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Preparation and swelling of polymeric absorbent containing hydroxamic acid group from polymer grafted sago starch

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Abstract

Poly(methyl acrylate) (PMA) grafted sago starch was prepared from the reaction between methyl acrylate and sago starch by free radical initiating process in which ceric ammonium nitrate (CAN) was used as an initiator. The common procedure was used to prepare a new polymer containing hydroxamic acid functional group from PMA grafted sago starch and hydroxylamine under alkaline solution. The PMA grafted sago starch and poly(hydroxamic acid) was characterized by FT-IR spectroscopy. The water absorbency or swelling of the poly (hydroxamic acid) absorbent was measured as a function of different sago starch concentration in absorbent. It was observed that the swelling in distilled water and various salt solutions increases with decreasing sago starch concentration. The maximum absorbency in water was 192 g water g^{-1} at 31% sago starch content in absorbent. The absorbency in the various salt solutions decreases with the increasing salt concentration in solution. At the same salt concentration in solution, the swelling has the following tendency: $Na^+ > Ca^{2+} > Fe^{3+}$. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(methyl acrylate); Ceric ammonium nitrate; Sago starch

1. Introduction

Absorbents are widely used in many products such as disposable diapers, feminine napkins, soil for agriculture, water blocking tapes, medicine for drug delivery system, absorbent pads, etc. where water absorbency or water retention is important (Lee & Wu, 1997; Sakiyama, Chu, Fujii & Yano, 1993; Shiga, Hirose, Okada & Kurauchi, 1992, 1993; Tanaka, 1979; Yoshida, Asano & Kumakura, 1989). Several types of hydrophilic polymers such as ampholytic, anionic, cationic, nonionic and zwitterionic polymers have the potential swelling character, i.e. the swelling in salt solution is more than in pure water (Ogawa, Yamano & Miyagawa, 1993). Flory (1953) explained the mechanism of absorption of water for hydrophilic polymers in nonionic network or ionic network structure. The effect of initial total monomer concentration was investigated on the swelling and deswelling behavior of the gel in a saline solution (Lee & Yeh, 1997). The complete swelling-time curves serve a much more sophisticated purpose, that of calculating diffusion coefficients from swelling data. The polymeric absorbents containing hydroxamic acids are not reported in the literature, although some ampholytic monomers and cationic monomers containing absorbent polymer were studied comprehensively (Baker, Hong, Harvey, Blanch & Prausnitz, 1994; Katayama & Ohata, 1985). In the present study, we have prepared a series of poly(hydroxamic acid) absorbent from poly(methyl acrylate) (PMA) grafted sago starch, which contained various concentrations of sago starch. We studied the swelling behavior of these absorbents in distilled water and various salt solutions.

2. Experimental

2.1. Materials

Sago starch was purchased from Tepung Sago Ind. (Malaysia). To remove inhibitor, methyl acrylate (Merck) was passed through a column, which was filled with chromatographic grade alumina. Analytical reagent grade ceric ammonium nitrate (CAN) (BDH), hydroxylamine hydrochloride (Fluka) and other chemicals were used.

2.2. Graft copolymerization

To obtain various sago starch concentrations in the PMA grafted copolymers, a variable quantity of sago starch was used in the copolymerization. Four grafting reactions were carried out for absorbent preparation and the parameters are shown in Table 1. Detailed description of the procedure was

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Table 1
Experimental conditions for grafting of methyl acrylate (MA) onto sago starch using CAN

Experiment no.	Sago starch (g)	0.1 M of CAN (ml)	Methyl acrylate (ml)	Distill water (ml)	H_2SO_4 conc. (ml)	Reaction temp. °C	Reaction period (h)
1	4	20	16	200	4	50	1
2	6	20	16	200	4	50	1
3	8	20	16	200	4	50	1
4	10	20	16	200	4	50	1

presented elsewhere (Lutfor, Sidik, Wan, Zaki, Mansor & Haron, 2000).

2.3. Preparation of poly(hydroxamic acid) absorbent

Preparation of hydroxylamine (NH_2OH) solution: about 21.10 g of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) was dissolved in 150 ml methanolic solution (methanol:water; 5:1). The HCl of NH_2OH was neutralized by NaOH solution and the precipitate of NaCl was removed by filtration. The pH of the reaction solution was adjusted to pH 13 by the addition of NaOH solution. The reaction medium was methanol to water ratio of 5:1.

The absorbent preparation was carried out in a 1 l two neck flask, which was equipped with a mechanical stirrer, condenser and thermostat water bath. Exactly 10.00 g of PMA each grafted sago starch copolymer containing different % of sago starch was placed into the flask and hydroxylamine solution was added to the flask. The reaction was carried out at 72°C and 2 h duration. After completion of the reaction, the absorbent was separated from solution by filtration and washed several times with methanolic solution (methanol:water; 4:1). Then the absorbent was treated with 100 ml of methanolic 0.2 M HCl solution at least 5 min. Finally, the absorbent was filtered and washed several times with methanol: water (4:1), then dried at 50°C to constant weight.

2.4. Swelling kinetics of absorbent

Exactly 0.050 g of the dry absorbents containing different % of sago starch were weighed and packed into tea bags, and soaked into 50 ml distilled water. After the specific time intervals, the sample was removed from water. Adherent moisture was removed by tissue paper within 30 s and the swollen sample was weighed. An empty tea bag was used as a blank. The swelling parameters were obtained by the following formula.

$$\text{Swelling} = (M_t - M_\infty)/M_\infty \tag{1}$$

where M_t is the mass of swollen absorbent at time t and M_∞ the initial mass of absorbent.

2.5. Swelling equilibrium in various salt solution

Three series of swelling experiments were carried out in NaCl, $CaCl_2$ and $FeCl_3$ solutions and each series of salt concentrations were 0.1, 0.01, 0.001, 0.0005 and 0.0001 M. Exactly 0.050 g of dry absorbent samples were immersed in 50 ml of different salt solutions for 12 h. After 12 h, the samples were removed and the adherent moisture was removed by tissue paper immediately and the swollen absorbent weighed. The effect of saline solutions on water absorbency was determined using Eq. (1).

3. Results and discussion

3.1. Analysis of FT-IR spectra

Infrared spectrum of sago starch is shown in Fig. 1(a); it indicates the characteristic absorption bands of starch at 3402 and 1646 cm^{-1} due to O–H stretching and bending modes, respectively. Additional characteristic absorption bands of sago starch appear at 2930 and 1024 cm^{-1} due to C–H stretching and bending, respectively. IR spectrum of purified PMA grafted sago starch shows a new absorption band of PMA at 1741 cm^{-1} of C═O due to stretching mode in addition to the same absorption bands of sago starch (Fig. 1(b)). In Fig. 1(c), the C═O band of 1741 cm^{-1} disappeared and formed a new band of hydroxamic acid of C═O at 1646 cm^{-1}, and amide II band of N–H at 1568 cm^{-1}. Elemental analysis shows that N_2 content was 8.35%, but the calculated value is higher (10.4%), and a little unreacted C═O of PMA was present in the products; therefore a shoulder was observed in Fig. 1(c). However, these new spectra suggest that the material is poly(hydroxamic acid) from PMA grafted sago starch.

3.2. PMA grafted sago starch

The reaction mechanism of sago starch and methyl acrylate by ceric ion initiation was presented elsewhere (Lutfor et al., 2000). Four grafted copolymer products were prepared and the parameter used in Table 1. After the preparation of the grafted copolymer, the products were weighed and % PMA in the copolymer was calculated from the equation described elsewhere (Lutfor et al., 2000). The % sago starch concentrations in the grafted copolymers were calculated based on the known amount of sago starch used in Table 1. Therefore, 31, 43, 56 and 66% sago starch were found in the grafted copolymers at experiment 1, 2, 3 and 4, respectively (Table 1). These grafted copolymers containing different amounts of sago

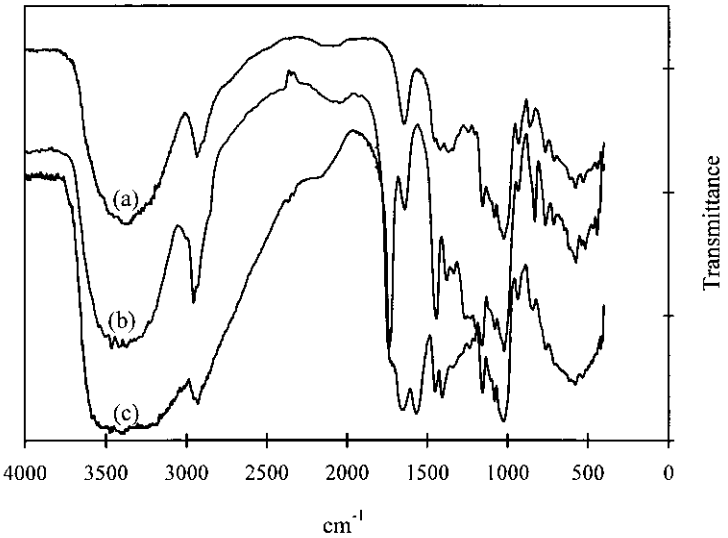


Fig. 1. FT-IR spectrum of: (a) sago starch; (b) PMA grafted sago starch; and (c) Poly(hydroxamic acid).

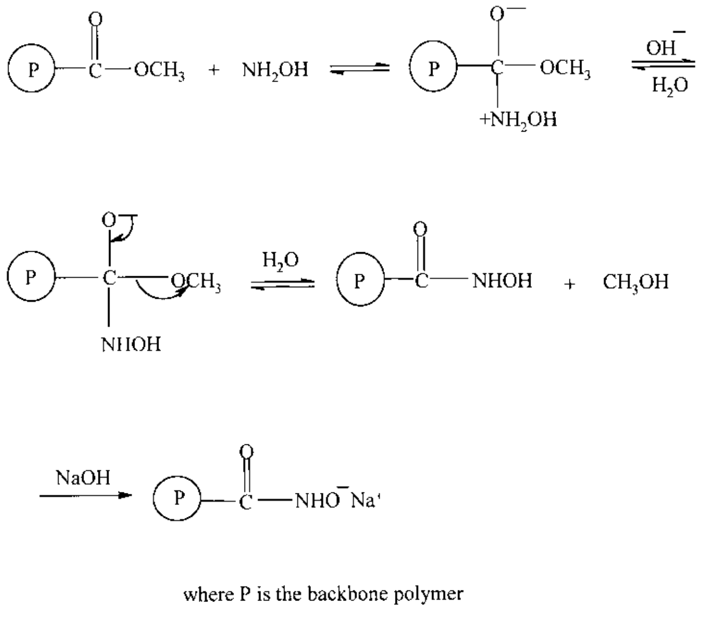
starch were used in the preparation of poly(hydroxamic acid) absorbent.

3.3. Poly(hydroxamic acid) absorbent

A series of poly(hydroxamic acid) was prepared from the grafted copolymers. The common method was used for hydroxamic acid preparation, which is the reaction between an ester and hydroxylamine in an alkaline medium. This method has been used to prepare poly(hydroxamic acid) from poly(acrylate ester) and hydroxylamine (Haron, Wan, Zaizi & Anuar, 1994; Kern & Schulz, 1957; Vernon & Eccles, 1976). The reaction mechanism of poly(acrylate ester) and hydroxylamine was presented in Scheme 1 (Reaction mechanism of poly(hydroxamic acid) with hydroxylamine in an alkaline medium), based on the mechanism suggested by Domb, Cravalho and Langer (1988).

3.4. Effect of sago starch concentration in the absorbent on the kinetics of swelling

The swelling of absorbents containing different % of sago starch were measured by tea bag method and the amounts of swelling were plotted as function of time (Fig. 2). The maximum swelling was 192 g water g^{-1} when 31% sago starch was used in the absorbent. The swelling decreased with the increase of sago starch concentration. The equilibrium swelling was reached at 120 min, approximately.



where P is the backbone polymer

Scheme 1.

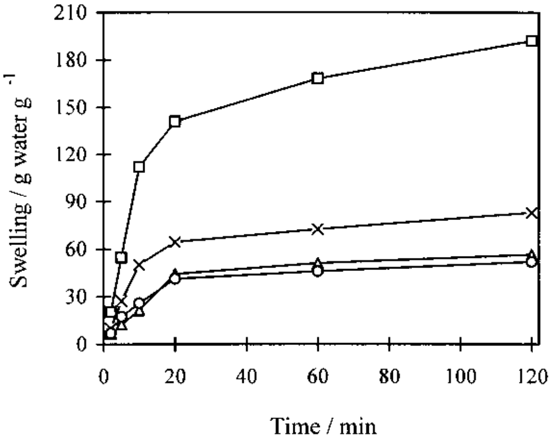


Fig. 2. Plots of swelling of absorbent in distilled water as a function of time at different sago starch % (-□- sago 31%; -×- sago 43%; -△- sago 56%; -○- sago 66%).

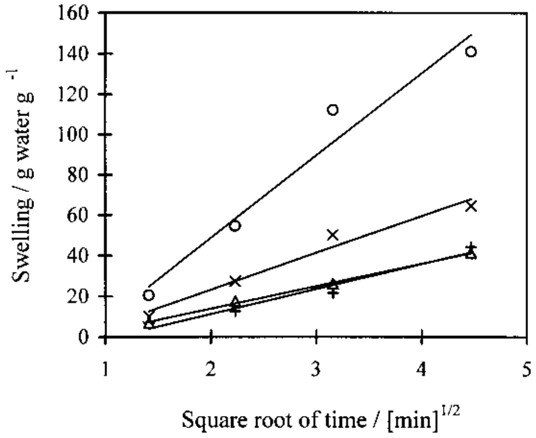


Fig. 3. Plots of swelling of absorbent in distilled water as a function of square root of time at different sago starch % (○ sago 31%; × sago 43%; + sago 56%; − sago 66%).

The swelling rate coefficients (k_s) were determined by the plotting of swelling as a function of square root of immersion time $(\text{min})^{1/2}$ (Fig. 3). The swelling rate coefficients were estimated from the initial stage of swelling (Saraydin, Karadag & Guven, 1995) and these rate coefficients were calculated from the slope of the lines (Fig. 3) and presented in Table 2.

The nature of diffusion of water was determined according to Fick's law, which was extended by Crank (1975).

$$F = kT^n \quad (2)$$

Here, $F = M_t/M_\infty$ where M_t is swelling at time t and M_∞ is equilibrium swelling.

Here, F denotes the amount of solvent fraction at time T, k is a constant incorporating characteristics of the macromolecular network system and the penetration, and n is diffusion exponent, which was indicative of the transport mechanism. This equation was applied to the initial stages of swelling and plots of ln F verses ln T are presented in Fig. 4. The values of exponent n and k were calculated from the slope and intercept of the lines, respectively (Fig. 4) and the parameters are listed in Table 2.

A useful classification scheme for the nonFickian diffusion and sorption associated with polymers is extended slightly by Crank (1975). The number n is meant to determine the type of diffusion and it was found over 0.50 (Table 2). Hence, the diffusions of water into the absorbent were nonFickian character in all the experiments.

Table 2
Swelling kinetics of poly(hydroxamic acid) absorbent at different sago starch concentration (%) (where, n is the diffusion exponent, and k is a constant incorporating characteristics of the macromolecular network system and its penetration)

Sago starch (%)	Swelling (g water g^{-1})	Swelling rate coefficient (k_s)	n	k
31	192.0	40.71	0.865	2.718
43	83.15	18.06	0.834	2.607
56	56.54	12.25	0.753	2.595
66	52.00	10.99	0.736	2.382

It was observed that swelling of absorbent was higher (192 g water g^{-1}) at lower sago starch concentration and swelling rate coefficient, n and k values were greater than those with high sago starch content in absorbent (Table 2). From the results, one can infer that sago starch contributed as the cross-linking agent. The lower cross-link content absorbents are more swollen than higher cross-linked absorbents (Helfferich, 1962). It is known that the network characteristics (cross-link density, etc.) are influenced not only by the cross-linking agent concentration, but also its chemical structure. The network characteristics parameters control the behavior of the polymer in the glassy state and especially, predict its swelling characteristics, where water or other penetrants are absorbed (Flory, 1953). The lower amounts of sago starch used, the more amount monomer (MA) is used in the graft copolymerization, and hence the excessive amount of homopolymer formed in the grafted

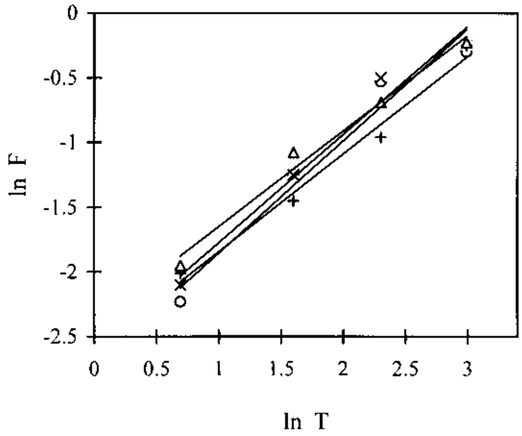


Fig. 4. Plots of ln T as a function of ln F at different sago starch % (○ sago 31%; × sago 43%; + sago 56%; − sago 66%).

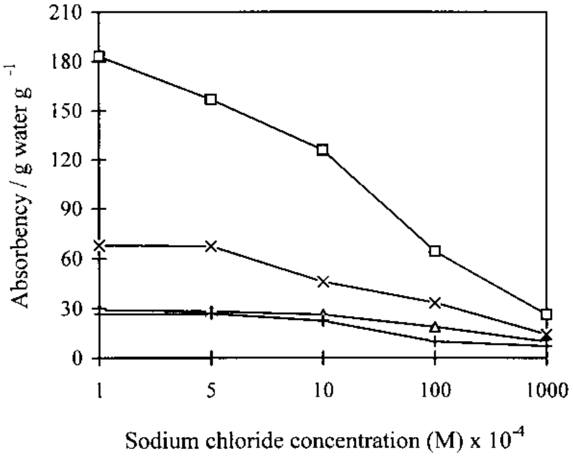


Fig. 5. Absorbency obtained in various concentration of sodium chloride solution (M) at different sago starch % (-□- sago 31%; -×- sago 43%; -△-sago 56%; + sago 66%).

copolymer cause impurities in the absorbent. However, PMA grafted sago starch was used in the preparation of poly(hydroxamic acid) absorbent and a significant swelling was obtained using 31% sago starch in absorbent.

3.5. *Effect of salts solution on the water absorbency*

The swelling behavior of the absorbents depends on the nature of the polymer and the characteristics of the external solution. The polymer's nature involves the following factors such as the amount of sago starch content, strength of the hydrophilic group, and elasticity of the polymer network, etc.

The effect of various salt concentrations in solution on the water absorbency was investigated. The typical absorbency of a series of hydroxamic acid as a function of concentration from 0.0001 to 0.1 M for NaCl, and $CaCl_2$, and $FeCl_3$ salt solutions were presented in Figs. 5–7, respectively. The results of the water absorbency in various salts solution show that the absorbency decreases with the increase of salt concentration in the solutions from 0.0001 to 0.1 M. The curves of water absorbency for the monovalent cationic salt solution (Fig. 5) are far flatter than are those in the divalent (Fig. 6) and trivalent (Fig. 7) cationic salt solutions, respectively. These results are due to the fact that the osmotic pressure differences exist between the polymeric absorbent and the external solution concentration (Flory, 1953). Comparing Fig. 5 with Figs. 6 and 7 reveals that the absorbency curves are much steeper for multivalent salt solutions. Moreover, the absorbency converged to very little in a high concentration for divalent and trivalent salt solutions, but not for the monovalent salt solutions. Restated for a given high concentration, the water absorbency in monovalent cation solutions was higher than that in multivalent cation solutions.

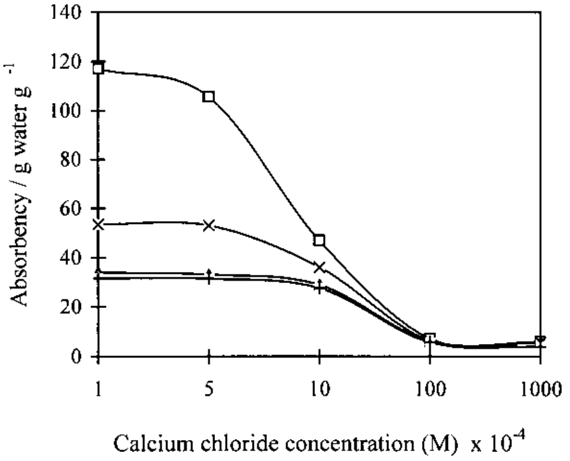


Fig. 6. Absorbency obtained in various concentration of calcium chloride solution (M) at different sago starch % (-□- sago 31%; -×- sago 43%; -△- sago 56%; + sago 66%).

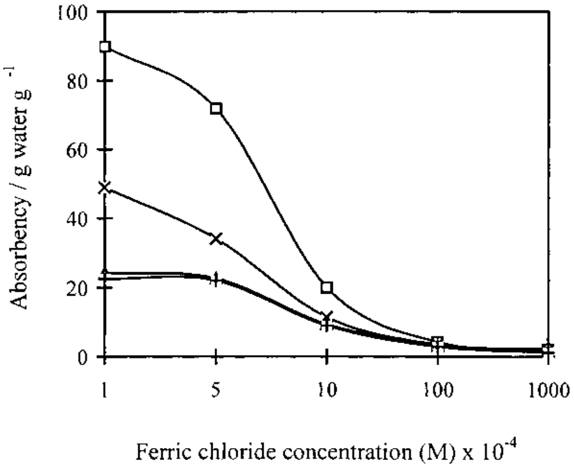


Fig. 7. Absorbency obtained in various concentration of ferric chloride solution (M) at different sago starch % (-□- sago 31%; -×- sago 43%; -△- sago 56%; + sago 66%).

The swelling behavior of poly(hydroxamic acid) absorbent was affected significantly by various factors of the external solution such as its valences and salt concentrations. The swellings were investigated in various salt solutions and it was found that the expansion of the gel network decreases, because the repulsive counter ion (hydroxamic group) on the polymeric chain is shielded by the bound ionic charge (cation). The osmotic pressure difference between the gel network and the external solution increases with an increase in the ionic strength of the salt solution. It is clear that multivalent salts were more absorbed by the polymeric absorbent and this absorbent can be used for the extraction of metal ions from aqueous solution.

4. Conclusions

The swelling behavior of poly(hydroxamic acid) absorbent was investigated using different concentrations of sago starch. It was observed that the swelling of absorbent was sensitive to sago starch concentration i.e. the maximum swelling was obtained at lower sago starch concentration (31%). The swelling kinetics were analyzed by Crank equation and nonFickian diffusion was found in all cases. The water absorbency in the salts solution decreases with increased salt concentration in the solution. The deswelling behavior of the absorbent occurred when the concentration of the external salt solution increased, especially for multivalent salt solution. This deswelling behavior can be accounted for the complexation of multivalent cation with hydroxamic acid ligands.

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