

Effect of Graft-Copolymerization with Poly(acrylamide) on Rheological and Thermal Properties of Cassava Starch

Alummoottil N Jyothi,¹ Moothandasery S Sajeev,¹ Subramoney N Moorthy,¹
Janardhanan Sreekumar²

¹Division of Crop Utilization, Central Tuber Crops Research Institute, Sreekariyam, Thiruvananthapuram 695 017, Kerala, India

²Section of Social Sciences, Central Tuber Crops Research Institute, Sreekariyam, Thiruvananthapuram 695 017, Kerala, India

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ABSTRACT: Graft copolymers of different grafting levels were synthesized by the free radical initiated reaction of cassava starch with acrylamide in presence of ceric ammonium nitrate. The viscosity properties of the native granular starch and the grafted starches were determined using a Rapid visco analyzer (RVA) and rheological properties by frequency sweep test under different conditions using a rheometer. Some of the grafted starches exhibited significantly higher and some others exhibited drastically reduced peak viscosity values irrespective of the percentage grafting. All the grafted starches exhibited very good viscosity stability as evidenced from the highly reduced breakdown and

higher final viscosity values in comparison to native cassava starch. Thermal analysis of the pure granular cassava starch and grafted starches was carried out using a differential scanning calorimetry (DSC) and thermogravimetry. DSC studies showed that in comparison to native starch, the grafted starches showed lower temperatures of transition. The thermal stability of cassava starch was enhanced by grafting as observed from the thermogravimetric data. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 337–346, 2010

Key words: cassava starch; acrylamide; grafting; rheological properties; thermogravimetry

INTRODUCTION

Starch graft copolymers are increasingly used in the manufacture of molded plastics, ion-exchange resins, plastic films, and in cosmetics.¹ Grafting of vinyl monomers onto starch has great potential in developing tailor-made products for industrial applications. Depending upon the conditions used for grafting, the properties of the graft copolymers also varied. There are many reports on the synthesis and characterization of starch graft-copolymers using various free radical initiation systems. However, most of them are confined to cereal and potato starches^{2–5} and a few are on cassava starch.^{6,7} Graft copolymerization is reported to alter the thermal stability of starch.^{1,5–9} Athawale and Lele¹ have studied the thermal stability, glass transition temperature, and kinetics of thermal degradation of graft copolymers of maize starch with vinyl monomers such as acrylamide, methacrylamide, acrylic acid, and meth-

acrylonitrile. Except starch-graft-acrylic acid, all other graft copolymers are reported to show enhanced thermal stability over pure maize starch.¹ No systematic studies seem to exist on the rheological properties of the gels of graft copolymers.

The reaction conditions for the synthesis of graft copolymers of cassava starch with poly(acrylamide) have been standardized in our laboratory. A range of graft copolymers with different levels of grafting could be synthesized and characterized by spectral and chemical methods, and reported elsewhere.¹⁰ The objectives of this study were to determine the rheological and thermal properties of those graft copolymers and to study the effect of reaction conditions and the level of grafting on the observed properties. The study was also aimed at comparing the properties among the grafted starches and also with the native starch.

MATERIALS AND METHODS

Cassava starch was extracted from freshly harvested tubers from CTCRI farm according to standard procedure.¹¹ The native starch contains about 9–10% moisture content. Acrylamide (AM), ceric ammonium nitrate (CAN), and Potassium bromide (KBr) were purchased from Sigma Aldrich Chemicals (St. Louis).

Correspondence to: A. N. Jyothi (sreejyothi_in@yahoo.com).

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Synthesis of cassava starch-g-copolymers

The detailed synthetic procedure has been reported¹¹ and is briefly described below: A 4-factor 3-level response surface Box-Behnken design with 27 treatments was used for the synthesis of graft copolymers of cassava starch with acrylamide using ceric ammonium nitrate as the free radical initiator. The factors were: concentration of AM [10, 15, and 20 g/10 g dry starch/200 mL (Starch: AM (g/g) = 1 : 1, 1 : 1.5, and 1 : 2)], concentration of CAN [1.65, 3.30, and 4.95 g/L (Starch: CAN (g/g) = 1 : 0.165, 1 : 0.329, and 1 : 0.493)], time (60, 120, and 180 min) and temperature (35, 45, and 55°C). The samples were labeled from S₁ to S₂₇. An aqueous solution of granular cassava starch (10 g/200 mL distilled water) was taken in a three necked flask. The flask was kept in a water bath at the specified temperature. Ceric ammonium nitrate was added in required quantities, kept for about 10 min to facilitate free radical formation and N₂ gas was passed through the solution. Acrylamide was then added and the reaction mixture was stirred for the required period. The reaction product was washed with distilled water several times to ensure the complete removal of the homopolymer. The product was then washed with 70% aqueous methanol, dried at 60°C and weighed. The percentage grafting was calculated from the weights of the original starch, grafted starch and the monomer used as follows⁵:

$$\% \text{ Grafting} = [(W_1 - W_0)/W_0] \times 100$$

$$\% \text{ Efficiency} = [(W_1 - W_0)/W_2] \times 100$$

where, W_0 , W_1 and W_2 denote the weights of the original starch, grafted starch, and the monomer used, respectively.

Viscosity studies

The viscosity parameters of the native and grafted starches were recorded using a Rapid visco analyzer (RVA-4, Newport scientific, Warriewood, Australia). For grafted samples, weighed quantities (2g starch in 20 g distilled water) were soaked in cold distilled water overnight. A 10% slurries thus obtained were subjected to RVA analysis at a constant speed of 160 rpm using standard I profile. The samples were heated from 50 to 95°C at 12°C/min and were then held at 95°C for 2 min. The pastes were cooled to 50°C at 12°C/min and finally maintained at 50°C for 2 min. The parameters recorded using the built-in software were peak viscosity, breakdown viscosity, final viscosity, setback viscosity, and pasting temperature. The ratio of breakdown to peak viscosity was expressed as the breakdown ratio.

Rheological properties

The dynamic rheological properties of the gels of grafted starches were determined using a Physica VT2 Rheometer (Anton Paar Germany GmbH, Ostfildern, Germany) at 30°C, using a parallel plate system (PP20-SN5912, 1mm diameter) at 1 mm gap. The types of gels were prepared as described below (hereafter represented as T1 and T2):

- T1- A weighed quantity of starch (2 g) was soaked in 20 g distilled water overnight to get a 10% gel.
- T2- The gels obtained from RVA analysis as described in section 2.3.

The mechanical spectra of the gels from both the treatments were obtained from frequency (f) sweeps over the range of 0.10–10Hz at a constant strain of 1%. The storage modulus (G'), loss modulus (G''), phase angle (δ) and complex viscosity (η) were recorded, and the measurements were conducted in triplicate. The frequency dependence of G' and G'' (n' and n'') were determined from the power law relationship of G' and G'' in the frequency sweep, $G' = G'_0 \omega^{n'}$ and $G'' = G''_0 \omega^{n''}$, where, G'_0 and G''_0 are the intercepts, $\omega = 2\pi f$ is the frequency in rad s⁻¹.¹² Depending up on the values of n' and n'' , the solid to liquid transition of a system can be ascertained. For n' , values close to 2 or 0, and for n'' , values close to 1 or 0 represent liquid or solid behaviors respectively.

Differential scanning calorimetry

The differential scanning calorimetry was performed according to Athawale and Lele.¹ The pure granular cassava starch and the graft copolymers (3–4 mg) were weighed out into aluminum pans and sealed hermetically. The samples were then tested in a Mettler Toledo DSC 822e instrument (Mettler-Toledo, Schcoerfenbach, Switzerland). An empty pan was used as reference and the sample was heated from 40 to 275°C at a heating rate of 20°C/min under nitrogen atmosphere. Temperatures corresponding to the onset of transition and midpoint of the transition region and enthalpy (ΔH) were recorded by means of the built-in software. To check the reassociation of the molecules during cooling, heating, cooling, and reheating cycle was performed as follows: heating from 30 to 250°C at 20°C/min, cooling back to 40°C and reheating to 250°C at 20°C/min.

Thermogravimetric analysis

The TG analysis of the samples was performed on a Diamond TG/DTA analyzer (Perkin Elmer Inc.,

TABLE I
The % Grafting and Grafting Efficiency of Cassava Starch-graft-copolymers
Synthesized Under Different Reaction Conditions

Sample	Conc. of AM (g/10g starch)	Conc. of CAN (g/L)	Time (min)	Temperature (°C)	% grafting	% efficiency
S ₁	10	1.65	120	45	31.91	31.91
S ₂	10	4.95	120	45	38.49	38.49
S ₃	20	1.65	120	45	75.95	37.98
S ₄	20	4.95	120	45	174.82	87.41
S ₅	15	3.30	60	35	2.9	1.93
S ₆	15	3.30	60	55	60.38	40.25
S ₇	15	3.30	180	35	104.48	69.65
S ₈	15	3.30	180	55	136.04	90.69
S ₉	10	3.30	120	35	20.66	20.66
S ₁₀	10	3.30	120	55	19.47	19.47
S ₁₁	20	3.30	120	35	91.26	45.63
S ₁₂	20	3.30	120	55	154.97	77.49
S ₁₃	15	1.65	60	45	32.66	21.77
S ₁₄	15	1.65	180	45	76.40	50.93
S ₁₅	15	4.95	60	45	53.05	35.37
S ₁₆	15	4.95	180	45	90.16	60.11
S ₁₇	10	3.30	60	45	28.81	28.81
S ₁₈	10	3.30	180	45	40.96	40.96
S ₁₉	20	3.30	60	45	14.48	7.24
S ₂₀	20	3.30	180	45	169.10	84.55
S ₂₁	15	1.65	120	35	8.72	5.81
S ₂₂	15	1.65	120	55	14.67	9.78
S ₂₃	15	4.95	120	35	37.34	55.95
S ₂₄	15	4.95	120	55	100.00	66.67
S ₂₅	15	3.30	120	45	156.81	71.21
S ₂₆	15	3.30	120	45	158.94	79.47
S ₂₇	15	3.30	120	45	162.44	81.22

Values are the mean of three replications.

Shelton, CT, USA). Heating was performed from 40°C to 630°C at a heating rate of 10°C/min.

Statistical analysis

All the determinations were performed in triplicate and the data were analyzed statistically using the package SAS 8.01 to perform ANOVA.¹³ The treatments were considered significantly different at 5% level of significance ($P \leq 0.05$). Simple correlation analysis was done to study the correlation between the percentage grafting and the observed properties of the grafted starches.

RESULTS AND DISCUSSION

The % grafting (%G) of the samples synthesized under different reaction conditions ranged from 2.9–174.82% and grafting efficiency from 1.93 to 90.69% (Table I). Second order polynomial relationships were obtained for %G, which explained the main, quadratic and interaction effects of factors. The linear and quadratic terms of all the four variables have significant effect on percentage grafting ($P \leq 0.05$) and the results showed that higher levels of all

the variables favored grafting reaction. The detailed results are reported elsewhere.¹⁰

Viscosity properties

The RVA viscosity parameters of the native cassava starch and the graft copolymers are presented in Table II. The peak viscosity of the native starch was 2442.0 cP with a breakdown ratio of 0.447. Some of the grafted starches exhibited lower and some others exhibited significantly higher peak viscosities than native starch. The results showed that in general, treatments with lower levels of AM, temperature and higher reaction duration showed reduced viscosities. Though correlation studies showed no significant correlation between %G and peak viscosity, the highest peak viscosity value of 8981cP was shown by the sample S₄, which also had the highest grafting percentage. This could be due to the higher amount of hydrophilic segment in the polymer, which resulted in increased swelling because the increasing hydrophilic fraction of the polymer chain tends to disperse better in the aqueous phase.⁷

Correlation studies have shown that there was no significant correlation between %G and any of the viscosity parameters. However, a few trends were

TABLE II
RVA Viscosity Data of the Native and Grafted Cassava Starch

Sample	Peak viscosity Final viscosity		Breakdown ratio
	(cP)		
Native starch	2442	1717	0.447
S ₁	4581	4178	0.159
S ₂	3631	3672	0.039
S ₃	3997	5198	0.019
S ₄	8981	8829	0.388
S ₅	2556	2840	0.055
S ₆	1732	2020	0.080
S ₇	400	691	0.115
S ₈	463	758	0.080
S ₉	1303	2027	0.021
S ₁₀	3595	3868	0.086
S ₁₁	889	2412	0.323
S ₁₂	2574	3463	0.458
S ₁₃	4624	4643	0.046
S ₁₄	2736	3310	0.024
S ₁₅	2934	4690	0.264
S ₁₆	1319	2193	0.065
S ₁₇	1054	1442	0.040
S ₁₈	832	1282	0.046
S ₁₉	3620	3339	0.157
S ₂₀	461	1173	0.095
S ₂₁	3096	2468	0.241
S ₂₂	1903	2992	0.201
S ₂₃	2174	3888	0.046
S ₂₄	1343	2318	0.160
S ₂₅	1359	2360	0.063
S ₂₆	1648	2328	0.064
S ₂₇	1630	2590	0.065

Values are the mean of three replications.

observed. For some samples all the viscosity properties were suppressed by grafting (samples S₇, S₈, S₁₇, S₁₈, S₂₀). This may be due to the high levels of bonding which prevents free swelling of the granules. In some other cases, peak viscosity considerably increased (S₁, S₂, S₃, S₄, S₁₀, S₁₃, S₁₉), when compared with the native starch. These samples also possess good viscosity stability. Here, the free swelling of granules is taking place and bonding is preventing their breakdown. This could be due to the small levels of crosslinking in these graft copolymers. According to earlier reports, AM grafts are hydrophilic and consequently higher swelling may be responsible for the high viscosity.⁷ In most of the cases, there was a steady and slow increase in viscosity properties to reach high final viscosity. This could be due to the restricted swelling of the samples. The RVA viscosgrams of the native cassava starch and some representative samples from the graft copolymers are shown in Figure 1.

The grafted starches also showed reduced breakdown, which was evident from the very low breakdown ratio shown by those samples (0.019–0.388). It could be observed that unlike the native starch, final viscosity is invariably higher than the peak viscosity

for all the grafted starches. The final viscosity of the native starch was 1717 cP, whereas those of the graft copolymers ranged from 691 to 8829 cP. The results proved the enhanced paste stability of the starch after grafting. Singh et al. earlier reported that grafting resulted in an increase in the viscosity of potato starch solutions; moreover the viscosities were more stable than those of native starch.⁵

Response surface analysis of the data showed that the positive quadratic effect of concentration of CAN was significant ($P = 0.013$) for the peak viscosity. Therefore, the peak viscosity increased with increase in CAN concentration, reached a maximum and then decreased with further increase in the variable. The linear effect of time ($P = 0.034$) and quadratic effect of concentration of CAN ($P = 0.004$) were significant on the final viscosity of the grafted starches. Higher final viscosities were observed for the samples synthesized under lower reaction durations. The breakdown ratio was significantly affected by the positive linear effect of concentration of AM ($P = 0.007$), and interaction of concentration of AM and CAN ($P = 0.022$). This indicates that breakdown was more when synthesis was carried out under higher levels of AM.

Unlike the native starch, since the grafted starches form gels in water even in the ambient temperature ($30 \pm 2^\circ\text{C}$), it may be difficult to use this information for studying the gelatinization properties, since RVA measures gelatinization properties during a cycle of heating and cooling. Hence, a rheometer has been

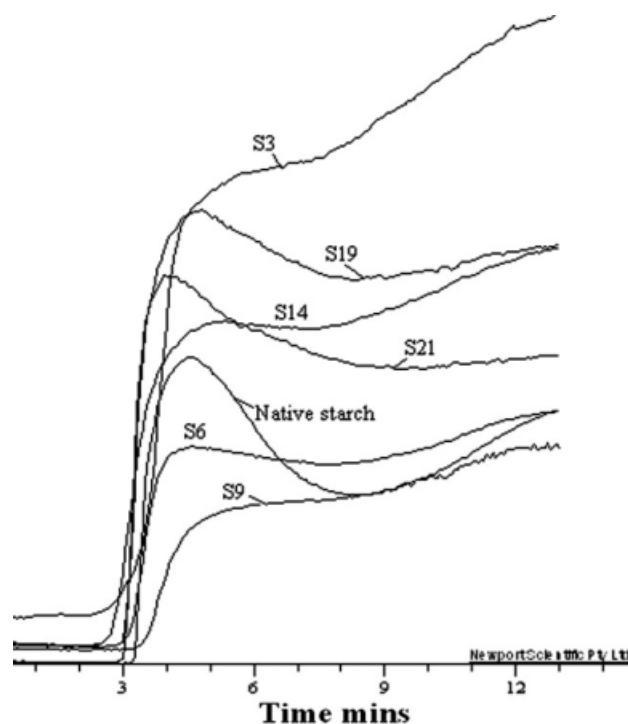


Figure 1 RVA viscosgrams of native cassava starch and its graft copolymers.

TABLE III
Mechanical Spectra^a of Native and Grafted Starch Gels at a Frequency of 10Hz

Sample	Overnight swelling				Overnight swelling and consequent heating/ cooling in RVA			
	G' (Pa)	G'' (Pa)	δ (°)	η (Pa s)	G' (Pa)	G'' (Pa)	δ (°)	η (Pa s)
Native starch	–	–	–	–	1060	959	42.2	22.7
S1	369.5	1425	75.55	23.45	1640	1260	37.6	32.9
S2	1235	1360	48.0	29.25	2150	1090	27.0	38.4
S3	479.5	913	62.6	16.45	1470	1200	39.1	30.2
S4	1535	1790	49.35	37.45	1540	1160	37.1	30.7
S5	547	1440	69.2	24.5	1390	1270	42.4	29.9
S6	228	1460	81.1	23.5	1060	1180	48.1	25.2
S7	1300	1510	49.3	31.7	3030	1890	32.0	56.8
S8	604	1830	71.7	30.6	893	1360	56.7	25.9
S9	977	1080	48.0	23.2	998	1240	51.2	25.3
S10	6790	1880	15.5	112.0	1770	1340	37.2	35.3
S11	1190	1200	45.2	26.9	940	1100	55.8	21.2
S12	3970	2670	33.9	76.1	556	1170	64.6	20.6
S13	1570	1060	34.1	30.3	1170	1550	52.8	30.9
S14	636	1300	64.0	23.1	1550	1720	47.9	36.8
S15	2000	1270	32.5	37.7	2360	1660	35.2	45.9
S16	568	980	59.9	18.0	934	1210	52.3	24.3
S17	746	1090	55.6	21.0	1180	1310	48.0	28.0
S18	467	1030	65.5	17.9	903	1220	53.6	24.2
S19	1180	1390	49.7	29.1	1240	1240	44.9	27.9
S20	1340	1720	52.1	34.7	2700	1560	30.1	49.7
S21	708	1710	67.6	29.5	1330	1070	38.6	27.2
S22	1270	1860	55.5	35.8	1240	1280	45.9	28.4
S23	820	1440	60.3	26.3	1450	1100	37.2	28.9
S24	337	1210	74.4	20.0	720	1640	66.2	28.5
S25	2130	1460	34.5	41.1	2100	2170	37.0	34.9
S26	1905	1320	34.3	38.3	1860	1800	39.5	35.0
S27	1900	1300	34.8	40.2	1985	1850	41.0	32.9

^a Values are the mean of three replications.

used to study the rheological properties of the gels at 30°C and also after RVA analysis.

Rheological properties

The dynamic rheological properties such as storage modulus (G'), loss modulus (G'') phase angle (δ) and complex viscosity (η) of the starch pastes were determined over a frequency sweep from 0.1 to 10 Hz for the native starch and the grafted starches. The G' , G'' , δ and η at a frequency of 10 Hz for the two types of gels (T1 and T2) as mentioned in section 2.4, are presented in Table III.

At 10Hz, the storage modulus and loss modulus for different grafted starch gels (T1), ranged from 228–6790Pa and 913–1880 Pa, respectively (Table III). The gels of most of the grafted starches showed liquid-like behavior since $G' < G''$. However, the samples S₁₀, S₁₂, S₁₃ and S₁₅ exhibited higher storage modulus than loss modulus showing more of a solid-like behavior. Also the G' values of the samples S₁₀ and S₁₂ were found to be significantly higher than that of the other samples (Fig. 2).

In Table III, the dynamic moduli for the gels T2 are presented. For the native cassava starch, G' and G'' were 1060 and 959 Pa, respectively, at a frequency of 10Hz. In the case of graft copolymers, majority of the samples exhibited liquid-like behavior ($G' < G''$) in this case also, during most of the frequency range. However, a few samples showed higher storage modulus than loss modulus exhibiting more solid like nature of the gels (Table III).

For both types of gels T1 and T2, the dynamic moduli showed frequency dependence and increased with increase in frequency for native as well as grafted starches (Figs. 2 and 3). In the case of grafted starches, the higher positive slopes for G' for the gels T2 showed that the frequency dependence was higher in this case than those observed for the gels T1.

Comparing the mechanical spectra of the two types of gels, two distinct behaviors were observed for the grafted starches. The graft copolymers which showed very low storage modulus for the gels from T1 showed significantly higher G' in the case of T2 (Table III). On the other hand, the samples S₁₀ and S₁₂ which had significantly higher G' (T1), showed a

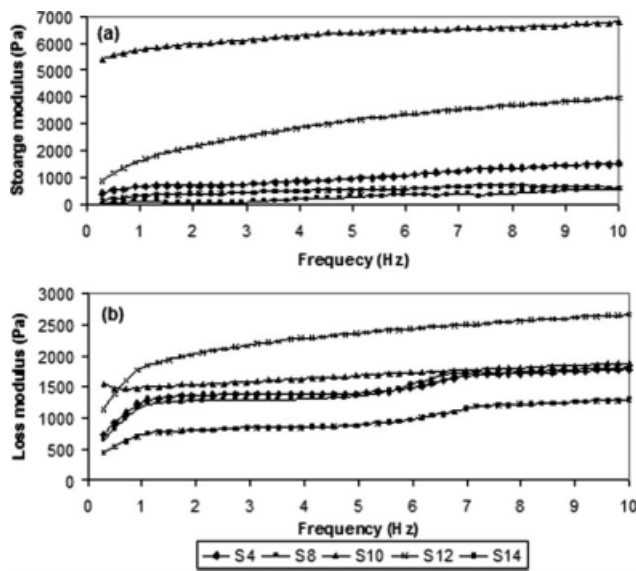


Figure 2 Dynamic moduli (a) storage modulus and (b) loss modulus against frequency for the grafted starch gels prepared by overnight swelling at ambient temperature.

decrease in the same for T2. The grafted starches with medium values for G' for the gels obtained by swelling at ambient temperature did not show much difference in G' after RVA analysis also. The observed effects could be attributed to the fact that the granules of the copolymers, which produced weak gels by overnight swelling at ambient temperature could produce stronger and compact gels when subjected to heating in RVA by the swelling and gelatinization of more granules under high temperature and shear. However, the samples S_{10} and S_{12} could produce stronger gels at ambient temperature and on further heating in RVA, the already swollen granules may undergo breakage resulting in lower G' . In the case of the samples with a medium value for G' the granules may be intact enough to overcome the disintegration of the gels during heating/cooling, and hence there was no significant change in G' values.

The grafted starch gels (T2) showed significantly higher storage moduli than native starch gel at the initial frequency levels. All the grafted starches showed higher loss modulus than native starch (959 Pa). In relation to G' of the native starch, the grafted starches were found to fall in two distinct groups. The samples S_8 , S_9 , S_{11} , S_{12} , S_{16} , S_{18} and S_{24} showed increase in storage modulus with frequency and up to a frequency of about 7–9 Hz, the values were higher than that of the native starch. With further increase in frequency, though G' continues to increase, it came down to lower values than that shown by the native starch gel. Hence at 10 Hz, these samples showed lower G' than that of the native starch gel. The rest of the samples had a very strong

dependency on frequency and showed higher storage moduli than native starch throughout the frequency range. The plots of G' and G'' versus frequency for representative samples from the two groups, along with the native starch are shown in Figure 3.

Table IV shows the frequency dependence of G' and G'' (n' and n'' respectively). Here also, liquid-like behavior of the gels was evident from the values of the exponents, n' and n'' in power law equation for the dynamic moduli. For the native starch gel (T2), the values of n' and n'' are 0.802 and 0.247 respectively, whereas, for the grafted starches, both the exponents were significantly lower and n' ranged from 0.114 to 0.689 and n'' from 0.115 to 0.277. Except for a few samples, the values of n' and n'' were significantly higher for the gels prepared by overnight swelling at ambient temperature (Table IV). This shows the more liquid-like nature of these gels in comparison with the gels obtained by RVA analysis.

Response surface analysis of the data showed that the interaction effect of acrylamide concentration and temperature had significant effect on storage modulus of the gels prepared at ambient temperature, whereas none of the variables or their interactions was directly related to the storage modulus of the gels from RVA analysis. None of the variables affected the loss modulus, phase angle and complex viscosity of the gels from the first set (T1). However, the quadratic terms of AM concentration, CAN concentration and temperature had high significant effect ($P < 0.001$) on the loss modulus of the gels

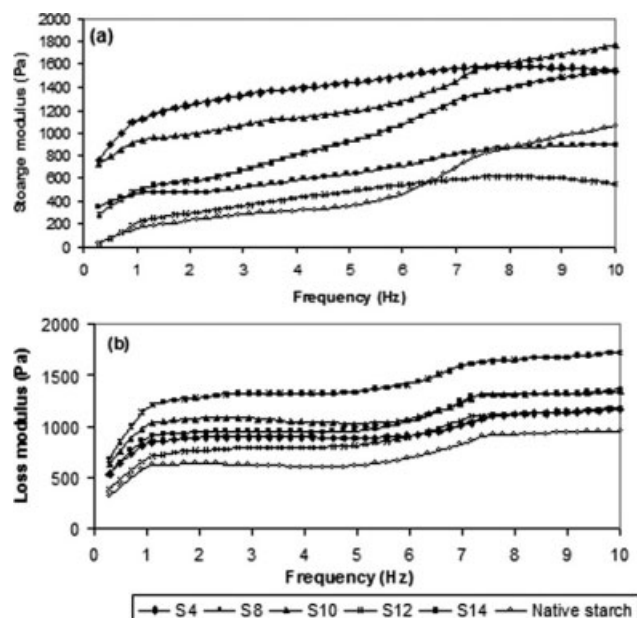


Figure 3 Plots of dynamic moduli against frequency for the native and grafted starch gels obtained by overnight swelling and consequent heating/cooling in RVA.

TABLE IV
Exponents in Power Equation for the Dynamic Moduli of the Gels of Native and Grafted Starches

Sample	Exponents in power equation ^a			
	Gels prepared by overnight swelling		Gels obtained after heating/cooling in RVA	
	n'	n''	n'	n''
Native starch	–	–	0.802	0.247
S1	0.687	0.248	0.171	0.152
S2	0.284	0.174	0.114	0.141
S3	0.462	0.287	0.386	0.186
S4	0.374	0.191	0.174	0.164
S5	0.921	0.264	0.246	0.193
S6	0.332	0.249	0.376	0.203
S7	0.514	0.252	0.264	0.158
S8	0.855	0.238	0.281	0.220
S9	0.568	0.212	0.543	0.229
S10	0.067	0.083	0.245	0.155
S11	0.569	0.222	0.687	0.277
S12	0.408	0.202	0.625	0.272
S13	0.331	0.169	0.152	0.159
S14	0.380	0.272	0.479	0.205
S15	0.118	0.111	0.232	0.115
S16	0.743	0.250	0.689	0.248
S17	1.683	0.248	0.606	0.246
S18	1.108	0.247	0.384	0.232
S19	0.436	0.195	0.279	0.195
S20	0.730	0.260	0.329	0.174
S21	0.283	0.188	0.234	0.200
S22	0.259	0.146	0.152	0.169
S23	0.359	0.217	0.390	0.207
S24	3.853	0.269	0.465	0.229
S25	0.337	0.198	0.198	0.116
S26	0.341	0.159	0.203	0.147
S27	0.324	0.293	0.219	0.115

^a r^2 ranged from 0.858–0.997 for n' and 0.672–0.941 for n'' for the gels after overnight swelling and 0.690–0.982 for n' and 0.683 – 0.959 for n'' for the gels after overnight swelling and RVA analysis.

from T2. With increase in concentrations of AM and CAN and time duration of reaction, there was a gradual decrease in loss modulus, which reaches a minimum and with further increase in these variables there was an increase in loss modulus for the gels. Correlation studies have shown that there was no significant correlation between the level of grafting and storage modulus, but percentage grafting was significantly ($P = 0.012$) correlated to loss modulus.

The phase angle of the native starch gel was 42.2°, whereas, for the grafted starches, it ranged from 27 to 66.2°. The early mentioned samples which showed lower storage modulus showed higher phase angles, indicating weak gel properties. However, the rest of the samples showed strong gel properties.

For most of the grafted starches, the dependency of phase angle on frequency was negligible, showing almost stable viscous and elastic properties under

frequency sweep. The complex viscosity showed a strong dependence on frequency in the initial frequencies and thereafter it showed almost steady values throughout the remaining frequency range. The highest complex viscosity (112.0 Pa s) was shown by the gel of sample S₁₀. The complex viscosity of the gel of S₄, which showed highest peak viscosity value in RVA analysis, was 35.5 Pa s.

The complex viscosity (η) ranged from 16.5 to 112.0 Pa.s for the gels T1 of the grafted starches and 20.6 to 56.8 Pa.s for the gels T2 at 10 Hz. The complex viscosity of most of the samples were higher after RVA analysis, however, some samples showed higher complex viscosity for the gels obtained by overnight swelling only. The sample S₁₀ could produce high viscous gels at room temperature and showed a significantly higher value of 112.0 Pa s for complex viscosity for its gel T1, and this was found to be higher than that observed for the gel T2.

DSC characteristics

The DSC data obtained for the native cassava starch and its graft copolymers are presented in Table V. According to Athawale and Lele,¹ the glass transition temperatures can be determined on the DSC curve either from the onset point of transition or from the mid-point of the transition region. In this study, the midpoint was used to determine the T_g , as it gives the average temperature at which most of macromolecules undergo the glass transition. Native cassava starch showed only one endotherm in the temperature range used. Some of the grafted starches showed two endotherms, while some others, especially those with a lower % grafting showed only one endotherm in the heating range (Fig. 4). This could be due to the still higher temperature for the second transition in those samples, since the maximum temperature used in this study was 275°C. According to earlier reports, copolymers synthesized from water soluble monomers such as acrylamide showed a second endotherm in the DSC curves around 250°C, and this was attributed to the fusion of the crystallites.¹

The first endothermic transition in each DSC curve corresponds to the glass transition of the respective polymer. The T_g of a semicrystalline polymer like starch is characteristic of its amorphous regions and hence hardly becomes affected by its crystallinity and is the temperature below which the changes in the position and the orientation of the molecules in the amorphous region cease.^{1,14} It has been reported that addition of plasticizers lowers the T_g of a polymer, making it easier for microlevel and macrolevel changes to occur.¹⁵ In this study, the glass transition of cassava starch having about 8–10% moisture

TABLE V
DSC Parameters for Cassava Starch and its Graft Copolymers

Polymer	First endotherm			Second endotherm		
	Onset of transition (°C)	Midpoint (°C)	ΔH (J/g)	Onset of transition (°C)	Midpoint (°C)	ΔH (J/g)
Native starch	160.28	162.46	138.56	–	–	–
S1	149.16	152.76	119.92	–	–	–
S2	155.15	159.12	116.15	–	–	–
S3	154.93	156.83	79.23	220.86	234.70	36.84
S4	157.65	160.66	137.47	235.54	250.78	17.09
S5	139.98	144.45	184.81	–	–	–
S6	154.29	158.13	108.26	240.49	255.13	14.03
S7	155.54	159.32	123.77	236.92	254.31	15.42
S8	153.43	157.09	124.37	238.18	253.69	16.68
S9	150.16	155.14	149.62	–	–	–
S10	151.86	154.74	180.23	255.53	272.56	14.93
S11	133.85	141.27	141.52	243.15	256.11	4.49
S12	153.95	159.10	157.09	244.77	253.81	2.14
S13	153.92	155.73	144.23	251.66	270.88	16.70
S14	157.38	161.14	130.78	–	–	–
S15	159.47	162.18	55.38	233.71	248.66	16.48
S16	155.90	159.27	149.62	241.45	256.78	14.21
S17	151.12	155.37	156.72	–	–	–
S18	156.42	158.76	9.269	250.33	272.53	12.07
S19	147.52	149.67	122.72	–	–	–
S20	155.72	157.63	91.00	242.08	257.09	11.94
S21	156.14	159.63	181.47	–	–	–
S22	154.72	158.38	43.59	–	–	–
S23	156.71	160.34	160.98	251.66	270.25	14.16
S24	154.51	157.72	99.37	234.56	245.35	25.25
S25	158.51	162.85	106.40	237.10	249.75	19.41
S26	155.20	157.54	103.16	231.39	252.73	14.55
S27	151.04	156.20	85.63	235.60	251.63	17.11

Values are the mean of three replications

showed the glass transition at 162.46°C and no other endotherm was present up to 275°C. However, Athawale and Lele¹ have reported that the glass transition temperature of maize starch was 91°C and

a second endothermic transition was appeared at around 245°C. The higher temperature for cassava starch shows more difficult molecular changes in comparison to maize starch.

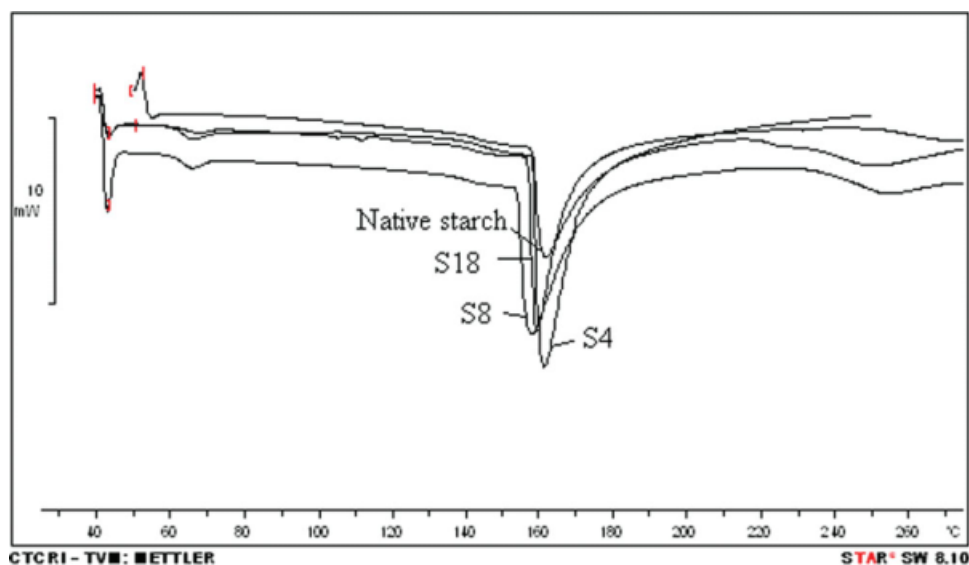


Figure 4 DSC curves for the native cassava starch and its graft copolymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

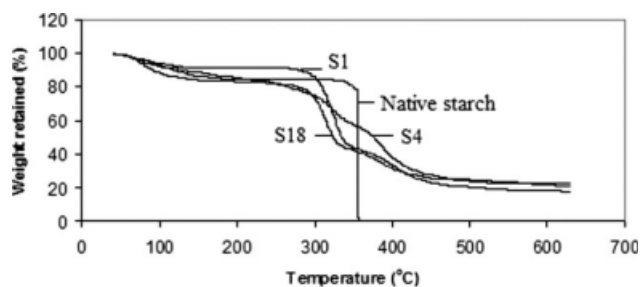


Figure 5 Thermograms for native cassava starch and starch-graft-poly(acrylamide).

The T_g values of the graft copolymers were close to each other and were lower than that of the native starch (Table V). This lowering could be due to the internal plasticization effect of the monomers when grafted on to the starch.¹ The enthalpy of transition was 138.56 J/g for the native cassava starch, whereas in the case of the grafted starches, some showed higher and some others showed lower values (9.27–184.81 J/g). In general, samples with very low or very high levels of % grafting showed significantly higher ΔH values and the samples having very low % grafting showed ΔH even higher than that of the native starch. However, there was a significant lowering in the enthalpy of the polymers with a medium level of grafting. The lowering in enthalpy for glass transition could be attributed to the decrease in crystallinity of starch on grafting of the monomers. However, at higher levels of grafting, due to some degree of crosslinking effect of the monomers more energy may be required for the transition.

Analysis of the pure granular starch and the graft copolymers by heating-cooling-reheating cycle showed that the grafted starches did not show any peaks in the reheating phase indicating that the graft melting is not reversible.

Thermo gravimetric analysis

Figure 5 shows the thermal behavior of native cassava starch and the grafted copolymers. Pure starch showed a characteristic three step thermogram, wherein the major weight loss (about 80%) occurred in the third step. The temperature for maximum decomposition was 346°C. The degradation was almost complete at 348°C. In the case of graft copolymers, five stages of decomposition were observed for all the samples. Unlike native starch, the grafted starches showed gradual decomposition. All the grafted starch samples showed higher thermal stability than native starch. The thermogravimetric data for the native and grafted starches are presented in Table VI. For the sample S_1 (%G = 31.91), about 17.43% of the sample remained undecomposed at 629.8°C. For other grafted starches also similar behavior was

observed. In the case of S_4 (%G = 174.82) and S_8 (%G = 136.04), 22.38% and 21.48% of the starch remained undecomposed even at 630°C. In general, acrylamide renders higher thermal stability to the grafted starch. Similar results have been reported earlier for starch-g-AM copolymers.^{1,4,5} According to earlier reports the grafting of vinyl monomers alters the thermal stability of starch and in most cases enhances it.^{8,9} Athawale and Lele¹ have studied the effect of percentage of grafting with different vinyl monomers, on the thermal stability of the starch by comparing the thermograms. They have observed that except starch-graft acrylic acid, all other graft copolymers showed enhanced thermal stability over pure maize starch. They also observed a characteristic three step thermogram for native maize starch and five stage decomposition for the grafted starches. Lanthong et al.,⁷ observed four stages of decomposition for cassava starch grafted with poly[acrylamide-co-(itaconic acid)]. Singh et al.,⁵ reported that grafted potato starch was more thermally stable than starch itself. The TGA

TABLE VI
Thermogravimetric Data of Cassava Starch and its Graft Copolymers

Sample	Number of decomposition stage	Temperature range (°C)	% Weight retained
Native starch	1	33.3–162.2	85.22
	2	162.2–346.7	77.33
	3	346.7–348.0	Nil
S_1 (%G = 31.91)	1	40.3–300.0	85.62
	2	300.0–337.5	48.27
	3	338.0–379.3	39.02
	4	380.0–425.0	26.84
	5	425.0–629.3	17.43
S_2 (%G = 38.49)	1	50.0–250.5	82.10
	2	250.5–312.7	71.33
	3	312.67–355.8	56.38
	4	355.8–452.3	27.23
	5	452.3–629.3	22.38
S_4 (%G = 174.82)	1	47.6–100.7	92.33
	2	100.7–317.3	74.63
	3	317.3–370.3	52.34
	4	370.3–435.5	29.20
	5	435.5–629.8	22.38
S_8 (%G = 136.04)	1	46.7–95.8	91.43
	2	95.8–289.7	78.45
	3	289.7–372.8	49.37
	4	372.8–439.2	27.98
	5	439.2–629.8	21.48
S_{18} (%G = 40.96)	1	46.7–121.3	85.92
	2	121.3–291.3	77.52
	3	291.3–344.0	43.22
	4	344.0–400.0	31.56
	5	400.0–623.7	21.33
S_{27} (%G = 172.44)	1	46.7–143.5	87.62
	2	143.5–293.0	78.77
	3	293.0–345.7	48.99
	4	345.7–425.5	25.49
	5	425.5–629.3	16.95

thermograms of polyethylene grafted membranes of potato starch have shown multistep degradation of PE backbone and grafted starch.^{16,17}

CONCLUSIONS

The rheological and thermal properties of cassava starch-*g*-copolymers with different % grafting were determined and compared. All the grafted starches showed higher final viscosities than peak viscosity, indicative of good paste stability. The graft copolymers also exhibited better thermal stability over native cassava starch. Because of the high water absorption capacity, viscosity stability and thermal stability, these water-soluble starch graft copolymers can find application in oil drilling for controlling filtrate loss for drilling muds, modifying viscosity in displacement fluids and inhibiting the hydration of clay and shale for enhanced oil recovery. Another potential field of application of these polymers is sizing and printing of cotton fabrics.

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