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Effects of amylose/amylopectin ratio on starch-based superabsorbent polymers

Wei Zou[a], Long Yu[a,b,*], Xingxun Liu[a], Ling Chen[a], Xiaoqing Zhang[b], Dongling Qiao[a], Ruozi Zhang[a]

[a] *Centre for Polymers from Renewable Resources, ERCPSP, South China University of Technology, Guangzhou 510640, China*
[b] *Commonwealth Scientific and Industrial Research Organisation, Division of Materials Science and Engineering, Clayton, Vic 3169, Australia*

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ABSTRACT

Biodegradable superabsorbent polymers (SAPs) were prepared by grafting acrylamide onto starches then crosslinking with N,N′-methylene-bisacrylamide. This work focused on the effects of the amylose/amylopectin ratio of starches from the same source (corn) on the grafting reactions and performance of the resultant starch-based SAPs. To characterise each SAP, the acrylamide groups grafted onto the starch were detected by FTIR; grafting ratio and grafting efficiency were evaluated by a gravimetric method; and graft position and the length of the grafted segment were investigated by NMR. The relationships between the microstructures of the starches, and the graft reactions and performance of the SAPs were studied based on the amylose content in the starches. It was found that under the same reaction conditions, the grafting ratio and efficiency increased with increasing amylose content, which corresponds with water absorption ratio. NMR results indicated that the acrylamide group mainly grafted onto C6, and that the length of the grafted segment decreased with increasing amylopectin content in general, and in particular for waxy starch. The high molecular weight and branched structure of amylopectin reduced the mobility of the polymer chains and increased viscosity, which could explain the graft reactions and performance of the starch-based SAPs.

1. Introduction

Superabsorbent polymer (SAP), a kind of hydrogel, can absorb and retain extraordinarily large amounts of water or aqueous solution (Athawale & Lele, 2001; Kazanskii & Dubrovskii, 1992; Mathur, Moorjani, & Scranton, 1996). SAPs can generally be classified into two groups: synthetic (petrochemical based) or natural (e.g. polysaccharide and polypeptide based). Most current superabsorbents are produced from acrylic acid, its salts, and acrylamide (AM) via solution or inverse-suspension polymerisation techniques. Biodegradable SAPs have been attracting increasing attention, because of their reduced environmental impact. They have been widely used in hygienic products, particularly disposable diapers and napkins, in which they are used to capture secreted fluids such as urine and blood. Agricultural grades of SAPs in granular form are used for holding soil moisture in arid areas.

Many attempts have been made to use natural polymers, such as starches and their derivatives, in developing SAPs. The first starch-based SAP was produced through alkaline hydrolysis of starch-graft-polyacrylonitrile (Fanta, 1973), and subsequent starch-based SAPs have been developed by grafting starch with acrylic monomer and AM (Athawale & Lele, 1998; Karadag, Uzum, & Saraydin, 2005; Mostafa, 1995), and ε-caprolactone (Chen, Ni, et al., 2005). They can also be formed by chemical copolymerisation (Athawale & Lele, 2000; Chen, Park, & Park, 1999; Chen, Liu, & Ma, 2005) and the use of gamma-ray (Caykara, Bozkaya, & Kantoglu, 2003; Kiatkamjornwong, Chomsaksakul, & Sonsuk, 2000; Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002). In general, in graft copolymerisation a polysaccharide reacts with an initiator in either of two ways. Firstly, neighbouring OHs on the saccharide units and the initiator (commonly Ce^{4+}) will interact to form redox pair-based complexes. These complexes subsequently dissociate to produce carbon radicals on the polysaccharide substrate via homogeneous cleavage of the saccharide C–C bonds. These free radicals initiate the graft polymerisation of the vinyl monomers and crosslinker on the substrate. Alternatively, an initiator such as persulphate may extract hydrogen radicals from the OHs of the polysaccharide to produce the initiating radicals on the polysaccharide backbone.

Various starches have been used to produce starch-based SAPs, such as potato (Shaikh & Lonikar, 2009; Zhang & Chen, 2001; Zhang & Hu, 2002), sago (Han, Kumar, Rozman, & Noor, 2003), cassava (Nakason, Wohmang, Kaesaman, & Kiatkamjornwong, 2010), and corn (Cho & Lee, 2002; Fanta, Felker, & Shogren, 2004; Ma, Manolache, Sarmadi, & Denes, 2004; Samaha, Nasr, & Hebeish, 2005; Song, Zhang, Ma, Wang, & Yang, 2007). Corn starch and its derivatives are the most popular base materials used to develop starch-based SAPs (Kaith, Jindal, Jana, & Maiti, 2010; Meshram, Patil, Mhaske, & Thorat, 2009; Mostafa & Morsy, 2004; Salam,

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* Corresponding author at: CSIRO CMSE, Vic. 3169, Australia.
Tel.: +61 3 9545 2797; fax: +61 3 9545 1128.
E-mail address: long.yu@csiro.au (L. Yu).

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Pawlak, Venditti, & El-tahlawy, 2010; Xu, Wei, Feng, Wang, & Li, 2004; Xu, Wang, Wu, & Wang, 2006). High amylose maize starch (Yamaguchi, Watamoto, & Sakamoto, 1988) and high amylopectin waxy corn starches (De Bruyn et al., 2006) have been used in previous work. Comer and Jessop (2008) studied the grafting efficiency of starch-g-poly(methyl methacrylate) prepared by emulsion photopolymerisation without a photoinitiator using two types of starch (high amylose and high amylopectin), and found that there were no significant differences. Rath and Singh (1997) reported that amylopectin-g-polyacrylamide (amylopectin-g-PAM) performed better in flocculation than amylose-g-PAM and starch-g-PAM, and that fewer and longer PAM chains were most effective. However, there are no reported systematic investigations of the effects of amylose/amylopectin ratio on starches from the same source on the grafting reactions and performance of starch-based SAPs.

Although the detailed microstructures of starch are still being elucidated, it has generally been established that starch is a heterogeneous material containing two microstructures: linear (amylose) and branched (amylopectin). Amylose is essentially a linear structure of α-1,4 linked glucose units; and amylopectin is a highly branched structure of short α-1,4 chains linked by α-1,6 bonds. The linear structure of amylose makes its behaviour more closely resemble that of conventional synthetic polymers. The molecular weight of amylose is about $\times 10^6$, which is 10 times higher than that of conventional synthetic polymers. Amylopectin, on the other hand, is a branched polymer and its molecular weight is about $\times 10^8$, which is much higher than amylose. The high molecular weight and branched structure of amylopectin reduce the mobility of the polymer chains, and interfere with any tendency for them to become oriented closely enough to permit significant levels of hydrogen bonding. Furthermore, most native starches are semi-crystalline, having a crystallinity of about 15–45% (Zobel, 1988). Amylose and the branching points of amylopectin form amorphous regions. The short branching chains in the amylopectin are the main crystalline component in granular starch (Veregin, Fyfe, Marchessault, & Taylor, 1986). Starches with different amylose/amylopectin ratio have different phase transition behaviours (Liu, Yu, Xie, & Chen, 2006; Liu, Yu, Chen, & Li, 2007; Liu, Yu, Simon, Dean, & Chen, 2009; Liu et al., 2010; Xue, Yu, Xiu, Chen, & Li, 2008) and rheological properties (Chen, Yu, Kealy, Chen, & Li, 2007; Della Valle, Vergnes, & Lourdin, 2007; Xie et al., 2009).

This work focused on the effects of amylose content in starches from the same source (corn) on the grafting reactions and performance of starch-based SAPs. Corn starches with different amylose contents (waxy, 4.3%; maize, 29.0%; Gelose 50, 50%; Gelose 80, 80%) were used as model materials. In the work, the starch-based SAPs were produced by grafting AM onto the corn starch using ceric ammonium nitrate as an initiator and N,N′-methylene-bisacrylamide as a crosslinker. The relationships between the microstructures of the starches, and the grafting reactions and performance of the SAPs were investigated based on amylose content, grafting ratio, grafting efficiency and water absorption.

2. Experimental

2.1. Materials

Commercially available corn starches with different amylose/amylopectin contents were used as model materials in this work, viz.:

- Waxy (4.3% amylose content), supplied by Shanxi Jinli Industry Group Co., Ltd.
- Maize (29.0% amylose content), supplied by Huanglong Food Industry Co., Ltd.
- Gelose 50 and Gelose 80 (50 and 80% amylose content, respectively), supplied by Penford, Australia.

The amylose contents of the starches were determined by the iodine-binding method as described previously (Morrison & Laignelet, 1983), and the moisture contents were measured using an infrared heating balance (Model DHS-20) to heat the samples to 110 °C for 20 min. The moisture contents of the four corn starches prior to extrusion were 15.2, 15.5, 15.0 and 14.9%, respectively. All formulations were prepared on a dry weight basis.

All other chemicals used in the work were also commercially available, viz.:

- Acrylamide (AM), from Tianjin Kemeou Chemical Reagent Co., Ltd.
- N,N′-methylene-bisacrylamide (N-MBA), from Shanghai Yuanju Biotechnology Co., Ltd.
- Ceric ammonium nitrate (CAN), from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of starch-based SAPs

The starch-based SAPs were prepared as follows (Meister, 1981; Wu, Lin, Zhou, & Wei, 2000):

- Gelatinisation of 15.00 g corn starch in distilled water (80 mL) for 15 min at 100 °C (for waxy and maize starches) or 121 °C (for G50 and G80 starches), using a Bilon high-pressure steam steriliser.
- The gelatinised starch solution was transferred into a four -neck round-bottom flask, equipped with a mechanical stirrer, condenser and nitrogen line, and 0.50 g of CAN was added at 60 °C to react for 10 min under nitrogen atmosphere.
- A mixed solution of AM (15.00 g) and N-MBA (0.07 g) was added at 60 °C to react for 120 min under nitrogen atmosphere.
- Sodium hydroxide solution of NaOH (6.84 g) in distilled water (125 mL) was added to the flask at 90 °C for 120 min.
- The saponified product was washed with distilled water to a pH of 7 to remove ungrafted molecules, monomer and base, and then rewashed with ethanol.
- The samples were dried to a constant weight in an oven at 90 °C, and were subsequently filtered through a 60-mesh screen to obtain the SAPs powder. All graft reactions were carried out under the same conditions.

2.3. Characterisations

2.3.1. Fourier transform infrared spectrometer (FTIR)

An FTIR (Bruker Tensor) was used to detect the functional groups on grafted starches. The transmittance spectra were computed between 4000 and 400 cm^{-1} at 4 cm^{-1} resolution with the triangular apodisation function in the standard PE OPUS software. Symmetrical interferograms on 128 scans were co-added for each spectrum. All spectra were baseline corrected and normalised.

2.3.2. Determination of grafting ratio and grafting efficiency

The percentages of graft polymer, free polymer and soluble starch were determined through separation by washing using distilled water, and acid hydrolysis using HCl (Lanthong, Nuisin, & Kiatkamjornwong, 2006). A 1.0 g sample of dried product was stirred in 300 mL of distilled water at room temperature for 24 h. The mixture was centrifuged to separate the graft polymer and dehydrated with methanol to give a fine precipitate. It was then dried in an oven at 65 °C for 24 h, before being weighed to examine the amount of free polymers. The weight of polymer after the removal of free polymer was calculated from the amounts of free PAM as by-product. Acid hydrolysis was carried out in a 125 mL Erlenmeyer flask mounted with a condenser. A 0.5 g sample of the grafted polymer was refluxed in 50 mL of 1 M HCl at 90 °C for 2 h. The polymer was filtered and washed with distilled water to a pH of 7, and then it was dried. Iodine solution was applied to the residual starch (substrate) after acid hydrolysis to observe the completion of reaction. The percentage weight of PAM in the graft polymer, or the so-called "percentage add-on" (AO), was computed from the weight difference between the graft polymer and the soluble starch previously removed by the acid hydrolysis. The AO, grafting ratio (GR) and grafting efficiency (GE) were calculated based on, respectively:

$$\text{AO}\quad(\%) = \frac{\text{Weight of graft polymer} - \text{Weight of soluble starch}}{\text{Weight of graft polymer}} \times 100 \tag{1}$$

$$\text{GR}\quad(\%) = \frac{\text{Weight of starch grafted polymer}}{\text{Weight of starch}} \times 100 \tag{2}$$

$$\text{GE}\quad(\%) = \frac{\text{Weight of starch grafted polymer}}{\text{Weight of free polymer} + \text{Weight of polymer grafted}} \times 100 \tag{3}$$

2.3.3. Nuclear magnetic resonance (NMR)

High-resolution NMR experiments were conducted using a Varian NMR 300 system at a resonance frequency of 75 MHz for 13C. Solution 13C NMR spectra were measured using a 10 mm solution probe-head via conventional methods at room temperature. The chemical shifts were determined using TMS (tetramethylsilane) as internal reference.

2.3.4. Multiple water absorbent capacity

To measure the water absorbent capacity of the polymer gels, samples were immersed in distilled water for 24 h at ambient temperature, so that they were completely swollen. Excess water from a swollen gel sample was removed via a 200-mesh screen, before the gel was weighed. After the measurement of first water absorbent capacity the swollen gel was dried at 90 °C to a constant weight for second measurement. Multiple water absorbent capacity was measured by repeating the swell-dry cycles.

3. Results and discussion

3.1. FTIR detection of functional groups grafted on starches

The grafted starches were characterised by the functional groups using FTIR. Fig. 1 shows the FTIR spectra of the various native starches and the grafted starches. It can be seen that the spectra of all native starches exhibited a similar pattern (Fig. 1a), as reported previously (Kačuráková & Mathlouthi, 1996; Liu et al., 2010), i.e. O–H stretching absorption in the region of 3500–3200 cm^{-1} (broad, s), C–H stretching at 3000–2800 cm^{-1} (m), and wavenumbers of 1158, 1081 and 1015 cm^{-1} (s) for C–O–C stretching (a triplet peak of starches).

The FTIR spectra of all grafted starches also exhibited a similar pattern (Fig. 1b). The spectra of starch-g-PAM after water extraction showed all the absorption peaks of the native starches. Additionally, the peaks detected at 3425, 1658 and 1600 cm^{-1} indicated N–H stretching, C–O stretching and N–H bending of the amide bands, respectively, which are characteristics of the –CONH$_2$ group contained in AM (Lanthong et al., 2006; Pal, Nasim, Patra, Ghosh, & Panda, 2010; Sen & Pal, 2009; Sen, Kumas, Ghosh, & Pal, 2009). In addition, the peak at 1409 cm^{-1} indicated –C–N stretching and that at 765–710 cm^{-1} indicated a weak band of N–H out-of-plane bending (Lanthong et al., 2006; Sen et al., 2009; Sen & Pal, 2009), which are the typical absorption bands of the amide. The results indicated that PAM was successfully grafted onto all starches.

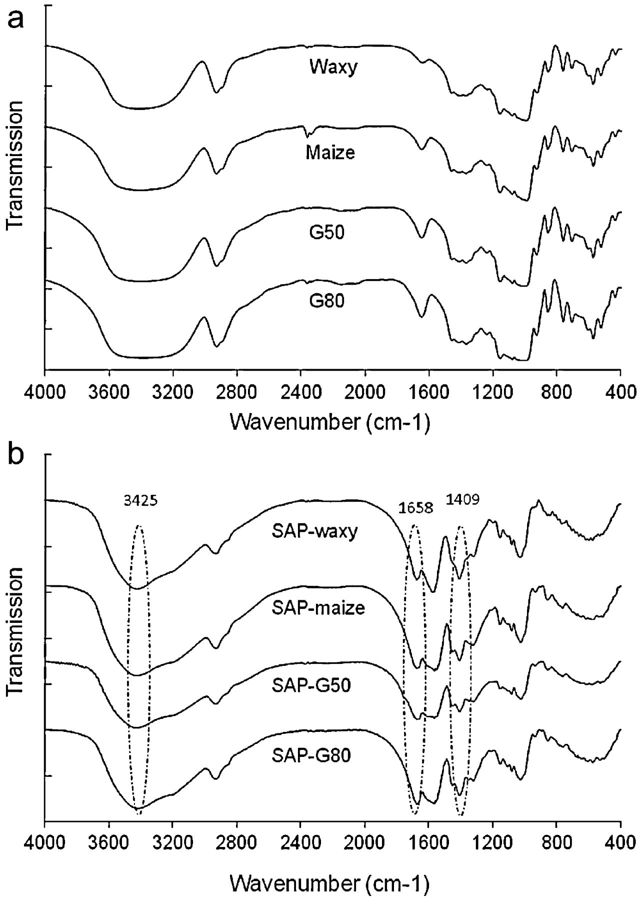

Fig. 1. FTIR spectra of various native starches (a) and starches-g-PAM (b).

3.2. Effects of amylose/amylopectin ratio on grafting ratio and efficiency

Grafting ratio and grafting efficiency were determined by a gravimetric method based on the separation and extraction of the various substances described in Section 2 (Section 2.3.2). In the results shown in Table 1, the add-on, grafting ratio and grafting efficiency were calculated using Eqs. (1)–(3), respectively. It can be seen that AO, GR and GE generally increased with increasing amylose content. Amylopectin is a branched polymer and it would appear that the double helix crystalline structure formed by its short branched chains (only 4–6 glucose), which are less flexible than the long chains in amylose, was torn apart during gelatinisation. Furthermore, these short branched chains remained in a regular pattern and retained a certain "memory" after gelatinisation (Yu & Christie, 2004). The short branched chains form gel-balls, each of which contains mainly the chains from the same sub-main chain. One amylopectin molecule could form a relatively separated large super-globe. It is suggested that the relatively tight structure of a gel-ball resists the chemical reaction of grafting.

In our experiments, the SAP-G50 samples achieved higher values for AO, GR and GE than SAP-G80. One possible explanation for this is that the G80 may not have been fully gelatinised during the first stage of the grafting reaction, since it has the highest gelatinisation temperature (Liu et al., 2006). It is suggested that the

Table 1
Effect of amylose/amylopectin ratio on the graft reactions and SAP compositions.

Samples	Grafting efficiency (%)	Grafting ratio (%)	Add-on (%)	Reaction ratio of C6 (%)	PAM segment length (number)
SAP-waxy	71.5 ± 1.6	105.2 ± 12.6	51.13 ± 3.1	53.2	4.4
SAP-maize	73.6 ± 3.8	123.0 ± 8.6	55.11 ± 1.7	21.6	12.7
SAP-G50	80.7 ± 2.7	161.7 ± 7.1	61.76 ± 1.0	18.3	19.8
SAP-G80	59.1 ± 2.2	144.6 ± 11.3	59.05 ± 1.9	20.1	16.3

multiphase transitions of G80 during heating, in particular at high temperature, could hinder the grafting reaction, and we intend to investigate this further in future work.

3.3. Effects of amylose/amylopectin ratio on graft position and length

The graft starches were characterised by NMR to study the graft positions and graft ratios on specific carbons in starches. Fig. 2 shows the peak assignments from the ^{13}C NMR spectra of a typical native starch (maize) and the different starch-g-PAM composites. Since the ^{13}C NMR spectra of PAM and starch-g-PAM have been widely reported previously (Gurruchaga, Goni, Varquez, Valero, & Guzman, 1992; Pal et al., 2010; Sen et al., 2009), the figures in this work focus on the carbons in starches. Carbons C1 to C6 in glucose can be clearly identified in native starches, as reported previously (Lan et al., 2010; Lawal, Lechner, Hartmann, & Kulicke, 2007). In Fig. 2, the low field peaks at $\delta = 103.2$ ppm are due to anomeric carbons (C1), while those at $\delta = 82.4$ ppm are due to C4. The peaks between 74 and 77 ppm are for carbon atoms (C2, C3, C5) connected by –OH groups. The peaks at $\delta = 63.5$ ppm are attributed to the carbon atoms (C6) of the CH_2OH group.

The ^{13}C NMR spectra of the grafted AM can be clearly identified. The peaks in the range 180–190 ppm represent amide carbonyl, and those at 35–50 ppm represent hybridised carbon atoms ($-(CH_2-CH)n$ units in the graft copolymer) (Pal et al., 2010; Sen et al., 2009). It should be noted that a new peak was detected at $\delta = 61.8$ ppm after AM grafting, which appeared close to the peak for C6 and indicated that some of the hydroxyl groups of C6 participated in the graft reaction (Zhang, Xu, & Wang, 2008). There were no observable differences in the peaks for other carbon atoms in starch, which means the graft reaction mainly occurred on C6.

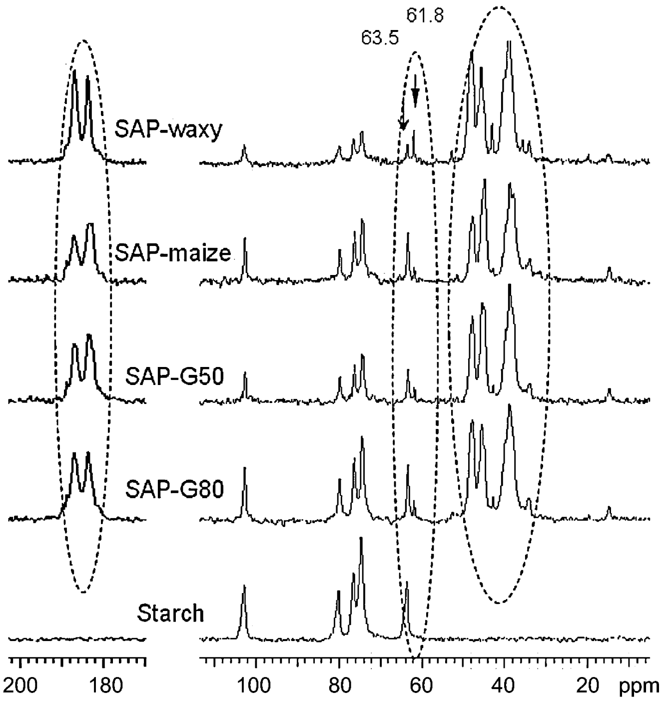

Fig. 2. ^{13}C NMR spectra of a typical starch (maize), and different starch-g-PAM composites.

The ratio of peaks at $\delta = 63.5$ ppm and at $\delta = 61.8$ ppm can be used to study the ratio of C6-AM grafting. Table 1 shows the compositions of the different SAP composites, in which “Add-on (%)” represents all the PAM segments in a SAP, and “Reaction ratio of C6” represents the number ratio of C6 linked to PAM in the SAP. All of the SAP samples contained about 51–62 wt% of PAM segments in the grafted SAP material. Note that 53.2% of C6 in the SAP-waxy was involved in the grafting reactions and was linked to the PAM segments in the grafted polymer, which is significantly higher than in the other three systems. Assuming that all the grafting occurred on C6 (as shown in Fig. 2), the length of grafted PAM segments in each system can be calculated, and this data is also listed in Table 1. The segment length for SAP-waxy was as short as 4.4, while the values for the other three systems ranged from 12 to 20. The high molecular weight and branched structure of amylopectin reduced the mobility of the polymer chains, resulting in higher viscosity and resistant chain growth.

3.4. Effects of amylose/amylopectin ratio on water absorption

The effects of amylose/amylopectin ratio on the water absorption of the starch-based SAPs is shown in Fig. 3. It can be clearly seen that the SAPs based on the starches with higher amylose content generally recorded higher water absorption, which corresponds with their higher grafting ratio and grafting efficiency. The high molecular weight and branched structure of amylopectin reduced the mobility of the polymer chains, and interfered with any tendency for them to become oriented closely enough to permit significant levels of hydrogen bonding. Furthermore, based on the NMR results, the longer grafted segments in high amylose starch may have also contributed to the higher water absorption.

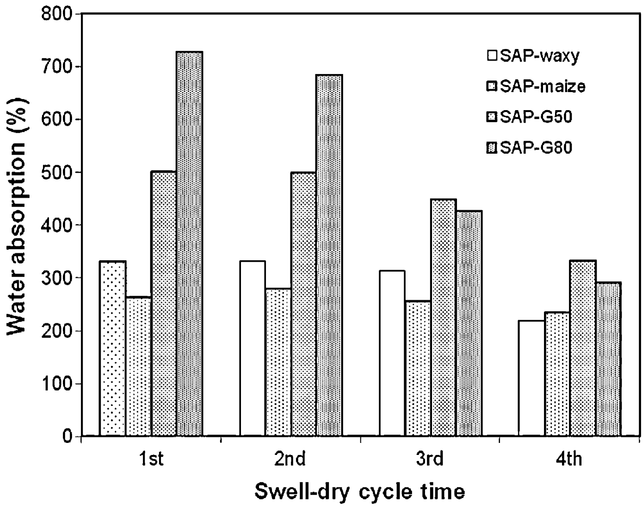

Fig. 3. Water absorption capacity of SAPs measured by multiple swell-dry cycles.

A previous study (Michaels, 1954) has shown that PAM with longer chains was more effective in the flocculation of clay suspensions, and a similar phenomenon has also been observed for graft copolymers of PAM on starches (Ghosh, Sen, Jha, & Pal, 2010; Pal et al., 2010; Rath & Singh, 1997, 1998). The rigid and branched structure of amylopectin hinders water movement in the gel, which results in lower water absorption.

4. Conclusions

The effects of amylose content in starches from the same source (corn) on the grafting reaction and performance of starch-based biodegradable superabsorbent polymers (SAPs) was investigated. Corn starches with different amylose contents (waxy, 4.3%; maize, 29.0%; Gelose 50, 50%; Gelose 80, 80%) were used as model materials. SAPs were prepared by grafting acrylamide onto starches, then crosslinking with N,N′-methylene-bisacrylamide.

The FTIR results indicated that polyacrylamide was successfully grafted onto all starches. The results of tests on the effects of amylose/amylopectin ratios showed a similar pattern of AO, GR and GE generally increasing with increasing amylose content.

NMR results indicated that the acrylamide group mainly grafted onto C6, and that the length of the grafted chains decreased with increasing amylopectin content, in particular for waxy starch. The high molecular weight and branched structure of amylopectin reduced the mobility of the polymer chains and interfered with any tendency for them to become oriented closely enough to permit significant levels of hydrogen bonding, resulting in higher viscosity and resistant chain growth.

The SAPs based on a higher amylose content recorded higher water absorption, which corresponded with their higher grafting ratio and grafting efficiency. The flexible linear chain structure of high amylose starches and the longer graft segments on them also contributed to this result.

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