslinking polymerization progression.

4. Conclusion

Alginate-g-PAMPS/MMT superabsorbent hydrogels were synthesized by using APS as a free radical initiator, in the presence of MBA as a crosslinking agent. FTIR indicates that the graft-copolymerization reaction occurs between alginate, AMPS, and MMT. SEM studies illustrate more finely dispersion of the MMT particle in the polymer matrix. In addition, XRD analysis shows that the polymerization reaction is performed on the surface of MMT. TGA implies that introduction of MMT into the polymer network leads to an increase in thermal stability of the composites. The impact of salts on water absorbency of Alginate-g-PAMPS/MMT superabsorbent hydrogel is relative to the concentration of salt solution and valence of cations. The swelling-loss behavior of the hydrogel occurred as the concentration of the external salt solution increased. The effect of various cationic salt solutions (NaCl, $CaCl_2$ and $FeCl_3$) and anionic salt solutions (NaCl and Na_2SO_4) on the swelling has the following order: $Na^+ > Ca^{2+} > Fe^{3+}$, $Cl^- > SO_4{}^{2-}$. The water absorbency for hydrogel is increased and then decreased. The swollen gel strength of the hydrogels was improved due to their nanocomposite structure. Gel strength enhancement was established through storage modulus obtained from rheological measurements.

Acknowledgements

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0023106).

References

EL-Rehim, H. A. A., Hegazy, E.-S. A., & Ali, A. M. (2000). Selective separation of some heavy metals by poly (vinyl alcohol)-grafted membranes. *Journal of Applied Polymer Science*, *76*, 125–132.

Abdel-Razik, E. A. (1997). Photoinduced graft copolymerization of ethyl acrylate, methyl methacrylate and methyl acrylate onto ethyl cellulose in homogeneous media. *Journal of Photochemistry and Photobiology A: Chemistry*, *107*, 271–274.

Amalia, P. S., Rivas, B. L., & Riquelme, F. J. (2007). Stimuli-responsive hydrogels from acrylamide with N-[3-(dimethylamine) propyl] metacrylamide. Synthesis and properties. *Journal of Chillean Chemical Society*, *52*, 1160–1162.

Andrade, J. D. (Ed.). (1976). *Hydrogels for medical and related applications, ACS symposium series*. Washington, DC: American Chemical Society.

Badwan, A. A., Abumalooh, A., Sallam, E., Abuhalaf, A., & Jawan, O. (1985). A sustained release drug delivery system using calcium alginate beads. *Drug Development and Industrial Pharmacy*, *11*, 239–256.

Bhat, S. D., & Aminabhavi, T. M. (2007). Pervaporation separation using sodium alginate and its modified membranes—A review. *Separation and Purification Reviews*, *36*, 203–229.

Broido, A. (1969). A simple, sensitive graphical method of treating thermogravimetric analysis data. *Journal of polymer science: Part A-2*, *7*, 1761–1773.

Cardona, F., & George, G. A. (2002). Copolymers obtained by the radiation-induced grafting of styrene onto poly (tetrafluoroethylene-co-perfluoropropylvinyl ether) substrates. 1. Preparation and structural investigation. *Macromolecules*, *35*, 355–364.

Chiang, C. L., Chang, R. C., & Chiu, Y. C. (2007). Thermal stability and degradation kinetics of novel organic/inorganic epoxy hybrid containing nitrogen/silicon/phosphorus by sol–gel method. *Thermochimica Acta*, *453*, 97–104.

Dargaville, T. R., George, G. A., Hill, D. J. T., & Whittaker, A. K. (2003). High energy radiation grafting of fluoropolymer. *Progress in Polymer Science*, *28*, 1355–1376.

Doyle, C. D. (1961). Estimating thermal stability of experimental polymers by empirical thermogravimetric analysis. *Analytical Chemistry*, *33*, 77.

Draget, K. I., Oestgaard, K., & Smidsrod, O. (1989). Alginate-based solid media for plant tissue culture. *Applied Microbiology and Biotechnology*, *31*, 79–83.

Durmaz, S., & Okay, O. (2000). Acrylamide/2-acrylamido-2-methyl propane sulfonic acid sodium salt based hydrogels. *Synthesis and Characterization Polymer*, *41*, 3693–3704.

Egboh, S. H., George, M. H., & Barrie, J. A. (1984). The γ-radiation induced grafting of unsaturated segmented polyurethanes with N-vinyl pyrrolidone. *Polymer*, *25*, 1157–1160.

El-Hag Ali, A., Abd El Rehim, H. A., Hegazy, E. A., & Ghobashy, M. M. (2006). Synthesis and electrical response of acrylic acid/vinylsulfonic acid hydrogels prepared by g-irradiation. *Radiation Physics Chemistry*, *75*, 1041.

Flory, P. J. (1953). *Principles of polymer chemistry*. New York: Cornell University Press.

Fujioka, R., Tanaka, Y., & Yoshimura, T. (2009). Synthesis and properties of superabsorbent hydrogels based on guar gum and succinic anhydride. *Journal of Applied Polymer Science*, *114*, 612–616.

Galaev, I. Y., & Mattiasson, B. (1993). A review—Thermoreactive water-soluble polymers, nonionic surfactants, and hydrogels as reagents in biotechnology. *Enzyme and Microbial Technology*, *15*, 354–366.

Golebiewski, J., & Galeski, A. (2007). Thermal stability of nanoclay polypropylene composites by simultaneous DSC and TGA. *Composites Science and Technology*, *67*, 3442.

Haraguchi, K., Li, H. J., Matsuda, K., Takeshia, T., & Elliott, E. (2005). Mechanism of forming organic/inorganic network structures during in situ free-radical polymerization in PNIPA-clay nanocomposite hydrogels. *Macromolecules*, *38*, 3482.

Jiang, H., Su, W., Mathera, P. T., & Bunninga, T. J. (1999). Rheology of highly swollen chitosan/polyacrylate hydrogels. *Polymer*, *40*, 4593–4602.

Jianming, Lin, Jihuai, Wu, Zhengfang, Yang, & Minli, Pu. (2001). Synthesis and properties of poly(acrylic acid)/mica superabsorbent nanocomposite. *Macromolecular Rapid Communications*, *22*, 422.

Jihuai, Wu, Jianming, Lin, Meng, Zhou, & Congrong, Wei. (2000). Synthesis and properties of starch-graft-polyacrylamide/clay superabsorbent composite. *Macromolecular Rapid Communications*, *2000*, 21.

Kabanov, V. Y., & Kudryavtsev, V. N. (2003). A review—Modification of polymers by radiation graft polymerization. *High Energy Chemistry*, *37*, 1–5.

Kabiri, K., Mirzadeh, H., & Zohuriaan-Mehr, M. J. (2010). Chitosan modified MMT-poly(AMPS) nanocomposite hydrogel: Heating effect on swelling and rheological behavior. *Journal of Applied Polymer Science*, *116*, 2548–2556.

Kabiri, K., & Zohuriaan-Mehr, M. (2003). Superabsorbent hydrogel composites. *Journal of Polymer Advanced Technology*, *14*, 438.

Kabiri, K., Omidian, H., Hashemi, S. A., & Zohuriaan-Mehr, M. J. (2003). Synthesis of fast-swelling superabsorbent hydrogels: Effect of crosslinker type and concentration on porosity and absorption rate. *European Polymer Journal*, *39*, 1341.

Kim, S. J., Lee, C. K., & Kim, S. I. (2004). Electrical/pH responsive properties of poly(2-acrylamido-2-methylpropane sulfonic acid)/hyaluronic acid hydrogels. *Journal of Applied Polymer Science*, *92*, 1731–1736.

Kulkarni, A. R., Soppimath, K. S., Aminabhavi, T. M., & Rudzinski, W. E. (2001). In vitro release kinetics of cefadroxil-loaded sodium alginate interpenetrating network beads. *European Journal of Pharmaceutics and Biopharmaceutics*, *51*, 127–133.

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

Lim, B. L., Kawai, H., Hori, H., & Osawa, H. (1986). Molecular evolution of 5S ribosomal RNA from red and brown algae. *Idengaku Zasshi*, *6*, 169–176.

Lohmann, D. D. (1992). Biodegradable polymers and additives in agricultural controlled release systems. In J. Kopecek (Ed.), *Proceedings of the international symposium on controlled release of bioactive materials, vol. 19* (pp. 170–171). Controlled Release Society.

Luo, W., Zhang, W., Chen, P., & Fang, Y. (2005). Synthesis and properties of starch grafted poly[acrylamide-co-(acrylic acid)/montmorillonite nan superabsorbent via γ-ray irradiation technique. *Journal of Applied Polymer Science*, *96*, 1341.

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

Martinsen, A., Skjak-Braek, G., & Smidsrod, O. (1989). Alginate as immobilization material, I. Correlation between chemical and physical properties of alginate gel beads. *Biotechnology and Bioengineering*, *33*, 79–89.

Medlin, L. K., Kooistra, W. H. C. F., Potter, D., Saunders, G. W., & Andersen, R. A. (1997). Phylogenetic relationships of the 'golden algae' (haptophytes, heterokont chromophytes) and their plastids. *Plant Systematics and Evolution*, *11*, 187–219.

Murali Mohan, M. Y., Keshava Murthy, P. S., & Mohana Raju, K. (2005). Synthesis, characterization and effect of reaction parameters on swelling properties of acrylamide–sodium methacrylate superabsorbent copolymers. *Reactive & Functional Polymers*, *63*, 11–26.

Omidian, H., Hashemi, S. A., Sammes, P. G., & Meldrum, I. A. (1998). Model for the swelling of superabsorbent polymers. *Polymer*, *39*, 6697.

Ozmen, M. M., & Okay, O. (2005). Superfast responsive ionic hydrogels with controllable pore size. *Polymer*, *46*, 8119–8127.

Painter, T. J., & Aspinall, G. O. (Eds.). (1983). *Algal polysaccharides: The polysaccharides*. (pp. 195–285). New York: Academic Press.

Peppas, N. A., (1986). (Ed.), Hydrogels in medicine and pharmacy. Boca Raton, FLa: C.R.C. Press, 180, 171.

Pourjavadi, A., Samadi, M., & Ghasemzadeh, H. (2008). Fast-swelling superabsorbent hydrogels from poly (2-hydroxy ethyl acrylate-co-sodium acrylate) grafted on starch. *Starch/Stärke*, *60*, 79–86.

Pourjavadi, A., Bardajee, G. R., & Soleyman, R. (2009). Synthesis and swelling behavior of a new superabsorbent hydrogel network based on polyacrylamide grafted onto salep. *Journal of Applied Polymer Science*, *112*, 2625–2633.

Pourjavadi, A., Kurdtabar, M., Mahdavinia, G. R., & Hosseinzadeh, H. (2006). Synthesis and super-swelling behavior of a novel protein based superabsorbent hydrogel. *Polymer Bulletin*, *57*, 813–824.

Pourjavadi, A., Zeidabadi, F., & Barzegar, Sh. (2010). Alginate-based biodegradable superabsorbents as candidates for diclofenac sodium delivery systems. *Journal of Applied Polymer Science*, *118*, 2015–2023.

Pourjavadi, A., Amini-Fazl, M. S., & Hosseinzadeh, H. (2005). Partially hydrolyzed crosslinked alginate-graft-polymethacrylamide as a novel biopolymer-based superabsorbent hydrogel having pH-responsive. *Properties Macromolecular Research*, *13*, 45–53.

Ramazani-Harandi, M. J., Zohuriaan-Mehr, M. J., Yousefi, A. A., Ershad-Langroudi, A., & Kabiri, K. (2006). Rheological determination of the swollen gel strength of superabsorbent polymer hydrogels. *Polymer Testing*, *25*, 470–474.

Renken, A., & Hunkeler, D. (2007). Polyvinylamine-based capsules: A mechanistic study of the formation using alginate and cellulose sulphate. *Journal of Microencapsulation*, *24*, 323–336.

Rhim, J. (2004). Physical and mechanical properties of water resistant sodium alginate films. *Lebensmittel Wissenschant und-Technologie*, *37*, 323–330.

Rinaudo, M., & Kamerling, J. P. (Eds.). (2007). *Seaweed polysaccharides: Comprehensive glycoscience*. (pp. 691–735). Amsterdam: Elsevier.

Sakiyama, T., Chu, C. H., Fujii, T., & Yano, T. (1993). Preparation of a polyelectrolyte complex gel from chitosan and k-carrageenan and its pH-sensitive swelling. *Journal of Applied Polymer*, *50*, 2021–2025.

Santacruz, I., Gutiĕırrez, C. A., Nieto, M. I., & Moreno, R. (2002). Application of alginate gelation to aqueous tape casting technology. *Material Research Bulletin*, *37*, 671–682.

Sayil, C., & Okay, O. (2002). Swelling-shrinking hysteresis of poly (N-isopropyl)acrylamide) gels in sodium dodecyl benzene sulfonate solutions. *Journal of Applied Polymer Science*, *83*, 1228–1232.

Schacht, E. H. (2004). Polymer chemistry and hydrogel systems. *Journal of Physics: Conference Series*, *3*, 22–28.

Shi, X., Wang, W., & Wang, A. (2011). Synthesis, characterization and swelling behaviors of guar gum-g-poly(sodium acrylate-co-styrene)/vermiculite superabsorbent composites. *Journal of Composite Materials*, *45*, 2189–2198.

Shiga, T., Hirose, Y., Okada, A., & Kurauchi, T. (1992). Bending of poly (vinyl alcohol)–poly (sodium acrylate) composite hydrogel in electric fields. *Journal of Applied Polymer Science*, *44*, 249.

Shiga, T., Hirose, Y., Okada, A., & Kurauchi, T. (1993). Bending of ionic polymer gel caused by swelling under sinusoidally varying electric fields. *Journal of Applied Polymer Science*, *47*, 113.

Takashi, M., Atsushi, J., Katsuhiko, N., & Allan, S. H. (2004). Preparation of reversibly glucose-responsive hydrogels by covalent immobilization of lectin in polymer networks having pendant glucose. *Journal of Biomaterials Science, Polymer Edition*, *15*, 1085–1098.

Toti, U. S., Kariduraganavar, M. Y., & Soppimath, K. S. (2002). Sorption, diffusion, and pervaporation separation of water–acetic acid mixtures through the blend membranes of sodium alginate and guar gum-grafted-polyacrylamide. *Journal of Applied Polymer Science*, *83*, 259–272.

Toti, U. S., & Aminabhavi, T. M. (2002). Pervaporation separation of water–isopropyl alcohol mixtures with blend membranes of sodium alginate and poly (acrylamide)-grafted guar gum. *Journal of Applied Polymer Science*, *85*, 2014–2024.

Tsuji, K. (1995). In Y. Dohi (Ed.), *Handbook of biodegradable plastics: Applications to pesticide slow release systems* (pp. 556–566). Tokyo: MTS.

US 3 981 100. (1976). United States Dept. of Agriculture, invs.: Weaver, M. O., Bagley, E. B., Fanta, G. F., Doane, W. M.; *Chem. Abstr. 85*, 161504n.

Vyazovkin, S., & Sbirrazzuoli, N. (2006). Isoconversional kinetic analysis of thermally stimulated processes in polymers macromol. *Rapid Communication*, *27*, 1515–1532.

Wang, W., & Wang, A. (2009). Preparation, characterization and properties of superabsorbent nanocomposites based on natural guar gum and modified rectorite: Original research article. *Carbohydrate Polymers*, *77*, 891–897.

Bao, Y., Jianzhong, M., & 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.

Yadav, M., Mishra, D. K., Sand, A., & Behari, K. (2011). Modification of alginate through the grafting of 2-acrylamidoglycolic acid and study of physicochemical properties in terms of swelling capacity, metal ion sorption, flocculation and biodegradability. *Carbohydrate Polymers*, *84*, 83–89.

Zheng, Y., Gao, T., & Wang, A. (2008). Preparation, swelling, and slow-release characteristics of superabsorbent composite containing sodium humate. *Industrial and Engineering Chemistry Research*, *47*, 1766–1773.

Yoshida, M., Asano, M., & Kumakura, M. A. (1989). New temperature-sensitive hydrogel with α-amino acid group as side chain of polymer. *European Polymer Journal*, *25*, 1197.

Yoshioka, T., Tsuru, K., Hayakawa, S., & Osaka, A. (2003). Preparation of alginic acid layers on stainless-steel substrates for biomedical applications. *Biomaterials*, *24*, 2088–2894.

Zhang, J., Wang, Li., & Wang, A. (2007). Preparation and properties of chitosan-g-poly(acrylic acid)/montmorillonite superabsorbent nanocomposite via in situ intercalative polymerization. *Industrial and Engineering Chemistry Research*, *46*, 2497–2502.

Zhang, Chi, & Easteal, A. J. (2003). Study of poly(acrylamide-co-2-acrylamido-2-methylpropane sulfonic acid) hydrogels made using gamma radiation initiation. *Journal of Applied Polymer Science*, *89*, 1322–1330.

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