

Preparation of Cassava Starch-based Superabsorbent Polymer Using a Twin-roll Mixer as Reactor^{*}

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Abstract Cassava starch-based superabsorbent polymer was successfully synthesized using a new technology that based on modification of a Haake twin-roll mixer as reactor. The cassava starch was first gelatinized then modified by grafting under external shear stress in the reactor. The torque and temperature curves as a function of time can reflect the variations in the reactor and also offer some information about the copolymerization reaction. The advantages of this system include starch modification can be carried out (1) with high starch concentration, (2) under controlled time and (3) smaller amount of sample (60 g) required. The technology provides useful guides for reactive extrusion. The starch grafted composites were characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) and thermal gravimetric analysis (TGA). The TGA was also used for determining the percentage of grafting ratio. The results show that the cassava starch has been successfully grafted with acrylamide then crosslinked by *N,N'*-methylene-bisacrylamide using this reactor. The ultimate water absorbent capacity of the cassava-based superabsorbent polymer impacted by various pH values illustrated that the acid and basic solutions inhibit the ability of imbibing water. Additionally, gel properties of the cassava-based superabsorbent polymer were investigated. It can be concluded that the structure of cassava gel is stable, while the three dimensional network of cassava-based superabsorbent polymer is rigid but its structure could not resist external force effectively and everlastingly since G' was decreased with increasing amplitude.

Keywords: Graft; Acrylamide; Superabsorbent; Extrusion; Starch; Cassava.

INTRODUCTION

Development of superabsorbent polymers (SAPs) has made remarkable progress due to the strenuous efforts by researchers for various utilization purposes during the last three decades^[1–5]. For examples, they have been used as retainers of water and solutes in the agricultural field based on its ability of keeping the materials moist and absorbing unnecessary excess water as for storage. Other superabsorbent polymers, such as pH and temperature sensitive hydrogels, are also used in control delivery systems for drugs and perfumes^[6–9]. Disposable diapers and sanitary napkins are alternative use of a superabsorbent polymer known as a water absorbing material. As most of those superabsorbent materials are used in disposable articles and most of them are disposed at landfills or by incineration, there is a perceived environmental problem with superabsorbent polymers. Incorporating starch into synthetic polymers has attracted increased attention, which not only reduces our dependence on

^{*} This work was financially supported by the National Natural Science Foundation of China (Nos. 31130042, 21174043, 31301554 and 31101340).

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Received December 13, 2013; Revised January 23, 2014; Accepted March 7, 2014

doi: 10.1007/s10118-014-1516-8

petrochemical-derived monomers but also provides materials that can biodegrade rapidly in the environment^[10, 11].

Traditionally, starch-based superabsorbent polymers grafted with acrylamide and acrylic acid were prepared by solution polymerization^[12, 13], inverse suspension polymerization, and emulsion polymerization. In the solution polymerization, the solvent acted as a heat sink and monomers grafted onto the starch backbone under the function of crosslink agent and initiated system. The polymerization is initiated thermally, by UV-irradiation, or by a redox initiator system. In inverse suspension polymerization, the monomer solution is dispersed in the non-solvent forming fine monomer droplets and the system is stabilized by the addition of stabilizer, in which spherical SAP microparticles with size range of 1 μm to 1 mm are prepared. The chemical reaction is initiated by radicals from thermal decomposition of an initiator. In polymerization by irradiation, ionizing high energy radiation, such as gamma rays^[14] and electron beams^[15], has been used as an initiator to prepare the starch-based SAPs. Kiatkamjornwong^[16] synthesized graft copolymerization of acrylamide and/or acrylic acid onto cassava starch by a simultaneous irradiation technique using gamma-rays as the initiator. In these cases, only about 10%–15% starch in water suspension is used in these conventional technologies, which results in low efficiency and large quantities of waste water.

Recently, the development of reactive extrusion for starch modification has attracted increased attention, and the technology has been reviewed by Xie *et al.*^[17] and Graeme^[18]. Compared with the traditional solution method, reactive extrusion has many advantages including high efficiency, accelerated processing rates, and less waste water. However, there are many concerns, like the possibility of jamming, the requirement of a certain amount of materials, and uncertainty of product handling, appeared when using an extruder in research work, especially a new system. In addition, conventional extruders have limitations due to barrier length when studying the effect of longer times (> 10 min) on modification reaction. We have been working on developing a reactor that can provide shear stress similar as extruder but can be easily controlled based on a internal mixer^[3, 4].

Cassava starch is cheaper compared with the potato and maize starches since the cassava tubers lack lipids and other extraneous compounds; the extraction of starch is easier and the yield is very high compared to cereal and other tuber starches. Furthermore, cassava starch is very pure and possesses characteristic features like bland taste and flavour and high paste clarity. Many works have reported about the synthesis of cassava-based superabsorbent polymers. For examples, Lanthong *et al.*^[10] synthesized biodegradable superabsorbent polymers by graft copolymerization of acrylamide (AM)/itaconic acid (IA) onto cassava starch *via* a redox initiator system of ammonium persulfate (APS) and *N,N,N',N'*-tetramethylethylenediamine (TEMED), in the presence of *N,N*-methylenebisacrylamide (*N*-MBA) crosslinking agent, sodium bicarbonate foaming agent, a triblock copolymer of polyoxyethylene/polyoxypropylene/polyoxyethylene as a foam stabilizer. Superabsorbent polymers (SAPs), which can imbibe 425.2 g/g water, were prepared from cassava starch by graft copolymerization of acrylamide on to starch using ceric ammonium nitrate (CAN) as free radical initiator, followed by alkali saponification^[19]. Also, response surface methodology (RSM) was employed for the synthesis of cassava starch-graft-poly(acrylamide) using ceric ammonium nitrate as free radical initiator^[20].

The purpose of this work is to develop a smaller batch reactor that can serve as an important preliminary instructor for the development of a new starch modification system using an extruder. Cassava starch was used as a modal material that grafted with acrylamide then crosslinked by *N,N*-methylene-bisacrylamide (MBA) to produce biodegradable superabsorbent polymers using this reactor system. The cassava starch grafted composites were characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) and thermal gravimetric analysis (TGA). The TGA was also used for determining the percentage of grafting ratio. The ultimate water absorbent capacity of the cassava-based superabsorbent polymer impacted by various pH values was evaluated. Gel properties of the cassava-based superabsorbent polymer were also investigated by a rheometer.

EXPERIMENTAL

Establishing Reactor Based on a Twin-roll Mixer

A Haake rheometer incorporating a twin-roll mixer was modified as a reactor system that can provide high shear stress to handle high viscose materials. Figure 1 shows a schematic presentation and photos of reactor based on a twin-roll mixer. Since the graft polymerization between the starch and the acrylamide/acrylic acid needs oxygen free conditions, the gaps of the three parts of the twin-roll mixer were sealed by Teflon films, and the feeder on top was sealed by a silicon rubber cover to prevent moisture loss during reaction. Also, there is a funnel used for adding liquid chemicals on the silicon rubber cover and a tube connected with nitrogen gas used for flush out air. The holes between gear box and the two rollers were sealed by rubber rings.

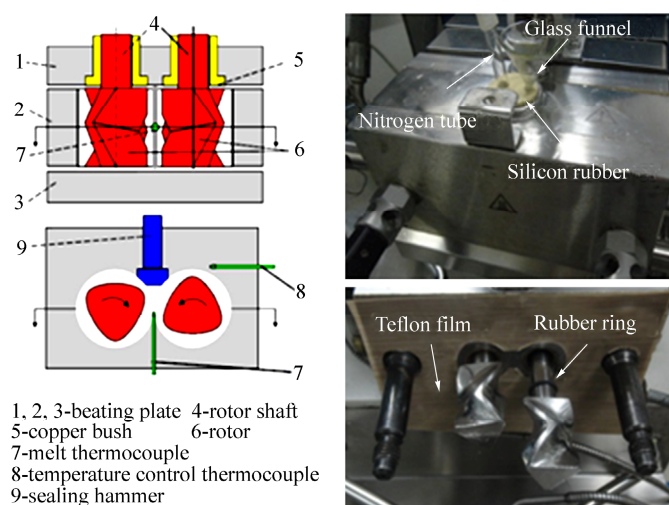


Fig. 1 Photo and schemata of reactor based on a twin-roll mixer

Materials

All materials used in this work are commercially available, viz.:

i) Cassava starch, from Huanglong Food Industry Co., Ltd. China; ii) Acrylamide, sodium hydroxide from Tianjin Kermel Chemical Reagent Co., Ltd. China; iii) *N,N*-Methylene-bisacrylamide, from Shanghai Yuanju Biotechnology Co., Ltd. China; iv) Ceric ammonium nitrate (CAN), from Sinopharm Chemical Reagent Co., Ltd. China.

Graft Polymerization

i) Dried starch (12 g), acrylamide (18 g) and distilled boiling water (45 g) were added into the mixer at 80 °C and on 80 r/min for 10 min to gelatinize the starch under shear stress.
 ii) Then nitrogen was introduced into the mixer to flush out oxygen and temperature of the mixer was decreased to 60 °C for the starch modification at the same time.
 iii) After 10 min, CAN (0.75 g) and MBA (0.14 g) solution was added into the batch at 60 °C to initial graft copolymerization and crosslinking of polymer chains, respectively.
 iv) After the reaction finished (about 10 min), NaOH (10.14 g) was added to the mixer at 60 °C and on 80 r/min to turn the amide group into carboxyl. Starch-based superabsorbent polymer was synthesized by twin-roll Haake Mixer.

Fourier Transform Infrared Spectrometry (FTIR)

The functional groups on grafted starches were detected by Bruker Tensor. The transmittance spectra were computed with the triangular apodisation function between 4000 and 400 cm^{-1} at 4 cm^{-1} resolution in the standard PE OPUS software. Symmetrical interferograms on 128 scans were co-added for each spectrum. All

spectra were baseline corrected and normalized.

Nuclear Magnetic Resonance (NMR)

High-resolution NMR experiments were conducted using a Varian NMR 300 system at a resonance frequency of 75 MHz for ^{13}C . Solution ^{13}C -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.

Thermal Gravimetric Analysis (TGA)

A Perkin Elmer Diamond thermogravimetric analysis (TGA) system was used to determine the grafting ratio of the graft copolymer, according to the identified decomposition temperatures of the starch and grafted groups. Samples investigated were heated from 35 °C to 600 °C at 10 K/min in a nitrogen atmosphere.

Determination of Add-on (AO) and Water Absorbent Capacity (WAC)

The starch ratio (SR), the percentage weight of PAM in the graft polymer, or the so-called “percentage add-on” (AO) were computed through TGA.

Water absorption capacity (WAC) of the polymer gels was measured by immersing samples in distilled water for 24 h at ambient temperature. Each swollen gel sample was passed through a 200-mesh screen to remove excess water, and then weighed.

Water Absorbent Capacity in Various pH Solutions

200 mg starch-based SAP (Cassava-SAP, 200 mesh) were packed into a bag made by 300 mesh screen cloth and dispersed in distilled water and kept in 200 mL various pH solutions for 1 h. Stock NaOH (pH 14.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Next, a centrifuge separated the free water from the starch-g-PAM under 4000 r/min for 10 min, and then weighted.

Dynamic Rheometry

The rheological properties of the gels of native cassava and grafted starch were determined using a controlled stress rheometer (Rheostress RS600, Haake, Germany) with parallel geometry (35 mm diameter). A gap of 1 mm was employed. To measure the rheological properties of samples, cassava starch and cassava-based SAP were prepared as follows: 30 mg cassava-based SAP was dispersed in 3mL distilled water and kept in ambient temperature for 12 h. Starch paste (10 wt%) was prepared at 90 °C for 30 min in the water bath.

RESULTS AND DISCUSSTION

The reactor has been developed successfully based on the Haake twin-roll mixer and was used to gelatinize starch and carry out chemical modification. Figure 2 shows a typical curve of starch gelatinization and chemical modification based on the measurement of torque and temperature variation with time in the mixer. The four stages in the curve represent the four steps during the copolymerization reaction. At beginning, temperature in the mixer dropped due to the cold materials added and then it got back to the initial temperature gradually. Correspondingly, there is a small sharp peak of torque that represents materials loading. The temperature in the mixer was cooled to 60 °C for graft reaction in a time range of about 10 min. Since the reaction is exothermic, the temperature increases rapidly in the third stage. At the same time the torque also increase since viscosity is increased significantly after grafting with AM, which indicates the copolymerization occurred. The reaction was taken about 10 min. Finally, NaOH was added into the mixer to saponify the SAP. Since neutralization reaction the temperature was increased sharply in the fourth stage. The torque also increased significantly since the water absorption capacity of the graft starch increased dramatically due to the saponification, which results in decrease of free water in the mixer and increase of the gel strength.

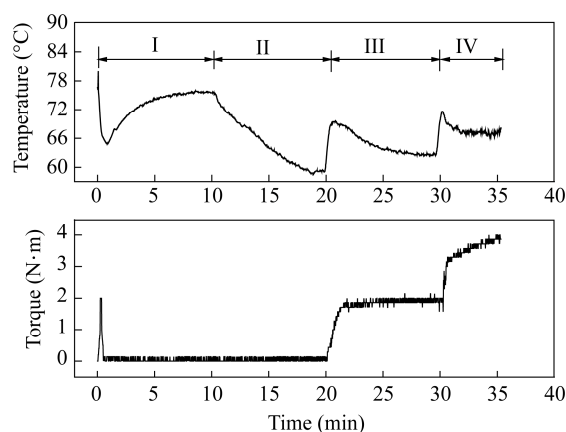


Fig. 2 Typical reaction curves of torque and temperature in the reactor for the starch graft polymerization

The native cassava starch and grafted starch were characterized by the functional groups using FTIR. Figure 3 shows that the spectrum of cassava exhibits typical absorption bands, as reported previously^[21, 22], *i.e.* O—H stretching absorption in the region of 3500–3200 cm^{-1} , C—H stretching at 3000–2800 cm^{-1} , and wavenumbers of 1158, 1081 and 1015 cm^{-1} for C—O—C stretching (a triplet peak of starches). All the absorption peaks of the native starch were shown in the spectrum of starch-g-PAM. 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 —CONH₂ group contained in acrylamide^[10, 23–25]. In addition, there are typical absorption bands of amide in the spectra of starch-g-PAMs, that is, the peak at 1409 cm^{-1} indicating —C—N stretching and 765–710 cm^{-1} indicating a weak band of N—H out-of-plane bending. The results indicated that PAM was successfully grafted onto starches. For the sample studied, this procedure was repeated for three times.

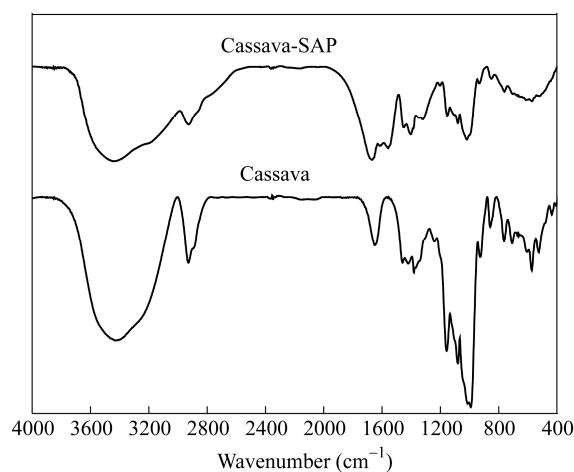


Fig. 3 FTIR spectra of cassava and cassava-SAP

The graft starch was also characterized by NMR to confirm graft modification on specific carbons in starches. Figure 4 shows the peak assignments from the ^{13}C -NMR spectra of native cassava starch and a cassava starch-g-PAM sample. Since the ^{13}C -NMR spectra of PAM and starch-g-PAM have been widely reported previously^[10, 24, 26, 27], the figures in this work focus on the carbons in starches. Carbons C1 to C6 in glucose can be clearly identified in the native starch, as reported previously^[28, 29]. In Fig. 4, the low field peaks at $\delta = 103.2$ are due to anomeric carbons (C1), while those at $\delta = 82.4$ are due to C4. The peaks between $\delta = 74$ and 77 are

the carbon atoms (C2, C3, C5) connected by $-\text{OH}$ groups. The peaks at $\delta = 63.5$ are attributed to the carbon atoms (C6) of the CH_2OH group.

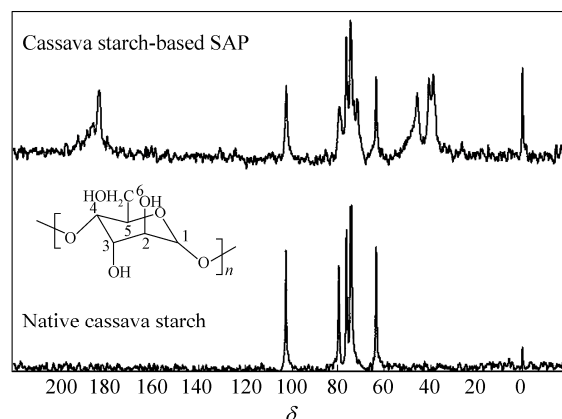


Fig. 4 NMR spectra of native cassava and cassava starch-based SAP

The ^{13}C -NMR spectra of the grafted AM can be clearly identified. The peaks in the range of $\delta = 180\text{--}190$ represent amide carbonyl, and those at $\delta = 35\text{--}50$ represent hybridised carbon atoms ($-(\text{CH}_2-\text{CH})_n$ units in the graft copolymer)^[25, 26]. It should be noted that a new peak was detected at $\delta = 61.8$ 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^[26, 30]. There were no observable differences in the peaks for other carbon atoms in starch, which means the graft reaction mainly occurred on C6.

The percentage of add-on and the starch ratio on the grafted polymer were calculated by TGA weight loss measurements. Figure 5 presents the TGA thermograms of the dried cassava starch, as well as cassava-SAP. The thermogravimetric curve for the native cassava shows that significant weight loss began at about 290°C . Correspondingly, there is a peak in the derivative thermogravimetric curve at about 340°C due to cassava decomposition. It also can be seen that three degradation steps occurred for the grafted starch, with the first peak P1 at about 70°C being assigned to the loss of water in the samples, the second peak P2 at about 300°C due to the thermal degradation of starch backbone of cassava-based SAP, and the third peak P3 standing for the polyacrylamide chain decomposition or chain scission. Correspondingly, W1, W2, W3 in the TG curve represents the weight loss of water, the starch backbone and the polyacrylamide, respectively. A phenomenon should be pointed out that the decomposition temperature for the modified starch was lower than the one for the

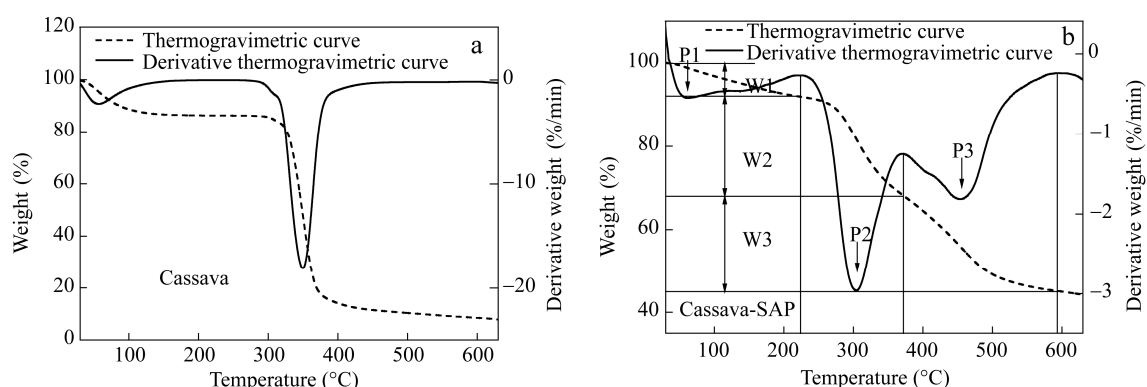


Fig. 5 TGA and DTA curves of cassava (a) and cassava-SAP (b)

native starch, which can be explained by the destruction of the crystalline structure in the starch granules during gelatinization and modification^[31, 32]. Similar results have previously been observed^[10, 33, 34]. The percentage weight loss detected by TG for starch and starch-based SAP can be converted to the percentage of starch and PAM grafted onto the starch respectively. Add-on was calculated based on W2 and W3 in Fig. 5 by^[26]:

$$\text{Add-on (\%)} = \frac{\text{Weight loss at W3} \times 100}{\text{Weight loss at (W2 + W3)}} \quad (1)$$

$$\text{Starch ratio (\%)} = 100 - \text{Add-on(\%)} \quad (2)$$

Table 1 gives the results. It is seen that Add-on, the ratio of acrylamide grafted onto the starch-based superabsorbent polymer, is about 50%, which depends on the ratio of starch and monomer, the amount of initiator and the cross-linking agent^[8].

Table 1. AO, SR and WAC of cassava-SAP

Sample	Add-on (%)	Starch ratio (%)	Water absorbent capacity
Cassava-SAP	50.21	49.79	80.80 ± 0.6

Water absorbent capacity of starch-based superabsorbent polymer was measured according to the tea-bag method. It can imbibe about 80 times amounts of water in the ambient temperature under the normal pressure.

Figure 6 shows the influence of the solution pH (1–14) on the water absorption capacity of the synthesized graft copolymer, which has the highest water absorption in distilled water (pH 7). The water retaining capacity of starch-based SAP decreased gradually with the increasing of the concentration of H^+ and OH^- in the swelling media. The primary mechanism of water absorption is the diffusion of water molecules into the three dimensional network of starch-based SAP coupled with relaxation of the polymer chains. The initial diffusion of water inside the hydrophilic polymer causes ionization of the neutralized acrylate groups into negative carboxylate ions and positive sodium ions, which causes osmotic effects between the inside and outside of the polyelectrolyte network. Also, the negative electrical charges along the polymer backbone cause mutual repulsion of carboxylate ions. This in turn results in expansion and swelling of the polymer chains due to associated water^[35]. The inhibitor effect of acid on the water absorbent capacity of starch-based SAP has a relationship with the hydrolysis equilibrium as Eq. (3):



When a relatively small amount of sample was immersed in a large volume of water with great deal of H^+ , the hydrolysis equilibrium should shift to the right-hand side to provide little COO^- ions in the starch-based SAP network, which can decrease the osmotic effects in the system and naturally decrease the amount of water absorbed by the starch-based superabsorbent polymer. The swelling-loss of the highly basic solutions (pH 8–14)

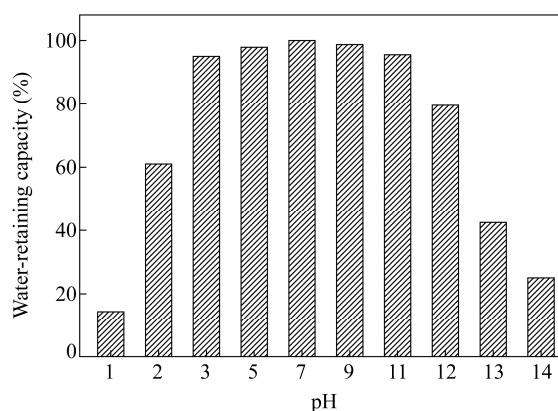


Fig. 6 Effect of pH on water-retaining capacity measured at room temperature (25 °C)

has a relationship to the charge screening effect of excess Na^+ in the external solution which shields the carboxylate anions from each other and prevents anion-anion repulsion^[8]. Similar pH swelling behaviors have been reported in the case of other hydrogel systems^[36–38]. The water absorbent capabilities of the samples in this work are not as high as the results reported by conventional methods, and need to be improved through optimizing processing conditions.

Figure 7 presents the rheological properties of both native and modified cassava starch. Figure 7(a) shows the variations of storage modulus (G') and loss modulus (G'') with strain under 1 Hz at 25 °C for cassava and cassava-based superabsorbent polymers respectively. It is seen that native cassava starch displayed an apparent linear viscoelastic region (LVR), where the strain is linear with the stress. However, the LVR range of starch-based superabsorbent polymer is relatively narrower. With the strain increasing, shear thinning sets in and the structure of cassava-based superabsorbent polymer starts to be destroyed. The conclusion can be made that the structure of cassava gel is stable, while the three dimensional network of cassava-based superabsorbent polymer is rigid but its structure could not resist external force effectively and everlastingly with the decreasing of G' as a function of amplitude.

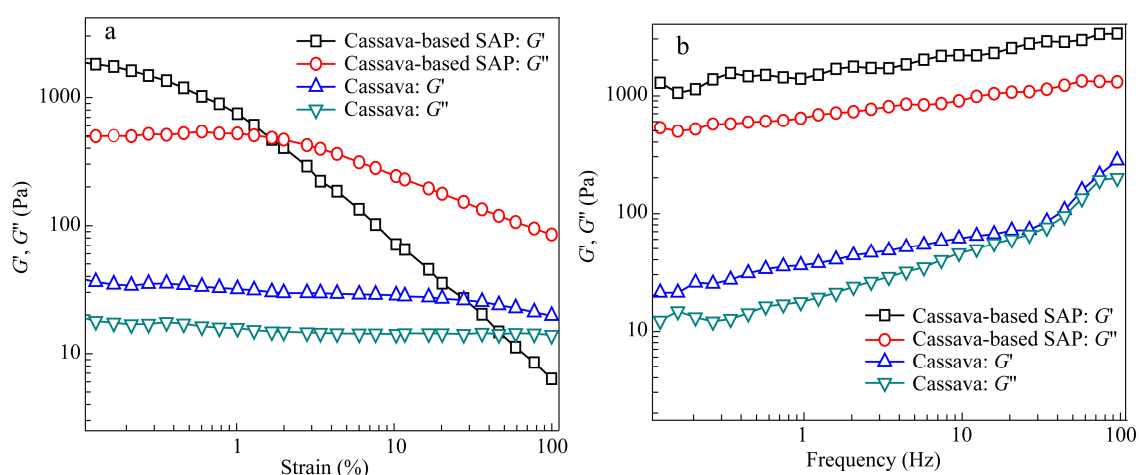


Fig. 7 Gel properties of the samples: (a) G' and G'' curves under 1 Hz at 25 °C and (b) G' and G'' at 25 °C with 0.5% strain

The frequency scanning curves of G' , G'' of cassava and cassava-based superabsorbent polymers are shown in Fig. 7(b). G' and G'' reflect the amount of energy stored (elastic response) by the system and the energy dissipated (viscous response) by the system respectively. It is seen that the G' and G'' of the cassava starch-g-PAM composites increased slightly as the function of frequency. The G' value of starch-g-PAM sample is higher than G'' , which indicates the cassava and cassava-based superabsorbent polymer display a predominantly solid-like behavior, and the elastic response of the material is stronger than the viscous response.

CONCLUSIONS

A starch modification reactor has been established based on a Haake rheometer with a twin-roll mixer. The torque and temperature curves as a function of time can reflect the variations in the reactor and also offer some information about the copolymerization reaction. The reactor provides shear stress similar as an extruder. Cassava starches was used as modal material and successfully grafted with acrylamide then crosslinked by N,N' -methylene-bisacrylamide to produce biodegradable superabsorbent polymers using the reactor. FTIR, NMR and TGA studies indicate that PAM has successfully grafted onto the cassava starch. Both the acid and basic solutions decreased the amounts of water imbibed by the cassava-based superabsorbent polymer. The water absorbent capability needs to be improved through optimizing processing conditions. The cassava and cassava-based superabsorbent polymer displayed a predominantly solid-like behavior, and the elastic response of the

material was stronger than the viscous response. Optimized graft conditions, such as concentration, ratios, temperature and time *etc.*, will be studied to achieve higher water absorbent capacity.

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