Rheological and Thermal Properties of Saponified Cassava Starch-*g*-Poly(acrylamide) Superabsorbent Polymers Varying in Grafting Parameters and Absorbency

Prabha C. Parvathy, Alummoottil. N. Jyothi

Division of Crop Utilization, Central Tuber Crops Research Institute, Sreekariyam, Thiruvananthapuram, Kerala, India
Correspondence to: A. N. Jyothi (E-mail: sreejyothi_in@yahoo.com)

ABSTRACT: Cassava starch-graft-poly(acrylamide) superabsorbent polymers (SAPs) with varying absorbencies were synthesized. Weight average molecular weight (M_w) of the hydrolyzed starch-graft-copolymers ranged from 1.6×10^6 to 2.8×10^6 g/mol, the largest being shown by the sample with highest percentage grafting. The storage (G') and loss modulus (G'') of hydrogels were determined as a function of frequency. G'' was larger than G' for the hydrogels with higher absorbencies and exhibited a liquid-like behavior. However, hydrogels with lower absorbencies showed a reverse viscoelastic behavior. The viscosity of hydrogels determined using a Brookfield viscometer at different shear rates was found to be larger for the hydrogels with higher absorbencies. The melting temperature (T_m) and enthalpy change of fusion (ΔH_f) of the SAPs ranged from 149.7 to 177.7°C and 65 to 494.9 J/g, respectively and showed a positive correlation with grafting parameters and M_w. Heavy metal ion removal capacity of hydrogel followed the order $Cu^{2+} > Pb^{2+} > Zn^{2+}$. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40368.

INTRODUCTION

Hydrogels are polymeric materials having the capacity to hold large quantities of water within their three-dimensional network structure. These materials absorb on contact with water and shrink on drying.[1] Recently, considerable attention has been focused on superabsorbent hydrogels not only due to their capacity to absorb very large quantities of water, but also the ability to change properties as well as volume in response to external stimuli. Superabsorbent polymers (SAPs) are widely used in personal care products, biomedical applications, agricultural and horticultural applications etc.[2,3] However, most of the presently available commercial SAPs are synthetic and petrochemical based polymers. Due to environmental concerns, replacing the synthetics by "greener" options is getting importance and incorporation of natural polysaccharides or carbohydrates in such materials helps in reducing the load of monomer component in the final product. Incorporation of natural polysaccharides such as cellulose, starch, chitosan, etc. without affecting the absorption characteristics, is an option to reduce the synthetic polymer component in such products.

The properties of the hydrogels such as gel strength, thermal stability, and viscoelastic properties are important in many of their practical applications. Several methods are used to quantify the gel strength of hydrogels.[4–7] A SAP sample with good gel strength may be rapidly identified by various qualitative indications in the swollen state; such as, (a) it has a geometrically stable shape with sharp edges and corners and (b) its strength can be felt when the particles are held between fingers.[4,8] The measurement of gel strength using conventional methods is not possible for the commercial SAPs, since they are highly hygroscopic sugar like particles having irregular size and shape. Hence, a rheological method for the determination of swollen gel strength of hydrogels was proposed.[8,9] Although there are several studies on the absorption pattern and swelling kinetics of SAP hydrogels,[10–13] the literature available on the viscoelastic properties of the hydrogels and melting characteristics of the xerogels (dry polymer) are very few.

Application of synthetic adsorbents for removal of metal toxicity from aqueous media may not be practical due to exorbitant costs. Recently adsorbents based on natural products and their derivatives have gained much importance due to their ability to remove heavy metal ions from solution. Crosslinked polymeric materials having functional groups such as carboxylic acid, amine, hydroxyl, amidoxime, sulphonic acid groups, etc. could be used as complexing agents for the removal of metal ions from aqueous solutions.[14] Easy handling and reusability make the hydrogels promising candidates for water purification.

Among natural polymers starch is particularly used due to its easy availability, biodegradability, low cost, and renewability. However, starch by itself does not possess any chelating or metal interacting property and thus cannot be applied in adsorbing heavy metal ions. There are some reports on the application of starch-based polymers for the removal of heavy metal ions from aqueous solutions.[15,16]

In our laboratory, we have successfully synthesized cassava starch-based superabsorbent polymers by ceric ammonium nitrate (CAN) initiated polymerization reaction of starch with acrylamide (AM) under different reaction conditions and consequent saponification of the grafted copolymers.[17,18] The structural properties, water absorption pattern, and swelling kinetics of these SAPs were studied and reported previously.[13,18] The objective of this study was to investigate and compare the viscoelastic and thermal properties of cassava starch-based SAPs and correlate these properties with grafting parameters and water absorbency. The study was also aimed at determining the ability of the polymer in removing heavy metal ions from aqueous solution.

EXPERIMENTAL

Cassava starch was extracted from the freshly harvested tubers according to a reported procedure.[19] Acrylamide (AM), ceric ammonium nitrate (CAN), and alpha amylase were purchased from Sigma Aldrich Chemicals (St. Louis). The other chemicals used were of analytical grade.

Synthesis of Superabsorbent Polymers
The detailed description of the procedure employed for the synthesis of cassava starch-based SAP is reported previously.[13,18] In brief, a set of 27 samples of SAPs with different absorbencies were synthesized by a two-step process which involved the free radical initiated polymerization reaction of cassava starch with acrylamide and the alkali saponification of the graft-copolymers, using a 4-factor-three-level response surface Box-Behnken design. The factors and their levels used were as follows: weight of acrylamide (10, 15, and 20 g/10 g dry starch), weight of CAN (1.65, 3.29, and 4.95 g/L), reaction time (60, 120 and 180 min), and temperature (35, 45, and 55°C). The percentage grafting and absorbencies of all the SAP samples were determined according to standard procedures and reported previously.[17,18] The above data were reused in this study for obtaining the correlations with vicsoelastic properties, thermal properties and weight average molecular weight of the polymers.

Viscoelastic Properties of the SAP Hydrogels
The dynamic viscoelastic properties of the superabsorbent hydrogels were determined using a Physica VT2 rheometer (Anton Paar Germany GmbH, Ostfildern, Germany). The measurement was done at 30 ± 2°C using a parallel plate system (PP20-SN5912, 1 mm diameter) at 1 mm gap. The effect of duration of hydration of the polymer on the viscoelastic properties of the hydrogel was studied. The xerogel was hydrated in excess of distilled water for different time durations *viz.*, 1, 2, and 24 h and the swollen gel particles were then dewatered using a sieve. The hydrogel was placed on the parallel plate of

the rheometer for the viscoelastic measurements. Strain (1%) was used, which was within the linear viscoelastic region (LVR) obtained by dynamic strain sweep experiments. The mechanical spectra of the gels were obtained from frequency (f) sweeps over the range of 0.10 to 10 Hz. The storage modulus (G'), loss modulus (G''), damping factor (tan δ), phase angle, and complex viscosity (η) were recorded. All the measurements were done in triplicate.

Viscosity of the Hydrogels
A 1% hydrogel solution was prepared by hydrating the polymer in distilled water, which was then homogenized and kept undisturbed for 2 days to obtain a viscous solution. The viscosity was determined at three different rpm (60, 120, and 180) using a Brookfield viscometer (Brookfield Instruments, Middleboro, MA) at 30 ± 2°C.

Thermal Properties
The melting temperature (T_m) and enthalpy change of fusion (ΔH_f) of the dry SAPs (xerogels) were determined using a Mettler Toledo DSC 822e instrument (Schcoerfenbach, Switzerland). The polymer (3–5 mg) was accurately weighed into an aluminium pan and sealed hermetically. Heating of the sample was performed from $-10°C$ to $250°C$ at a rate of $20°C/min$ in nitrogen atmosphere. The onset, conclusion, and the peak maximum temperatures along with the enthalpy change for phase transition were recorded by means of the built-in software.

Percentage Add On, Intrinsic Viscosity, and Weight Average Molecular Weight
The starch-graft-poly(acrylamide) copolymers were subjected to enzymatic hydrolysis using an α-amylase (E.C 3.2.1.1,280 Units) and NaCl as enzyme stabilizer for 48 h for the complete removal of the starch moiety. The resulting PAM chains were subjected to iodine test to ensure the complete removal of the starch. The percentage add on was calculated from the weight loss of the graft copolymers after removal of the starch moiety.[20]

The weight average molecular weight (M_w) of hydrolyzed starch-graft-copolymers was determined by intrinsic viscosity method.[21] The intrinsic viscosity of the hydrolyzed polymer solutions in $0.1M$ sodium nitrate solution was determined using an Ubbelohde capillary viscometer at 30 ± 2°C. Relative viscosity ($\eta_{rel} = t/t_0$) was obtained from the time of flow of aqueous polymer solution (t) and that of the pure solvent (t_0). Specific viscosity (η_{sp}) of the polymer solution was obtained from the relation $\eta_{sp} = (t - t_0)/t_0$. Knowing the concentration of the polymer (g/dL), reduced viscosity ($\eta_{red} = \eta_{sp}/C$) and inherent viscosity ($\eta_{inh} = \ln\eta_{rel}/C$) were calculated for different polymer concentrations. The intrinsic viscosity [η] was then obtained by extrapolating the plots of reduced and inherent viscosities to zero polymer concentration (C = 0 g/dL). Weight average molecular weight was determined from the intrinsic viscosity (η) using Mark-Houwink equation given below.

$$[\eta] = KM^\alpha$$

where K and α values are constants for a particular polymer/solvent/temperature system. The K and α values for PAM are given in the following equation:

Table I. Absorbency of the SAP Samples Synthesized Under Different Reaction Conditions

Sample	Concentration of AM (g/10g of starch)	Concentration of CAN (g/L)	Time (min)	Temperature (°C)	Absorbency (g/g)
S1	10	1.65	120	45	65.6 ± 1.0
S2	10	4.95	120	45	102.9 ± 2.7
S3	20	1.65	120	45	68.3 ± 2.30
S4	20	4.95	120	45	425.2 ± 3.8
S5	15	3.30	60	35	81.2 ± 5.20
S6	15	3.30	60	55	67.7 ± 2.60
S7	15	3.30	180	35	76.8 ± 3.60
S8	15	3.30	180	55	109.1 ± 0.7
S9	10	3.30	120	35	28.5 ± 0.70
S10	10	3.30	120	55	28.8 ± 0.10
S11	20	3.30	120	35	139.1 ± 1.0
S12	20	3.30	120	55	325.1 ± 4.3
S13	15	1.65	60	45	41.4 ± 0.70
S14	15	1.65	180	45	78.1 ± 5.10
S15	15	4.95	60	45	84.8 ± 3.00
S16	15	4.95	180	45	108.4 ± 3.6
S17	10	3.30	60	45	54.8 ± 2.90
S18	10	3.30	180	45	87.6 ± 1.60
S19	20	3.30	60	45	98.1 ± 1.80
S20	20	3.30	180	45	143.4 ± 3.2
S21	15	1.65	120	35	34.4 ± 2.90
S22	15	1.65	120	55	39.7 ± 2.30
S23	15	4.95	120	35	88.5 ± 2.20
S24	15	4.95	120	55	108.8 ± 1.7
S25	15	3.30	120	45	110.4 ± 5.9
S26	15	3.30	120	45	129.5 ± 9.3
S27	15	3.30	120	45	159.6 ± 6.4

$$[\eta] = 6.31 \times 10^{-5}(M_w)^{0.80}$$

where M_w is the weight average molecular weight.[21]

Graft Frequency

Graft frequency (N_{AGU}), which is a measure of the average number of anhydroglucose unit (AGU) per grafted PAM chain was determined using the following equation.

$$N_{AGU} = M_w(1-g)/2M_{AGU} \cdot g$$

where M_w is the weight average molecular weight, M_{AGU} is the AGU molecular weight (162 g/mol), and g is the percentage add on.[22]

Statistical Analysis

The data were analyzed using the package SAS 9.3 to perform ANOVA.[23] The treatments were considered significantly different at 5% level of significance ($P \leq 0.05$). Simple correlation analysis was done to study the correlations among the various properties.

Removal of Heavy Metal Ions by Saponified Starch Graft Copolymers

Saponified starch graft copolymers were used for the competitive removal of three metal ions namely Cu(II), Pb(II), and Zn(II). Adsorption of metal ions was determined using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Aqueous metal salt solutions Cu(II), Pb(II), and Zn(II) were prepared and pH was adjusted to be 4.5. The metal salt solutions were mixed with 0.25 g of saponified graft copolymer (S4). The solution was stirred for 2 h at room temperature. After filtration the remaining metal ions in the solution were determined using ICP spectrometer. Percentage of metal ions adsorbed was determined using the equation:[24]

$$\% \text{ Adsorption} = \text{Metal ions adsorbed by the polymer/Metal ions in the feed} \times 100$$

RESULTS AND DISCUSSION

A total of 27 SAP samples were synthesized according to the response surface Box-Behnken design using different levels of the reaction variables. Table I shows the different variables used in the synthesis of SAPs. The absorbency of the SAPs were in the range of 28.8 to 425.2 g/g respectively (Table I).[18]

Table II. Grafting Parameters, Intrinsic Viscosity, and Weight Average Molecular Weight of the Cassava Starch-Graft-Poly(Acrylamide) Copolymers

Sample	% Grafting	Add on (%)	Intrinsic viscosity, $[\eta]$ (dL/g)	M_w ($\times 10^6$ g/mol)	Graft frequency (N_{AGU})
S1	31.9	26.2	5.8	1.60	13,914
S2	38.4	38.4	5.6	1.53	7,584
S3	75.9	36.4	6.9	1.98	10,723
S4	174.8	56	9.1	2.81	6,815
S5	2.9	40.2	6.5	1.85	8,473
S6	60.3	36.8	6.0	1.67	8,851
S7	104.4	40.2	6.5	1.85	8,473
S8	136.0	48.2	7.4	2.17	7,198
S9	20.6	28.0	5.7	1.57	12,429
S10	19.4	26.4	5.5	1.49	12,887
S11	91.2	46.8	6.3	1.77	6,227
S12	154.9	54.6	8.5	2.58	6,623
S13	32.6	26.2	6.1	1.70	14,819
S14	76.4	33.2	6.0	1.67	10,369
S15	53.0	46.1	6.1	1.7	6,151
S16	90.1	47.8	6.8	1.95	6581
S17	28.8	29.1	5.7	1.57	11,776
S18	40.9	30.4	5.8	1.6	11,309
S19	14.4	31.8	5.7	1.56	10,366
S20	169.1	50.8	8.3	2.51	7,488
S21	8.7	28.4	6.0	1.67	12,993
S22	14.6	23.8	5.5	1.49	14,799
S23	37.3	36.3	5.6	1.53	8,296
S24	100.0	49	6.7	1.92	6,157
S25	156.8	48.7	7.1	2.06	6,700
S26	158.9	48.9	7.2	2.09	6,764
S27	162.4	48.7	7.5	2.21	6,893

Percentage Add On, Intrinsic Viscosity, and Weight Average Molecular Weight and Graft Frequency

Percentage add on, intrinsic viscosity, weight average molecular weight, and frequency of grafts (N_{AGU}) of some of the SAP samples are presented in Table II.

Percentage Add On. The percentage add on of the samples ranged from 23.8 to 56.0%. This was found to be in agreement with that reported earlier for starch-graft-acrylamide/itaconic acid polymers when the ratio of starch to monomer was 1:2, where, a maximum % add on of 50% was reported.[25] Our results also agree with that of Kiatkamjornwong et al.[26] that higher percentage add on was obtained at high monomer to starch ratio for graft copolymers of cassava starch-g-acrylamide/acrylic acid. The add on (%) was highest for the sample S4.

Analysis of the data showed that the linear as well as quadratic effects of concentration of monomer, initiator, and time significantly affected the percentage add on values. The effect of the different reaction variables on add on values can be explained as follows. The initial rise in add on with increase in concentra-tion of initiator might be due to the greater number of active free radical sites generated on the starch backbone.[27] Thereafter, excess initiator is used up either in faster termination of the growing poly(acrylamide)chains or in the initiation of homo-polymer.[28] The nonavailability of sites on starch molecule at which initiator can react to generate more free radicals may be another reason for the decline in % add-on at high CAN con-centration. The initial increase in % add on with increase in monomer concentration is due to the greater availability of monomer in the proximity of starch molecules. However, fur-ther increase in monomer concentration might result in homo-polymerization. This was evident from the increase in viscosity of the reaction medium and the sticky nature of the graft copolymers. These homopolymer lumps may hinder the rate of diffusion of monomer molecules to the starch macro radicals resulting in a decrease in % add on. The initial increase in add on values with reaction time could be due to the increase in number of grafting sites in the initial stages of reaction and fur-ther decrease could be attributed to initiator exhaustion with time.

Intrinsic Viscosity and Weight Average Molecular Weight.
Intrinsic viscosity (η) of a polymer is a measure of its hydrodynamic volume in solution, which in turn depends upon its molecular weight, structure, nature of solvent, and temperature of the medium.[29] The η and weight average molecular weight of different graft copolymers ranged from 5.5 to 9.1 dL/g and 1.49×10^6 to 2.81×10^6 g/mol, respectively (Table II). It was observed that both the parameters were higher for the grafted samples with higher percentage grafting and the sample S4 exhibited the highest weight average molecular weight. This could be due to the long poly(acrylamide) (PAM) side chains formed during grafting.[30,31] Higher levels of AM resulted in longer PAM chains whereas higher concentration of CAN could lead to more frequency of grafting sites on the starch backbone. A combined effect of these two has been observed in the case of sample S4. In the case of samples S9 and S10, the monomer concentration was lower and this might have caused the formation of shorter PAM side chains on the starch backbone which resulted in their lower η and molecular weight. Graft-copolymers with maximum percentage grafting possessed the highest η because a higher % grafting at a fixed initiator concentration indicated that longer PAM chains were grafted on to starch backbone which instantly increased the hydrodynamic volume of the polymer in solution.[29] Correlation analysis indicated a positive linear correlation between M_w and η with % grafting. The increase in η and M_w with increase in % grafting could be due to the increase in side chain length of the copolymer.

Our previous observations on nitrogen content, acrylamide content, and absorbency also confirm this explanation.[18] The maximum nitrogen content, acrylamide content, and absorbency were obtained for the sample S4. The grafting parameters as well as absorbency were significantly lower for the samples S9 and S10. Reports suggest that for a branched polymer the longer the branching, the higher is its η.[28,31] Statistical analysis of the data indicated that concentration of monomer and reaction time had a linear effect ($P < 0.05$) on η and molecular weight of grafted chains. The increase in η with increased amount of monomer may be due to the increase in the molecular weight of PAM side chains.[30,31] The η and M_w was also affected by the quadratic effect of concentration of initiator. The initial increase in η and M_w with increase in concentration of initiator may be due to the formation of active free radical sites on the polysaccharide backbone. However, further increase in concentration of initiator resulted in a decrease in η and M_w values which might be due to faster termination of growing PAM chains.

Similar observations were reported by Ghosh et al.[32] and Brostow et al.[33] that graft copolymers with highest percentage grafting showed the highest η. Similarly, Sen and Pal[29] have obtained the highest molecular weight (40.15×10^5 g/mol) for carboxymethyl tamarind-g-PAM with a highest percentage grafting of 50%. Using Mark-Houwink equation, Krishnamoorthi et al.[34] obtained a highest M_w value of 1.31×10^6 g/mol for dextran-g-PAM with the highest η of 7.21 dL/g. Eutamene et al.[30] and Song et al.[35] have observed that the weight average molecular weight of starch-g-poly(acrylamide) and starch-g-poly(AM-co-AMPS) copolymers increased with increase in concen-

tration of the monomer due to the presence of longer PAM side chain molecular weight.

Graft Frequency. The graft frequency, which is represented in terms of average number of anhydroglucose (AGU) unit per grafted polyacrylamide chain, is presented in Table II. The highest $N_{AGU/graft}$ value was shown by the sample S13 (14,819) and lowest by the sample S15 (6151). The values are in consistent with previous reports.[36] When concentration of initiator used was high, more number of grafting sites was generated on the polysaccharide backbone and consequently the N_{AGU}/graft was low as observed in the case of the samples S4, S15, etc. The high $N_{AGU/graft}$ values obtained for the sample S13 could be due to the fewer grafting sites on the polysaccharide backbone since the concentration of initiator used was lowest. Analysis of the results showed that the negative linear effect of concentration of monomer and initiator had significant effect on graft frequency. At low initiator concentration, few grafting sites were generated on starch backbone where monomers can be grafted resulting in high $N_{AGU/graft}$ values. Correlation analysis indicated that graft frequency was negatively correlated to absorbency, i.e., the graft copolymers with higher N_{AGU} values exhibited lower absorbency and *vice versa*.

Viscoelastic Properties of SAP Hydrogels
The storage modulus (G'), loss modulus (G''), phase angle, damping factor, and complex viscosity of the SAP hydrogels, at different levels of hydration, were determined as a function of frequency. The plots of dynamic moduli versus frequency of the hydrogels prepared by the hydration of the xerogel in distilled water for 2 h are shown in Figure 1. The frequency dependence of the dynamic moduli was evident from the figure and G' and G'' increased with frequency for all the samples. For S4, G' was smaller than G'' at lower frequencies. But as the frequency increased to 4.2 Hz, a crossover point (where $G' = G''$) was observed which denoted the existence of a concentrated solution (Figure 1). With further increase in frequency, G' predominated over G''. However, this crossover pattern was not observed in the case of the hydrogel S12, which showed the second higher absorbency (325.1 g/g). In this case, G'' was greater than G' at all frequencies which indicated the liquid like nature of the hydrogel. The occurrence of crossover for certain samples might be characteristic of that particular hydrogel and differences in the polymer structure. No direct relation was observed between the absorbency of the sample and the occurrence of crossover pattern. Earlier, Rao has explained the existence of concentrated solutions of semi-solid food samples, where, G'' was larger than G' at lower frequency until a crossover (critical) frequency was reached and G' became higher than G'' beyond the crossover frequency.[37]

In the case of the hydrogels S9 and S10 with comparatively smaller absorbencies, G' was considerably higher than G'' at all frequencies indicating the more solid-like (gel) nature of the hydrogel. Hence the gel strength was more in these hydrogels in comparison to those with higher water absorbencies. Seetapan et al.[38] reported that the strength of fully swollen poly(acrylamide/itaconic acid) SAP particles was inversely related to their absorbency which is in accordance with our observation.
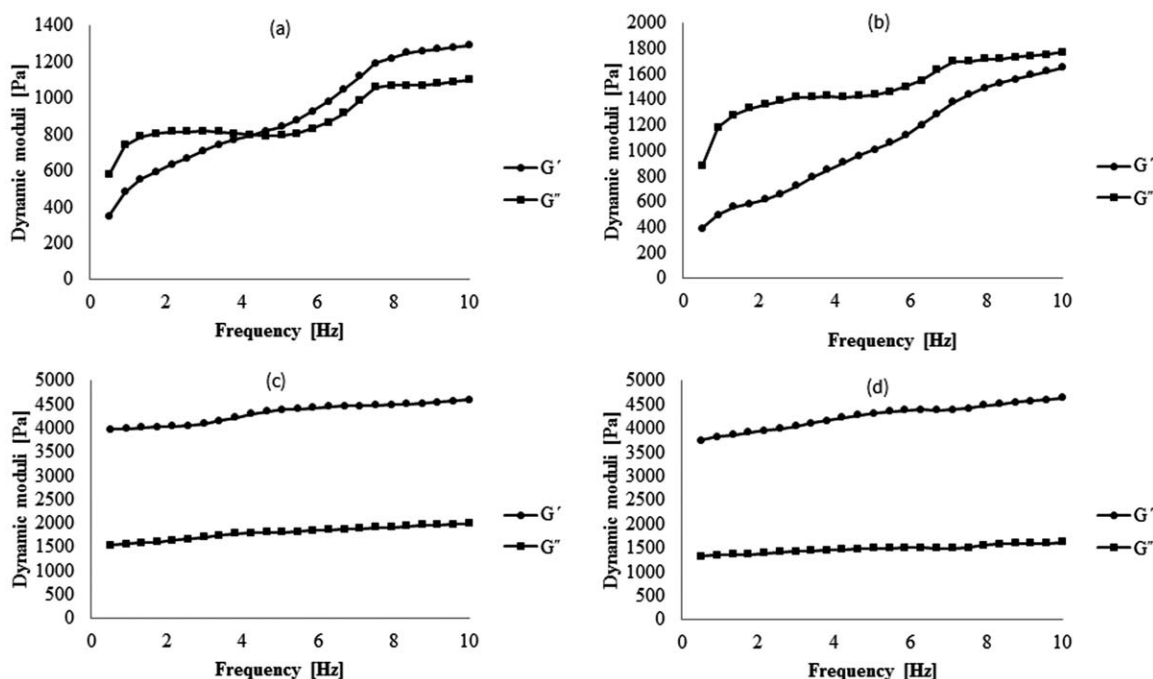
Figure 1. Plots of dynamic moduli as a function of frequency of (a) S4, (b) S12, (c) S9, and (d) S10 hydrated for 2 h.

In general, the hydrogels with higher absorbencies exhibited larger G'' values than G' (i.e., $G'' > G'$), while those with comparatively lower absorbencies showed a reverse effect, i.e., $G' > G''$. G' is a measure of the elastic component of the system. Since higher G'' values for highly absorbing hydrogels indicate that the viscous component predominated over the elastic component and such hydrogels showed a liquid-like nature.[38] This liquid-like behavior of the highly absorbing hydrogels could be probably due to the higher amount of water in their network structure. The systems with higher absorbencies possessed greater percentage of small water molecules within them. The reason for higher G'' exhibited by such hydrogels is that these systems can dissipate more energy.[38] However, in the case of the hydrogel S4, this trend was present up to the cross over point and thereafter G' predominated over G'', exhibiting the property of a concentrated solution. The G' and G'' at a frequency of 10 Hz for hydrogels at equilibrium absorbency are presented in Table III. The G' ranged from 1240 to 4650 Pa and G'' from 1100 to 2060 Pa. The G' obtained was comparatively smaller for the hydrogel S4 and higher for S10.

Figure 2 shows the effect of duration of hydration of the dry polymer on the dynamic moduli of the hydrogels S4 and S10, which exhibited the maximum and minimum absorbencies respectively. The gels were prepared by hydrating the xerogel for 1, 2, and 24 h. In the case of the hydrogel S4, the storage modulus steadily increased with frequency (Figure 2). The sample which was hydrated for 1h showed that $G'' > G'$ at all frequencies, indicative of the more liquid-like behavior of the gel [Figure 2(a)]. However, when the polymer was hydrated for 2 and 24 h, the system exhibited a crossover at frequencies 4.2 and 8.7 Hz, respectively [Figure 2(b,c)]. For the sample

S10, which had a lower absorbency, no such crossover point was observed and G' was found to be larger than G'' for the gels [Figure 2(d–f)] indicative of their solid like (gel) nature after hydration for 1, 2, and 24 h.[38] Correlation analysis indicated a significant ($P < 0.5$) negative correlation of G' with the absorbency of the gels.

The phase angles of some representative hydrogels are shown in Table III and it ranged from 19.3 to 47°. A perfectly elastic material possesses a phase angle of 0° and a perfectly viscous material possesses a phase angle of 90°. In the present study, the highly absorbing hydrogels exhibited relatively larger phase angle than the hydrogels with smaller absorbencies exhibiting a more viscous nature.

An important rheological parameter for determining the gel strength of hydrogels is the damping factor. Damping is a measure of how well a material can get rid of the energy and is reported as the tangent of the phase angle. The strength of the interaction within the system or internal structure can be measured by the magnitude of tan δ. If the value of tan δ is greater than 1, the system behaves like a liquid and if the value is smaller than 1, the system shows solid-like (gel) behavior. The smaller the value of tan δ, the stronger will be the interaction within the polymer system.[39] In the present study, a range of hydrogels with different gel properties were developed. The tan δ values of representative hydrogels are presented in Table III. For the highly absorbing hydrogels, tan δ value was greater or close to 1, indicating a more liquid-like behavior.[38]

The complex viscosity of the hydrogels ranged from 27.0 to 79.6 Pa s (Table III). SAP hydrogels S9 and S10 with smaller absorbencies possessed larger complex viscosities, whereas highly

Table III. The Equilibrium Absorbency and Rheological Parameters of SAP Hydrogels After Hydration for 2 h in Distilled Water

Sample	Absorbency (g/g)	Storage modulus (G')	Loss modulus (G'')	Damping factor	Complex viscosity (Pa s)	Phase angle (°)
S1	64.8 ± 1.0	3150 ± 15	1550 ± 30	0.492 ± 0.007	55.9 ± 2.1	26.1 ± 1.6
S2	102.5 ± 2.4	1630 ± 20	1470 ± 10	0.902 ± 0.005	34.9 ± 1.8	42.2 ± 2.3
S3	68.7 ± 2.0	1920 ± 30	1640 ± 15	0.854 ± 0.005	40.2 ± 2.5	40.6 ± 1.1
S4	425.9 ± 3.0	1240 ± 20	1100 ± 15	0.887 ± 0.002	27 ± 1.5	47.0 ± 0
S5	81.2 ± 5.6	655 ± 35	1510 ± 20	2.31 ± 0.090	30.2 ± 2.0	66.5 ± 1.8
S6	65.7 ± 2.6	2490 ± 25	2240 ± 10	0.899 ± 0.014	53.4 ± 1.6	41.9 ± 2.9
S7	76.7 ± 5.6	2130 ± 35	1240 ± 20	0.582 ± 0.001	39.3 ± 0.8	30.3 ± 1.0
S8	105.8 ± 3.9	1435 ± 15	1500 ± 20	1.05 ± 0.002	32.7 ± 1.7	46.2 ± 0.4
S9	28.6 ± 2.8	4585 ± 5	2060 ± 70	0.45 ± 0.01	79.6 ± 0.7	23.4 ± 4.2
S10	28.6 ± 0.3	4650 ± 20	1655 ± 35	0.36 ± 0.002	78.0 ± 4.3	19.3 ± 6.2
S11	137.8 ± 5.0	2700 ± 10	2060 ± 5	0.762 ± 0.001	54.1 ± 2.3	37.3 ± 3.1
S12	325.1 ± 4.3	1610 ± 40	1705 ± 65	1.06 ± 0.01	37.3 ± 1.2	46.6 ± 0.4
S13	40.6 ± 0.8	4150 ± 15	2700 ± 30	0.65 ± 0.005	78.9 ± 0.8	33 ± 1.4
S14	76.4 ± 3.8	2390 ± 5	2610 ± 15	1.09 ± 0.006	56.3 ± 2.3	47.5 ± 1.4
S15	87.4 ± 2.5	3520 ± 20	2070 ± 10	0.587 ± 0.001	52.3 ± 1.0	30.4 ± 0.5
S16	105 ± 3.6	2370 ± 10	2030 ± 20	0.857 ± 0.004	49.7 ± 1.4	40.6 ± 0.8
S17	54.8 ± 2.5	2520 ± 25	1960 ± 10	0.778 ± 0.004	50.8 ± 2.6	37.9 ± 1.4
S18	84.8 ± 4.4	2830 ± 5	1670 ± 10	0.59 ± 0.003	52.3 ± 3.0	30.6 ± 2.4
S19	98.1 ± 1.8	2060 ± 10	1420 ± 15	0.689 ± 0.004	39.9 ± 1.3	34.7 ± 1.5
S20	140.8 ± 4.6	2300 ± 0	2055 ± 35	0.893 ± 0.016	46 ± 2.8	42.3 ± 0.9
S21	34.3 ± 2.0	2660 ± 20	2130 ± 15	0.80 ± 0.0	54.3 ± 2.1	38.7 ± 1.6
S22	39.5 ± 2.0	3770 ± 35	1810 ± 25	0.480 ± 0.002	66.6 ± 2.6	25.7 ± 0.8
S23	83.9 ± 5.0	1630 ± 15	1210 ± 5	0.742 ± 0.003	32.3 ± 1.0	36.6 ± 2.4
S24	105.8 ± 4.2	2470 ± 25	2280 ± 20	0.923 ± 0.001	53.5 ± 2.6	42.8 ± 3.2
S25	107.1 ± 5.0	2690 ± 25	1820 ± 20	0.677 ± 0.0	56.1 ± 3.2	34.9 ± 2.0
S26	129.5 ± 5.0	2685 ± 30	1830 ± 20	0.677 ± 0.004	48 ± 2.0	36.7 ± 1.3
S27	154.4 ± 5.5	2645 ± 15	1725 ± 5	0.652 ± 0.002	50.9 ± 0.5	32.8 ± 0.2

absorbing hydrogels possessed comparatively smaller viscosities. Table IV shows the frequency dependence of G' and G'' (exponents, n' and n'' respectively in power law equation for the dynamic moduli). The n' and n'' values ranged from 0.03 to 0.54 and 0.07 to 0.20, respectively. The liquid-like behavior of the highly absorbing gels was evident from the higher values of the exponents.

The results of the present study agree with those of earlier reports. Ramazani-Harandi et al.[8] have studied the swollen gel strength of acrylic based SAP hydrogels and obtained the storage modulus of the swollen hydrogels above 1000 Pa at 25°C. Seetapan et al.[38] observed that systems containing a higher level of smaller molecules (such as water) within them can dissipate more energy and thus an increase in the G'' is expected for such highly absorbing systems. The study also showed that acrylamide-protic acid superabsorbent copolymers which possessed a large absorbency had less gel strength and for all the samples within the frequency range (0.1–10 Hz), G' was greater by 10-fold than the G''.[38]

Viscosity of SAP Hydrogels

Figure 3 shows the plots of viscosity at different rpm of some of the SAP samples at 1% concentration, measured using a Brookfield viscometer. The viscosity of the hydrogels ranged from 6.3 to 77.4 mPa s. For all the samples, viscosity was found to be reduced at higher rpm. The sample S4 showed the largest viscosity of 77.4 mPa s at 60 rpm, whereas, the smallest viscosity (6.3 mPa s) was exhibited by S9. Analysis of the results confirmed that viscosity was significantly affected by linear effects of concentration of initiator and monomer. As the concentration of initiator increased, more number of active free radical sites were generated onto starch backbone where the monomer molecules can be grafted. The larger viscosity of the highly absorbing hydrogels could be due to the presence of more hydrophilic segments in the polymer which could disperse better in the aqueous phase.[40] Correlation analysis showed a highly significant ($P < 0.0001$) positive correlation of viscosity to the absorbency of the SAPs. The results agree with some of the earlier reports. Singh et al.[41] reported a viscosity of 19.4 mPa s at
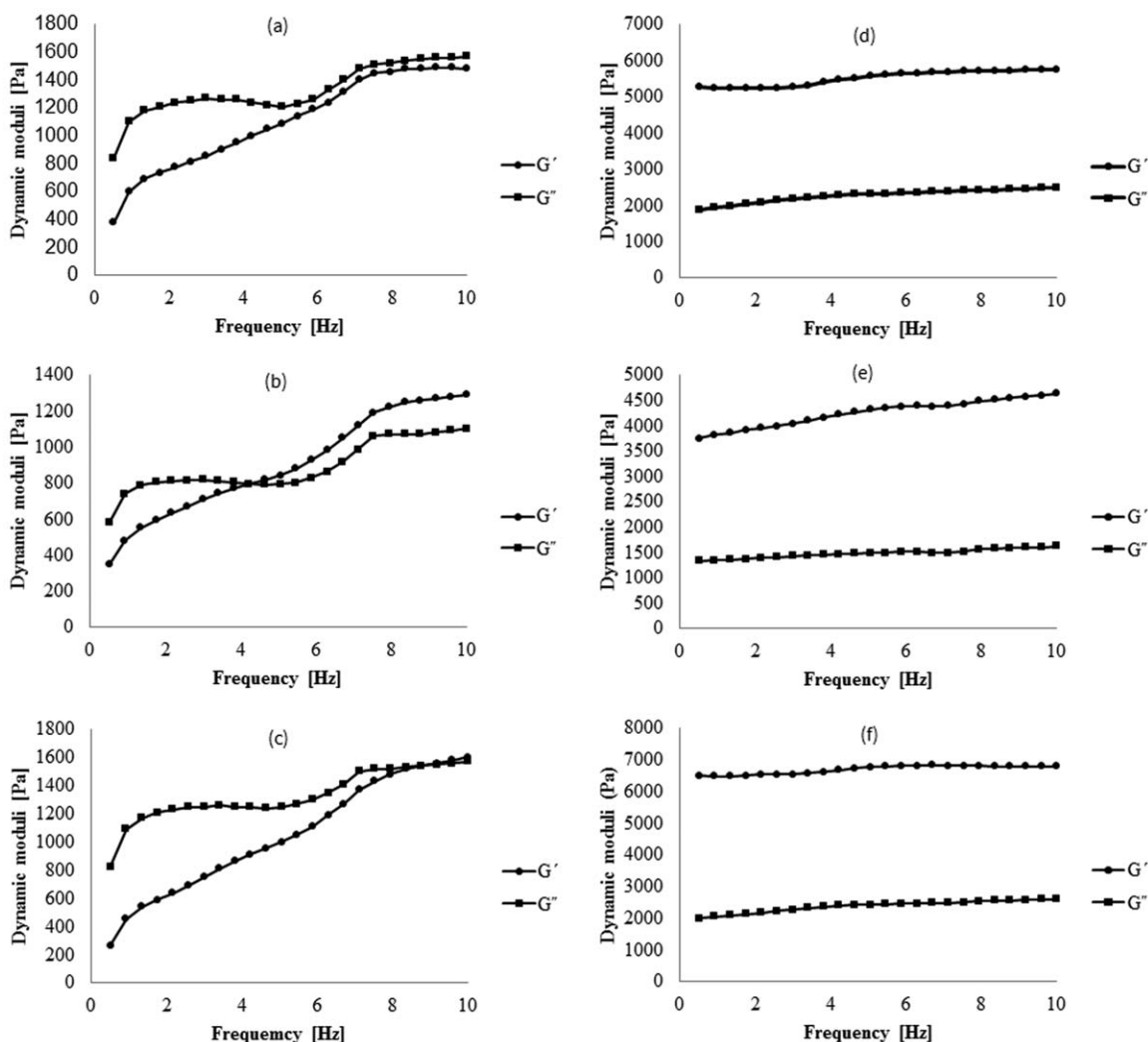
Figure 2. Plots of dynamic moduli versus frequency of the hydrogel S4 (a, b, and c) and S10 (d, e, and f) hydrated for 1, 2, and 24 h.

25°C for a 1% solution of potato starch-g-poly(acrylamide) at 100 rpm. Krishnamoorthi et al.[34] determined the viscosity behavior of dextran-g-PAM at different shear rates and observed that grafting of long PAM chains onto dextran backbone resulted in an increased viscosity.

Thermal Properties

The melting temperature and the enthalpy of fusion of SAPs are presented in Table V and the thermograms are shown in Figure 4. The melting temperatures of the SAP samples ranged from 149.7 to 177.7°C and the highest melting temperature was obtained for the sample S4 and lowest for the sample S9. Enthalpy of fusion (ΔH_f) of the polymers determined from the area under the curve ranged from 65.1 to 494.9 J/g. The sample S4 with the highest T_m exhibited the highest ΔH_f. Correlation analysis showed positive correlation of T_m and ΔH_f with grafting parameters such as percentage grafting and weight average molecular weight whereas, a negative correlation with graft frequency.

In the present study, T_m values were higher for those samples which possessed longer chains, i.e., as the chain length of the

polymer increased, the melting temperature also increased. Our observation is in agreement with that of Rubinstein and Ralph.[42] In the case of polymers with longer chain (higher molecular weight), due to increased interactions, the individual chains are fixed firmly in position which resist deformation and require more energy to break. This might be the reason for the observed higher ΔH_f values for higher molecular weight polymers. It is also reported that increase in chain length can lead to decrease in chain mobility and increase in chain strength and toughness. This is due to increase in chain interaction such as van der Waal's attractions and entanglements that come with increase chain length.[43] Short chain polymers are generally weaker in strength and allow the crystalline layers to slip past one another causing a break in the material.[44] This explanation is in consistent with our observation since in the present study, low molecular weight polymers exhibited relatively lower ΔH_f values.

The melting temperature (T_m) obtained in the present study agree with previous reports by Labet et al.[45] where, broad endothermic peaks were observed in the DSC curves of nanostarch-

Table IV. Exponents in Power Equation for the Dynamic Moduli of the Hydrogels of SAP Obtained After Hydrating the Hydrogels to their Equilibrium Absorbency
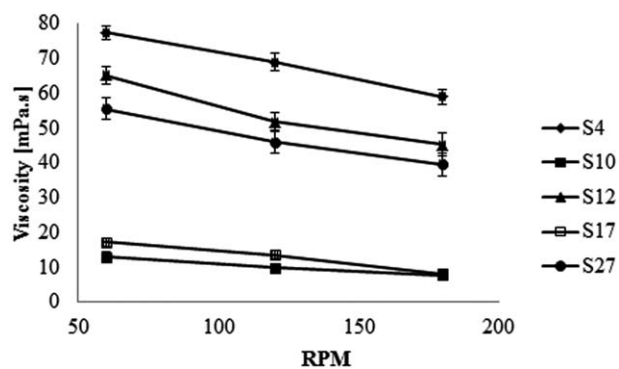
Sample	Exponents in power equation	
	n'	n''
S1	0.09 ± 0.01	0.07 ± 0.01
S2	0.39 ± 0.01	0.11 ± 0.02
S3	0.29 ± 0.02	0.14 ± 0.01
S4	0.44 ± 0.44	0.18 ± 0.22
S5	0.41 ± 0.04	0.21 ± 0.01
S6	0.16 ± 0.01	0.12 ± 0.02
S7	0.19 ± 0.01	0.12 ± 0.01
S8	0.56 ± 0.06	0.19 ± 0.02
S9	0.05 ± 0.02	0.09 ± 0.01
S10	0.08 ± 0.04	0.07 ± 0.04
S11	0.13 ± 0.01	0.12 ± 0.01
S12	0.54 ± 0.01	0.20 ± 0.01
S13	0.10 ± 0.04	0.11 ± 0.02
S14	0.25 ± 0.02	0.15 ± 0.01
S15	0.13 ± 0.01	0.13 ± 0.01
S16	0.23 ± 0.04	0.18 ± 0.02
S17	0.26 ± 0.01	0.14 ± 0.01
S18	0.07 ± 0.03	0.09 ± 0.01
S19	0.44 ± 0.01	0.14 ± 0.01
S20	0.29 ± 0.04	0.16 ± 0.02
S21	0.15 ± 0.04	0.11 ± 0.02
S22	0.03 ± 0.02	0.09 ± 0.02
S23	0.35 ± 0.06	0.13 ± 0.02
S24	0.21 ± 0.04	0.14 ± 0.03
S25	0.22 ± 0.03	0.12 ± 0.02
S26	0.18 ± 0.03	0.12 ± 0.02
S27	0.09 ± 0.05	0.09 ± 0.01

Figure 3. Viscosity of SAP hydrogels at different rpm for 1% solutions.

also by sorption in the bulk of SAP particles.[24] The structure of the polymeric hydrogel affects the level of polymer interaction with water and the provision of active sites to adsorb or coordinate metal ions. The sorption behavior and the quantity of metal ions taken up depend on not only the attributes of metal ions (such as ionic size, electropositivity, reactivity, etc.), but

Table V. Melting Temperature and Enthalpy of Fusion of Starch-Based SAP Samples

Sample	Onset of melting (°C)	Melting temperature (°C)	Endset of melting (°C)	Enthalpy of fusion (J/g)
S1	152.7	162.3	186.7	213.2
S2	159.4	160.5	173.5	289.5
S3	154.3	169.5	196.0	398.9
S4	152.7	177.7	196.6	494.9
S5	161.8	166.8	181.4	239.4
S6	144.9	159.2	181.9	220.2
S7	162.9	165.9	179.7	232.6
S8	162.2	169.2	195.7	343.2
S9	149.9	151.5	157.8	65.1
S10	143.9	149.7	172.4	158.6
S11	156.9	163.8	183.4	288.5
S12	141.1	171.6	193.9	416.6
S13	161.8	166.8	181.4	237.2
S14	152.0	166.0	194.2	244.7
S15	156.8	163.8	183.9	245.2
S16	162.9	165.9	179.7	232.6
S17	155.9	158.9	171.7	244.1
S18	154.2	161.9	184.1	233.9
S19	156.3	164.3	185.4	226.7
S20	150.6	173.1	198.9	247.1
S21	153.9	162.9	190.5	238.1
S22	148.1	151.7	164.8	125.6
S23	157.2	159.2	169.7	188.6
S24	157.9	169.8	194.8	269.9
S25	163.3	172.3	200.8	308.3
S26	159.3	172.2	196.7	305.8
S27	168.0	171.9	187.4	283.0

g-poly(tetrahydrofuran) and poly(caprolactone) in the temperature range of 110 to 180°C. Our results also agrees with the observation of Nayak and Singh[46] that for hydroxypropyl guar gum-g-PAM an endothermic peak was obtained at 195°C due to crystalline melting of grafted PAM.

Removal of Heavy Metal Ions

The heavy metal ion removal capacity of the superabsorbent polymer (S4) was determined at pH 4.5 at room temperature. Maximum adsorption capacity was obtained for the metal, copper (93%), followed by Pb (88.9%), and Zn (78%). The highest adsorption obtained for copper could be due to the fact that copper is the easiest metal to be complexed with ligands containing nitrogen and oxygen.[47] Our result agrees with the observation of Guclu et al.[15] that the order of affinity in competitive removal of heavy metals was observed to be greater for copper than lead.

Saponified starch-g-poly(acrylamide) could remove the metal ions by adsorption on COO^- group present in the SAP and
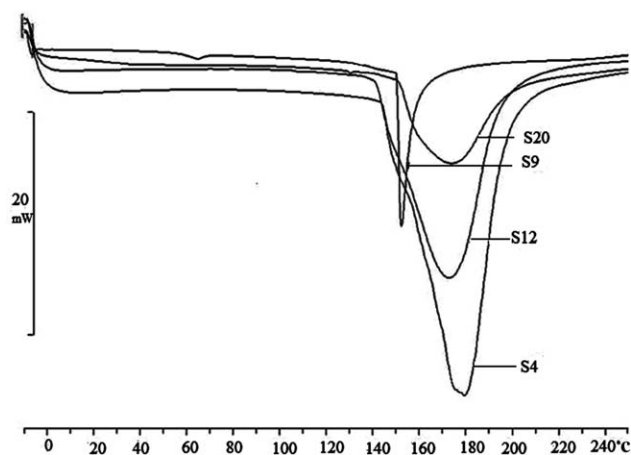
Figure 4. DSC thermograms of starch-based superabsorbent polymers.

also on the structural aspects of the polymer.[16,48] In this study, saponification of graft copolymer yielded polymer structure that contains carboxylate groups (COO^-) which can bind these metal ions. Pathania et al.[24] have determined the metal ion (Zn, Ni, and Mg) adsorption capacities of starch-graft-copolymers synthesized from potato starch and methacrylic acid and obtained a maximum adsorption for Mg (18.7%) followed by Ni (16%) and Zn (12.6%). However, in the present study, the adsorption capacity was found to be very high.

CONCLUSIONS

Superabsorbent polymers with different swelling capacities were synthesized from cassava starch by graft copolymerization with acrylamide and subsequent alkali saponification and the grafting parameters, dynamic rheological and thermal properties were determined. The percentage add on, graft frequency, and weight average molecular weights were found to be largest for the copolymer with highest percentage grafting. The mechanical stability of the hydrogels investigated by frequency sweep test indicated that, for the hydrogels with higher absorbency, the viscous component predominated over the elastic component in the frequency range of linear viscoelastic region and exhibited less mechanical rigidity. The highly absorbing hydrogels had relatively low gel strength compared to those with smaller absorbencies. The melting temperatures and enthalpies of fusion were determined for the xerogels synthesized under different reaction conditions. The information on mechanical properties of these hydrogels will be useful in exploiting their suitable end uses. The adsorption behavior of the starch-g-PAM hydrogels to metals such as Cu(II), Pb(II), and Zn(II) from aqueous solution was investigated to demonstrate the application of these materials for the removal of heavy metals in effluent water.

ACKNOWLEDGMENTS

REFERENCES

1. Athawale, V. D.; Lele, V. *Starch/Starke.* **2001**, *53*, 7.

2. Saraydin, D.; Karadag, E.; Guven, O. *Polym. Bull.* **1998**, *4*, 577.

3. Abedi-Koupai, J.; Asadkazemi, J. *Iran. Polym. J.* **2006**, *15*, 715.

4. Po, R. *J. Macromol. Sci. Polym. Rev.* **1994**, *34*, 607.

5. Sayil, C.; Okay, O. *Polymer.* **2001**, *42*, 7639.

6. Francesca, L.; Alessandro, S.; Giuseppe, M. *Macromol. Symp.* **2003**, *200*, 199.

7. Perera, D. I.; Shanks, R. A. *Polym. Int.* **1996**, *39*, 121.

8. Ramazani-Harandi, M. J.; Zohuriaan-Mehr, M. J.; Yousefi, A. A.; Ershad-Langroudi, A.; Kabiri, K. *Polym. Test.* **2006**, *25*, 470.

9. Ramazani-Harandi, M. J.; Zohuriaan-Mehr, M. J.; Yousefi, A. A.; Ershad-Langroudi, A.; Kabiri, K. *J. Appl. Polym. Sci.* **2009**, *113*, 3676.

10. Marandi, G. B.; Mahdavinia, G. R.; Ghafari, S. *J. Polym. Res.* **2011**, *18*, 1487.

11. Omidian, H.; Hashemi, S. A.; Sammes, P. G.; Meldrum, I. *Polymer.* **1999**, *40*, 1753.

12. Sadeghi, M.; Hosseinzadeh, H. *Turk. J. Chem.* **2008**, *32*, 375.

13. Parvathy, P. C.; Jyothi, A. N. *Starch/Starke.* **2012**, *64*, 803.

14. Karadag, D.; Saraydin, D.; Guven, O. *Sep. Sci. Technol.* **1995**, *30*, 3747.

15. Guclu, G.; Al, E.; Emik, S.; Iyim, T. B.; Ozgumus, S.; Ozyurek, M. *Polym. Bull* .**2010**, *65*, 333.

16. Ekebafe, L. O.; Ogbeifun, D. E.; Okieimen, F. E. *Afr. J. Environ. Sci. Technol.* **2012**, *6*, 275.

17. Jyothi, A. N.; Sreekumar, J.; Moorthy, S. N.; Sajeev, M. S. *Starch/Starke* **2010**, *62*, 18.

18. Parvathy, P. C.; Jyothi, A. N. *Starch/Starke* **2012**, *64*, 207.

19. Sajeev, M. S.; Moorthy, S. N.; Kailappan, R.; Rani, V. S. *Starch/Stärke* **2003**, *55*, 213.

20. Fanta, G. F.; Burr, R. C.; Doane, W. M.; Russell, C. R. *J. Polym. Sci.* **1974**, *45*, 89.

21. Biswal, D. R.; Singh, R. P. *Carbohydr. Polym.* **2004**, *57*, 379.

22. Willet, J. L.; Finkenstadt, V. L. *J. Appl. Polym. Sci.* **2006**, *99*, 52.

23. SAS/STAT Software Version 8; SAS Institute Inc: Cary, NC, 2000.

24. Pathania, D.; Sharma, R.; Kalia, S. *Adv. Matt.Lett.* **2012**, *3*, 259.

25. Lanthong, P.; Nuisin, R.; Kiatkamjornwong, S. *Carbohydr. Polym.* **2006**, *66*, 229.

26. Kiatkamjornwong, S.; Chomsaksakul, W.; Sonsuk, M. *Radiat. Phys. Chem.* **2000**, *59*, 413.

27. Kiatkamjornwong, S.; Mongkolsawat, K.; Sonsuk, M. *Polymer* **2002**, *43*, 3915.

28. Hao, X.; Chang, Q.; Duan, L.; Zhang, Y. *Starch/Starke* **2007**, *59*, 251.

29. Sen, G.; Pal, S. *Macromol. Symp.* **2009**, *277*, 100.

30. Eutamene, M.; Benbakhti, A.; Khodja, M.; Jada, A. *Starch/Starke* .**2009**, *61*, 81.

31. Lu, S.; Lin, T.; Cao, D. *Starch/Starke* **2003**, *55*, 222.

32. Ghosh, S.; Sen, G.; Jha, U.; Pal, S. *Bioresour. Technol* .**2010**, *101*, 9638.

33. Brostow, W.; Pal, S.; Singh, R. P. *Mater. Lett.* **2007**, *61*, 4381.

34. Krishnamoorthi, S.; Mal, D.; Singh, R. P. *Carbohydr. Polym.* **2007**, *69*, 371.

35. Song, H.; Zhang, S. F.; Ma, X. C.; Wang, D. Z.; Yang, J. Z. *Carbohydr. Polym.* **2007**, *69*, 189.

36. Shrogen, R. L.; Willet, J. L.; Biswas, A. *Carbohydr. Polym.* **2009**, *75*, 189.

37. Rao, M. A. In Rheology of Fluid and Semisolid Foods: Principles and Applications; Gustavo, B. C., Ed.; Food Engineering Series; Springer: Gaithersburg, Aspen, **1999**; p 59.

38. Seetapan, N.; Wongsawaeng, J.; Kiatkamjornwong, S. *Polym. Adv. Technol.* **2011**, *22*, 1685.

39. Pourjavadi, A.; Hosseizadeh, H. *Bull. Korean. Chem. Soc.* **2010**, *31*, 3163.

40. Jyothi, A. N.; Sajeev, M. S.; Parvathy, P. C.; Sreekumar, J. *J. Appl. Polym. Sci.* **2011**,*122*, 1546.

41. Singh, V.; Tiwari, A.; Pandey, S.; Singh, S. K. *Starch/Starke* **2006**, *58*, 536.

42. Rubinstein, M.; Ralph, C. H. In Polymer Physics; Oxford University Press: New York, **2003**; Vol. *1*, Chapter 1, p 1.

43. Bhatt, V. D.; Gohil, K.; Mishra, A. *Int. J. Chem. Tech. Res.* **2010**, *2*, 1771.

44. Ahmed, J.; Zhang, J. X.; Song, Z.; Varshney, S. K. *J. Therm. Anal. Calorim.* **2009**, *95*, 957.

45. Labet, M.; Thielemans, W.; Dufresne, A. *Biomacromolecules* **2007**, *8*, 2916.

46. Nayak, B. R.; Singh, R. P. *Eur. Polym. J.* **2001**, *37*, 1655.

47. Essawy, H. A.; Ibrahim, H. S. *React. Funct. Polym.* **2004**, *61*, 421.

48. Abd-Alla Nada, M. A.; Alkadi, M. Y.; Fekri, H. M. *Bioresources* **2007**, *3*, 46.