Cassava Starch-*graft*-Polymethacrylamide Copolymers as Flocculants and Textile Sizing Agents

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ABSTRACT: Cassava starch-*graft*-polymethacrylamide (PMAM) copolymers were synthesized by a free-radical-initiated polymerization reaction, and the products were tested for their efficiency as flocculants and textile sizing agents. The highest percentages of grafting and monomer conversion were 79.9 and 78.0%, respectively. The grafted starches were characterized by Fourier transform infrared spectroscopy, X-ray diffraction analysis, scanning electron microscopy, differential scanning calorimetry, and thermogravimetric analysis. The average molecular weight of PMAM chains in the grafted starches ranged from 15.9 to 30.8 × 10^5 g/mol. The grafted starches exhibited a higher peak viscosity and paste stability in comparison to the native starch (NS). Dynamic mechanical analysis showed that grafting provided fairly shear-stable hydrogels, and the highest storage modulus obtained was 17,900 Pa compared to 1879 Pa for NS. The flocculation studies demonstrated the superiority of starch-*g*-PMAM over cassava starch and PMAM as an efficient flocculant. The tensile strength of cotton yarns sized with the starch-grafted copolymer was significantly higher (104 MPa) compared to that sized with NS (34 MPa). © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2013**, *000*, 39810.

INTRODUCTION

Graft copolymerization is considered to be one of the most effective methods for gaining new and desired properties of natural and synthetic polymers.[1] Among natural polymers, starch has received much attention because of its low cost, easy availability, renewability, biocompatibility, and versatility of use.[2] Among the various sources of starch, cassava and maize starches have been commercially exploited for a long time and continue to be the major sources of starch. Because cassava roots contain a high starch content and a very low quantity of compounds such as proteins and lipids, they are recognized as an excellent source of pure starch suitable for a wide range of applications.

Starch-grafted copolymers are widely used as thickeners and sizing agents in the paper and textile industries, as flocculants for various kinds of industrial effluents,[3] as superabsorbents in diapers and sanitary napkins,[4] and in biodegradable plastics and films.[5] Many reports are available on the synthesis and characterization of starch-grafted copolymers with various free-radical initiation systems. The grafting of acrylamide and acrylonitrile onto starch has been extensively investigated[2,6–10] but with little attention to methyl analogues.[11–14] Athawale and Lele[15] synthesized graft copolymers of maize starch with acrylamide, methacrylamide, acrylic acid, and methacrylonitrile with ceric ammonium nitrate initiator. There are only a few reports on graft copolymerization onto cassava starch.[16,17]

The objective of this study was to optimize the reaction conditions for maximizing the grafting percentage of cassava starch-*graft*-polymethacrylamide (PMAM) by response surface methodology and to characterize the products and evaluate their efficiency as flocculants and textile sizing agents.

EXPERIMENTAL

Materials

Cassava starch was extracted from freshly harvested tubers according to a reported procedure.[18] Methacrylamide, ceric ammonium nitrate, kaolin, and α-amylase (from pancreatin porcine, E.C. 3.2.1.1, 280 units) was purchased from Sigma Aldrich Chemicals (St. Louis, MO). All of the other chemicals used were analytical grade.

Synthesis of Starch-*graft*-PMAM

A four-factor Box–Behnken design with 27 treatments, including three replicates of the central treatment, was used for the synthesis of the graft copolymers (Table I). A weighed quantity of starch dispersed in distilled water was gelatinized in a boiling water bath. It was then cooled to room temperature, ceric ammonium nitrate (CAN) was added in required quantities and kept for about 10 min in an N_2 atmosphere under mild stirring

Table I. %G, %GE, N_{AUG}, and R_g Values for the Starch-g-Copolymers under Different Reaction Conditions

Sample code	MAM (g)	CAN (g/L)	Time (min)	Temperature (°C)	%G	%GE	N_{AUG}	R_g (mol/L min)
A1	10	0.438	120	55	16.0 ± 2.1	16.0 ± 1.5	17,788 ± 156	1.57 ± 0.1
A2	10	0.878	120	55	19.6 ± 1.4	19.6 ± 1.7	16,238 ± 190	1.92 ± 0.4
A3	20	0.438	120	55	25.9 ± 1.4	13.0 ± 1.4	30,123 ± 213	2.02 ± 0.9
A4	20	0.878	120	55	79.9 ± 1.1	40.0 ± 2.3	12,645 ± 245	4.21 ± 1.0
A5	15	0.658	60	45	12.4 ± 3.6	8.3 ± 2.3	32,901 ± 390	7.83 ± 1.1
A6	15	0.658	60	65	23.8 ± 2.3	15.8 ± 2.5	27,991 ± 279	6.72 ± 0.5
A7	15	0.658	180	45	53.2 ± 3.2	35.4 ± 2.6	12,683 ± 121	5.87 ± 0.9
A8	15	0.658	180	65	60.4 ± 2.4	40.3 ± 2.8	11,819 ± 134	3.94 ± 0.4
A9	10	0.658	120	45	14.7 ± 1.5	14.7 ± 1.3	27,842 ± 145	1.44 ± 0.2
A10	10	0.658	120	65	14.5 ± 2.4	14.7 ± 1.4	28,888 ± 213	1.47 ± 0.5
A11	20	0.658	120	45	33.5 ± 3.3	16.8 ± 1.7	30,915 ± 224	3.28 ± 1.1
A12	20	0.658	120	65	64.4 ± 1.5	32.2 ± 1.9	16,932 ± 234	5.33 ± 1.0
A13	15	0.438	60	55	18.1 ± 2.6	12.1 ± 1.4	26,039 ± 312	3.55 ± 0.8
A14	15	0.438	180	55	26.9 ± 4.1	17.9 ± 1.8	30,789 ± 311	2.69 ± 1.1
A15	15	0.878	60	55	22.4 ± 3.2	14.9 ± 1.5	34,307 ± 267	4.39 ± 0.7
A16	15	0.878	180	55	27.7 ± 2.5	18.5 ± 2.3	30,831 ± 261	1.81 ± 0.8
A17	10	0.658	60	55	15.3 ± 2.2	15.3 ± 2.6	23,755 ± 210	3.06 ± 0.5
A18	10	0.658	180	55	22.6 ± 2.3	22.6 ± 3.1	25,124 ± 100	1.48 ± 0.3
A19	20	0.658	60	55	13.7 ± 1.9	6.9 ± 2.1	38,337 ± 121	2.68 ± 0.6
A20	20	0.658	180	55	68.6 ± 3.1	34.3 ± 2.2	24,456 ± 99	4.48 ± 0.7
A21	15	0.438	120	45	14.9 ± 2.5	14.6 ± 1.8	24,178 ± 222	1.46 ± 0.6
A22	15	0.438	120	65	13.4 ± 3.1	9.9 ± 1.6	34,506 ± 245	1.31 ± 0.2
A23	15	0.878	120	45	18.4 ± 2.7	12.3 ± 1.3	27,554 ± 265	1.80 ± 0.1
A24	15	0.878	120	65	49 ± 2.5	32.6 ± 1.1	21,984 ± 212	4.80 ± 0.4
A25	15	0.658	120	55	67.4 ± 1.2	44.9 ± 1.2	22,347 ± 234	6.61 ± 0.6
A26	15	0.658	120	55	68.3 ± 1.4	45.5 ± 1.2	22,156 ± 243	6.69 ± 0.7
A27	15	0.658	120	55	69.4 ± 1.3	46.3 ± 1.3	22,965 ± 235	6.73 ± 0.7

All measurements were taken in triplicate.

to facilitate free-radical formation. Methacrylamide dissolved in distilled water (100 mL) was then added, and the polymerization reaction was allowed to proceed at the required temperature for different time durations under continuous stirring. The product was precipitated with 200 mL of methanol and washed with 50% methanol three to four times to remove the homopolymer and unreacted monomer. The reaction product was dried in an air oven at 55°C and weighed. The percentage graft yield (%G) and grafting efficiency (%GE) were calculated as follows:[19]

$$\%G = [(W_1 - W_0)/W_0] \times 100$$

$$\%GE = [(W_1 - W_0)/W_2] \times 100$$

where W_0, W_1, and W_2 denote the weights of native starch (NS), grafted starch, and methacrylamide (MAM), respectively.

Graft Parameters

Graft frequency is a measure of the average number of anhydroglucose units (AGUs) between graft points,[20] and it was calculated with the following equation:

$$[N_{AGU}] = M_w(1-g)/162g$$

where $[N_{AGU}]$ is the graft frequency, M_w is the weight-average molecular weight of PMAM, g is the graft content, and 162 is the molecular weight of AGU. The rate of grafting (R_g) was calculated with the following equation:[13]

$$R_g = 1000 \quad \%G \times w_i/100VtM$$

where %G is the percentage graft yield, w_i is the weight of the starch, V is the total volume of the reaction mixture, t is the reaction time, and M is the molecular weight of MAM.

The nitrogen content in the graft copolymers (N_f) was determined with a Vario EL III CHNS elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). The monomer conversion (X_{MAM}) was calculated as follows:[7]

$$X_{MAM} = 100(N_f/N_i)$$

where N_i is the theoretical nitrogen content based on the feeding amount of the monomer. The mean average degree of polymerization (D_p) was estimated as follows:[7]

$$D_p = (X_{MAM} \times n_{MAM})/n_{CAN}$$

where n_{MAM} and n_{CAN} are the amounts of monomer and initiator, respectively.

Before the determination of the molecular weight and percentage add-on, the grafted branches were isolated from the starch moiety by enzymatic hydrolysis. A stirred suspension of 100 mg of the copolymer was treated with α-amylase at pH 6.9 and digested overnight with gentle agitation. The completion of starch hydrolysis was confirmed by testing with iodine solution. The grafted PMAM chains were separated by filtration and dried at 60°C. The percentage add-on was calculated as follows:

$$\text{Add-on}(\%) = (\text{Weight of synthetic part of graft copolymer}/ \text{Total weight ofgraft copolymer}) \times 100$$

The molecular weight of the grafted chains was determined by the intrinsic viscosity (η) method. η of the grafted PMAM was determined with an Ostwald viscometer at $30 \pm 2°C$ in a $1M$ NaNO$_3$ solution, and M_w was calculated according to the Mark–Houwink equation:

$$\eta = 6.80 \times 10^{-5} \times M_w^{0.80}$$

Fourier Transform Infrared (FTIR) Spectroscopy
The infrared spectra of the graft copolymers were recorded with a PerkinElmer FTIR instrument (Spectrum RX1) with a diffused reflectance accessory in the frequency range 4000–400 cm^{-1} to confirm the grafting reaction.

Scanning Electron Microscopy (SEM)
The surface morphology of the grafted polymers was studied with a scanning electron microscope (JEOL/EO model JSM-6390).

X-ray Diffraction (XRD) Analysis
The crystallinity was studied by XRD analysis (model D8 Advance, Bruker AXS, Inc., Madison, WI) with a Cu Kα radiation ($\lambda = 1.540A°$) source.

Differential Scanning Calorimetry (DSC)
The melting temperature (T_m) and the enthalpy of melting were determined with DSC (DSC 822e, Mettler-Toledo, Schcoerfenbach, Switzerland) in the temperature range 40–350°C at a heating rate of 20°C/min under a nitrogen atmosphere.

Thermogravimetric Analysis
The thermal properties were determined with a thermogravimetric/differential thermal analyzer (Diamond, PerkinElmer, Inc., Shelton, CT) in the temperature range 40–630°C at a heating rate of 10°C/min.

Viscometry
The viscosity profile of the samples was obtained with a rapid visco-analyzer (RVA; RVA-4, Newport Scientific, Australia). The samples were heated from 50 to 95°C at 12°C/min at a speed of 160 rpm and were cooled to 50°C at 12°C/min. The parameters, including the peak viscosity, breakdown viscosity, final viscosity, and pasting temperature, were recorded. The ratio of the breakdown to the peak viscosity was expressed as the breakdown ratio.

Dynamic Mechanical Properties
The dynamic mechanical properties, namely, the storage modulus (G') and loss modulus (G''), of the hydrogels were determined with a Physica VT2 rheometer (Anton Paar Germany GmbH, Ostfildern, Germany) at 30°C with a parallel-plate system (PP20-SN5912, 1 mm in diameter) by a frequency sweep test in the range 0.10–10 Hz at a constant strain of 1%. For this purpose, the grafted starch (2 g) was allowed to swell in cold water (20 g) overnight to obtain a 10% gel.

Flocculation Studies
The flocculation abilities of cassava starch, PMAM, and cassava starch-g-PMAM were evaluated with a kaolin clay suspension. The flocculants were suspended in 1000 mL of tap water, and the mixture was stirred for 15 min at 90°C. The solution was cooled and added to 1 mL of a 5% aqueous suspension of kaolin. The mixture was stirred at 100 rpm for 10 min,[21] and the supernatant solution was taken after another 10 min. The percentage transmission of the solution was estimated with an ultraviolet–visible spectrophotometer (T70/T80 series, P. G. Instruments, Wibtoft, Lutterworth, United Kingdom). The effects of the flocculant dose, N_f, and molecular weight of flocculants and pH of the medium on the flocculation efficiency were studied.

Textile Sizing Studies
We sized the cotton yarns by dipping in the cooked NS and the starch-g-PMAM solution (1% w/v) at 95°C with continuous stirring.[9] The yarns were then squeezed, dried at 100°C for 5 min, and kept at ambient temperature for 48 h before testing. The sized yarns were tested for tensile strength and elongation at break with a texture analyzer (TA HDi, Stable Micro Systems, United Kingdom).

Statistical Analysis
The data were analyzed with SAS 9.3 software to perform an analysis of variance to generate three-dimensional surface plots. The treatments were considered significantly different at a 5% level of significance.

RESULTS AND DISCUSSION

Optimization of Grafting Conditions
%G and %GE of the starch-grafted copolymers are presented in Table I. The highest %G of 79.9% was obtained under the following conditions: 20 g of MAM/10 g of starch, 0.878 g/L CAN, time duration = 120 min, and temperature = 55°C. The %G and %GE increased with increasing concentrations of MAM and CAN and reached a maximum, and a leveling off was noticed at still higher levels of the variables. This could have been due to the depletion of grafting sites on the starch molecule.[13] The initial increase with CAN concentration could have been due to the increasing number of free-radical sites on the starch backbone at which the monomer could be grafted,[2] and the decrease at higher concentration could have been due to the termination of the growing grafted chains by excess ceric ions.[16] The reaction duration showed a quadratic effect on %G and %GE; this could have been associated with depletion in monomer and initiator concentration as the reaction proceeded.[14] The coefficient of determination was calculated as 0.89 for %G and 0.87 for %GE; this showed the high prediction performance of the proposed regression model. The three-dimensional response surface plots showing the effects of the concentration
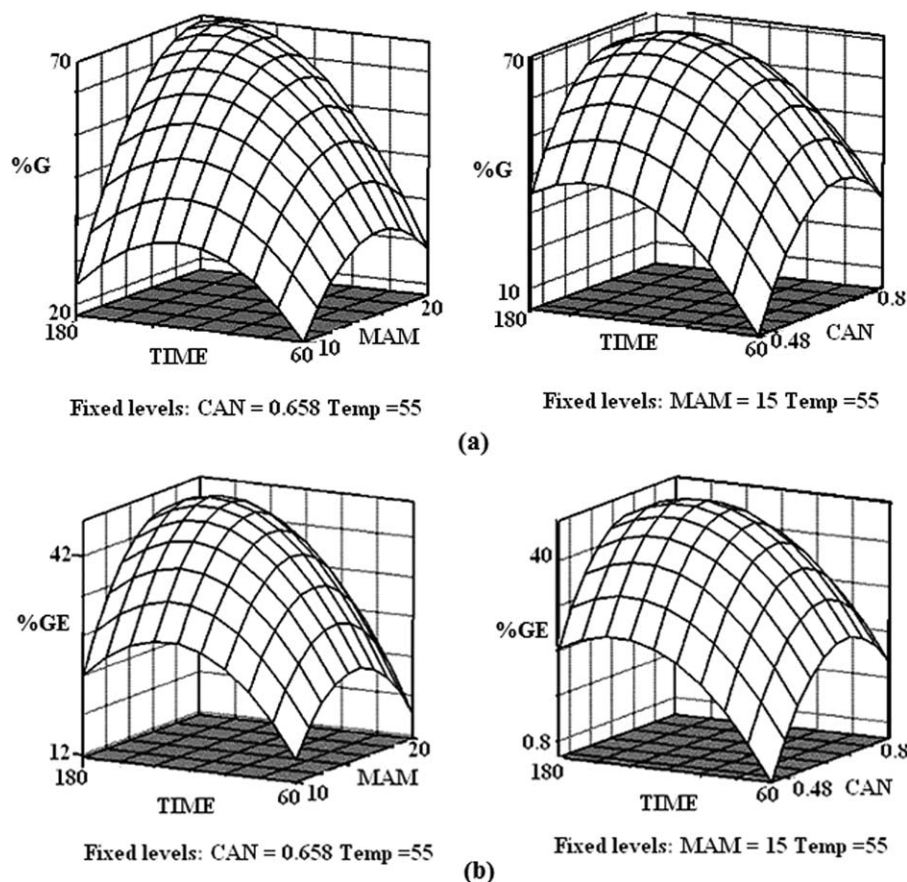
Figure 1. Response surface plots for (a) %G and (b) %GE as functions of the concentrations of MAM and CAN when the time and the temperature were kept constant.

of CAN and reaction time and the concentration of MAM and reaction time on %G and %GE when the other two variables were kept constant at the medium level are shown in Figure 1.

Graft Parameters

The graft frequency (N_{AUG}) and R_g values of the starch-grafted copolymers synthesized under different conditions are presented in Table I. The values of N_{AUG} ranged from 11,819 to 38,337. Response surface analysis indicated that the concentration of MAM was highly significant ($p < 0.05$) for N_{AUG}, and as the monomer concentration increased, the grafting frequency also increased. This could have been due to the greater probability of a free radical initiated on the starch reacting with MAM rather than oxidizing the starch.[22] R_g was in the range 1.31–7.83 mol L^{-1} min^{-1} and was highest under the following grafting conditions: 15 g of MAM, 0.656 g/L CAN, time duration = 120 min, and temperature = 55°C. The concentration of CAN had a positive quadratic effect ($p < 0.05$) on R_g. The increase of R_g with increasing CAN concentration could have been due to the formation of a greater number of active sites on the starch backbone.[2] As the free-radical concentration reached excess with increasing CAN, the rate of the termination reaction increased, and consequently, the homopolymers exceed the grafted polymer and thereby decreased R_g.[13]

Table II shows the various grafting parameters of the copolymers. N_f in the starch-g-PMAM ranged from 3.3–7.8 (Table II). Sample A4, having the highest percentage grafting, exhibited the

highest N content. The N_f was found to be significantly affected by the concentration of MAM ($p < 0.05$). X_{MAM} ranged from 39 to 78% (Table II), and the quadratic effect of the temperature significantly ($p < 0.05$) influenced it. At a lower temperature (45°C), fewer free radicals were formed, and at temperatures higher than 55°C, the rate of free-radical generation was high; it then recombined and hence reduced the efficiency of the initiator. D_p is the average number of monomer units contained in each grafted chain on the starch molecule, and it ranged from 41 to 124 for the grafted starches (Table II). The highest D_p of 124 was obtained when the grafting was carried out under following conditions: 20 g of MAM/10 g of starch, 0.878 g/L CAN, time duration = 120 min, and temperature = 55°C. The percentage add-on ranged from 14 to 53% (Table II) and decreased significantly with increasing concentration of CAN.

The η and M_w values of the grafted PMAM were in the ranges 5.8–9.8 dL/g and 15.9–30.8 × 10^5 g/mol, respectively (Table II). The sample A25 with η 9.8 dL/g, showed the highest M_w of 30.8 × 10^5 g/mol. η increased significantly ($p < 0.05$) with increasing concentration of CAN, reached a maximum value of 9.8 dL/g at an optimal CAN amount of 0.658 g/L, and then decreased thereafter. This could be explained by the increase in the molecular weight of the PMAM side chains. The decrease in η at higher CAN contents was attributed to the reduction of the molecular weight of the PMAM chains. As the initiator content increased, an excess of active free radicals were formed, and this increased

Table II. Properties of Cassava Starch-*g*-PMAM under Different Grafting Conditions

Sample code	N_i (%)	N_f (%)	X_{MAM} (%)	D_p	Add-on (%)	η (dL/g)	$M_w \times 10^5$ (g/mol)
A1	6.6 ± 0.1	3.3 ± 0.1	50 ± 3	70 ± 8	24 ± 2	5.9 ± 0.1	16.2 ± 1.5
A2	6.6 ± 0.2	3.9 ± 0.1	59 ± 1	41 ± 9	28 ± 3	6.3 ± 0.1	17.5 ± 1.6
A3	9.9 ± 0.1	6.9 ± 0.2	41 ± 2	112 ± 8	53 ± 3	7.1 ± 0.3	20.7 ± 1.8
A4	9.9 ± 0.1	7.8 ± 0.1	78 ± 2	124 ± 2	46 ± 2	8.2 ± 0.5	24 ± 1.3
A5	8.4 ± 0.3	4.3 ± 0.1	51 ± 1	75 ± 8	18 ± 4	6.9 ± 0.5	19.7 ± 1.5
A6	8.4 ± 0.2	4.8 ± 0.1	57 ± 2	83 ± 4	22 ± 2	7.3 ± 0.3	21.3 ± 1.5
A7	8.4 ± 0.1	4.9 ± 0.1	58 ± 1	85 ± 7	43 ± 3	8.3 ± 0.2	25 ± 1.6
A8	8.4 ± 0.1	5.3 ± 0.1	63 ± 3	93 ± 9	47 ± 1	8.9 ± 0.2	27.3 ± 1.3
A9	6.6 ± 0.2	3.5 ± 0.2	53 ± 2	49 ± 3	21 ± 2	7.0 ± 0.1	20.2 ± 1.4
A10	6.6 ± 0.1	3.7 ± 0.1	56 ± 1	52 ± 2	20 ± 3	6.9 ± 0.2	19.7 ± 1.7
A11	9.9 ± 0.1	6.7 ± 0.2	39 ± 2	82 ± 1	23 ± 4	8.1 ± 0.2	24.2 ± 1.8
A12	9.9 ± 0.1	6.8 ± 0.1	49 ± 3	968	37 ± 1	8.5 ± 0.2	25.7 ± 1.2
A13	8.4 ± 0.2	4.3 ± 0.3	51 ± 4	50 ± 5	38 ± 4	5.9 ± 0.3	16.3 ± 1.4
A14	8.4 ± 0.2	4.7 ± 0.3	56 ± 3	54 ± 4	19 ± 3	6.9 ± 0.1	19.8 ± 1.5
A15	8.4 ± 0.1	4.1 ± 0.1	49 ± 2	54 ± 8	18 ± 4	7.1 ± 0.2	20.7 ± 1.6
A16	8.4 ± 0.1	3.8 ± 0.1	45 ± 1	50 ± 7	17 ± 1	7.2 ± 0.1	20.8 ± 1.3
A17	6.6 ± 0.1	3.9 ± 0.1	59 ± 1	55 ± 2	21 ± 6	6.3 ± 0.2	17.5 ± 1.2
A18	6.6 ± 0.1	4.7 ± 0.1	71 ± 1	66 ± 8	22 ± 4	6.8 ± 0.1	19.4 ± 1.3
A19	9.9 ± 0.2	7.4 ± 0.2	42 ± 3	82 ± 7	15 ± 2	6.7 ± 0.1	19.1 ± 1.2
A20	9.9 ± 0.1	7.4 ± 0.1	56 ± 2	110 ± 2	30 ± 1	8.8 ± 0.1	26.7 ± 1.9
A21	8.4 ± 0.3	3.9 ± 0.2	46 ± 2	102 ± 4	43 ± 4	6.9 ± 0.2	19.7 ± 1.5
A22	8.4 ± 0.3	3.6 ± 0.2	43 ± 4	95 ± 6	44 ± 3	5.9 ± 0.2	16.2 ± 1.6
A23	8.4 ± 0.2	4.1 ± 0.2	49 ± 1	54 ± 5	17 ± 2	5.8 ± 0.2	15.9 ± 1.5
A24	8.4 ± 0.1	4.8 ± 0.1	57 ± 2	63 ± 3	19 ± 1	7.8 ± 0.1	23.1 ± 1.6
A25	8.4 ± 0.2	5.8 ± 0.1	69 ± 1	101 ± 6	34 ± 2	9.8 ± 0.3	30.8 ± 1.6
A26	8.4 ± 0.2	5.7 ± 0.2	68 ± 1	100 ± 8	33 ± 3	9.5 ± 0.1	29.7 ± 1.5
A27	8.4 ± 0.2	5.6 ± 0.2	70 ± 2	103 ± 7	34 ± 2	9.3 ± 0.2	28.9 ± 1.3

All measurements were taken in triplicate.

the number of grafting sites. This resulted in the formation of short and low-molecular-weight PMAM chains.[7] Similar behavior was observed in the grafting of *N-tert*-butylacrylamide on starch with ceric ammonium as an initiator.[1] On the other hand, increasing the amount of MAM showed an increase in η, which could have also resulted from the increase in the molecular weight of the PMAM side chains.[23]

FTIR Analysis

The FTIR spectra of the cassava starch-*graft*-PMAM showed the absorption bands that were characteristic of native cassava starch (Figure 2). The O—H absorption band was observed at 3244 cm^{-1}, the C—H stretching band was observed around 2935 cm^{-1}, the C=O stretching band was observed at 1688 cm^{-1}, and a triplet band for C—O—C stretching was observed at 954, 928, and 856 cm^{-1}. In addition, the absorption bands found at 1640.4 and 1600 cm^{-1} for the graft copolymers indicated the C=O stretching and N—H bending of the —CONH$_2$ group, respectively, which are characteristic of the amide group. The presence of these bands in the grafted copolymers confirmed the grafting reaction.[24–26]

SEM

The SEM micrographs of the native cassava starch and selected samples of the grafted starches, namely, A1, A4, and A25, having different levels of %*G*, are shown in Figure 3.
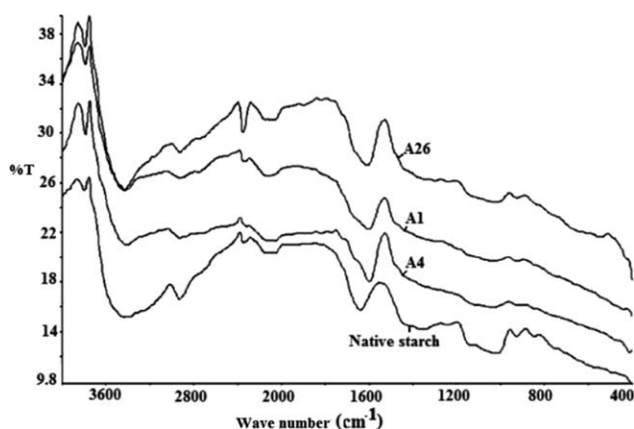

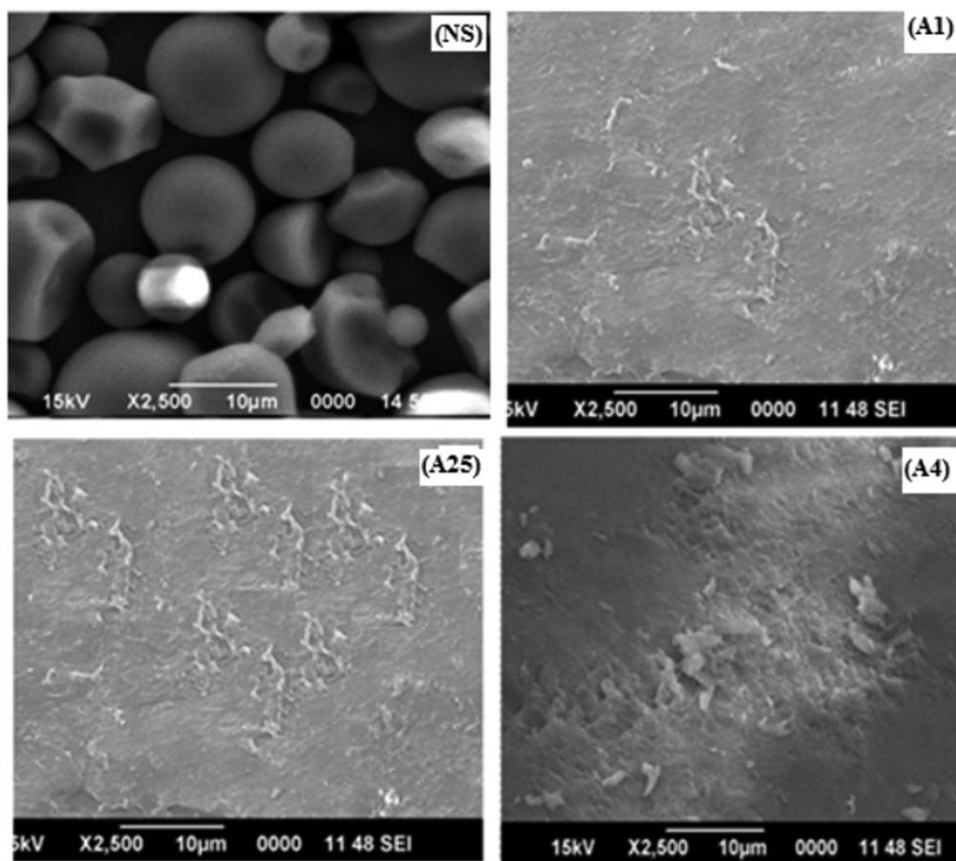**Figure 2.** FTIR spectra of the native cassava starch and starch-*g*-PMAM.

Figure 3. Scanning electron micrographs of the NS and grafted starches.

The native cassava starch granules were spherical, with a flat surface on one side containing one or more pits. However, the granular structure completely disappeared in the case of the grafted starches. The surface appeared continuous, non-planar, and nonuniform.[16] The alteration in the surface morphology confirmed the formation of the grafts.

XRD Studies
There were four major crystal peaks for native cassava starch at diffraction angles of $2\theta = 14.932°$ (d spacing = 5.928), $17.141°$ (d spacing = 5.169), $18.058°$ (d spacing = 4.908), $22.989°$ (d spacing = 3.866), and $23.408°$ (d spacing = 3.797); this indicated an A-type XRD pattern (Figure 4). A change in the type and the intensity of the XRD patterns was noticed for the graft copolymers. On grafting with methacrylamide, the four crystal peaks were merged into a smooth peak; this suggested that the crystal phase was also involved in the reaction and the grafting of methacrylamide modified the crystalline region of starch.[2,27] The decrease in intensity indicated a reduction in the crystallinity. The doublet observed around $17–18°$ for NS was found to be reduced in intensity, and it became a singlet in the case of the grafted starches.

DSC
DSC analysis showed that there was only one endotherm for the native cassava starch, whereas the grafted starches exhibited two endothermic transitions, and the second endotherm was attributed to the fusion of crystallites.[2] For the NS, the T_m was found to be 161.3°C (Table III). There was a shift in the peaks to lower temperature ranges for the grafted starches (145.9–160.9°C). The decrease in T_m was attributed to the internal plasticization effect of the monomers when grafted on to the starch; this made it easier for microlevel and macrolevel transitions to occur.[28] All of the grafted starches, except A4, exhibited a lower enthalpy change (ΔH) in comparison to that of the NS (Table III). This decrease could be attributed to the slight weakening of the granular structure as a result of a plasticization effect of the monomers and also a decrease in the crystallinity of the starch on grafting. In this case, the higher ΔH for A4 could have been due to the increased perfection of crystals, and hence, A4 required a higher energy than NS to gelatinize.[2,29]

Thermogravimetric Analysis
The thermal behavior of samples A1 and A4 is shown in the thermograms, along with that of the NS (Figure 5). Both the grafted starches showed a gradual thermal decomposition, and about 17.0 and 19.7% of the initial weights were retained by samples A1 and A4, respectively, at the end of the analysis. For sample A1, four stages were visible for thermal decomposition, and the major weight loss occurred in the temperature range 275.2–340.0°C. For sample A4, a five-stage decomposition was observed, and the major weight loss (47.5%) occurred in the third step in the temperature range of 280.5–360.1°C; this corresponded to the decomposition of the starch and
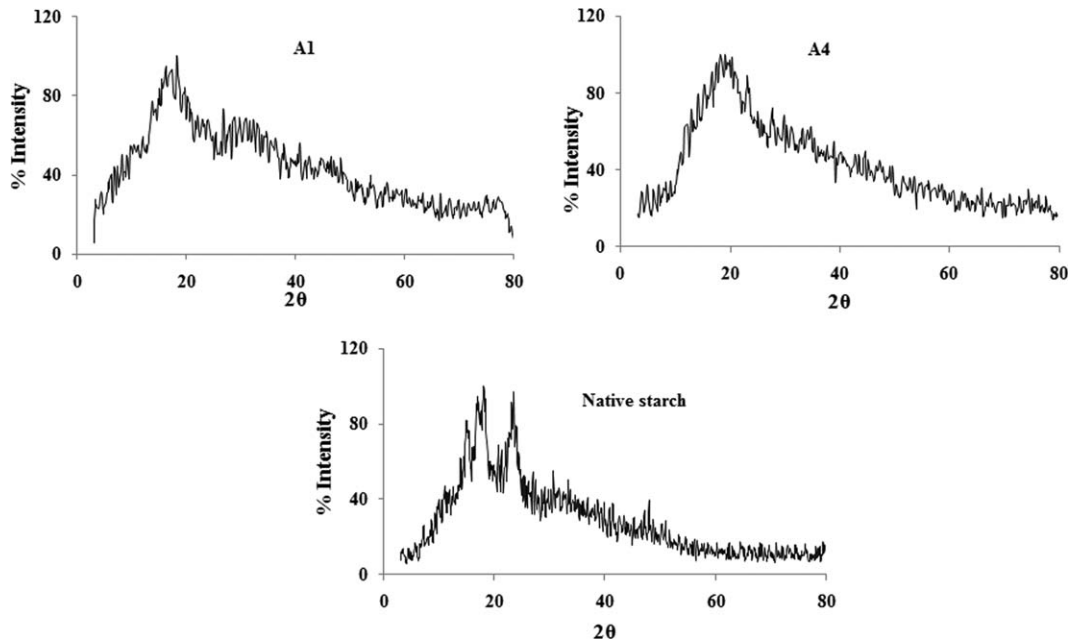
Figure 4. XRD patterns of the cassava starch and grafted starches.

Table III. DSC Parameters of NS and Its Graft Copolymers

Sample	First endotherm		Second endotherm	
	T_m (°C)	ΔH (J/g)	Midpoint of transition (°C)	ΔH (J/g)
A1	154.6 ± 1.5	113.9 ± 5.6	258.8 ± 2.1	3.6 ± 1.9
A2	160.4 ± 1.4	69.3 ± 5.9	254.5 ± 1.8	9.5 ± 1.6
A3	159.9 ± 1.6	36.5 ± 2.6	214.2 ± 1.6	3.4 ± 2.3
A4	147.3 ± 4.5	197.7 ± 3.5	267.3 ± 1.9	29.4 ± 2.5
A5	160.8 ± 1.8	68.5 ± 3.3	259.3 ± 1.5	1.3 ± 1.6
A6	154.9 ± 1.2	40.5 ± 2.6	311.9 ± 1.6	9.7 ± 1.5
A7	155.4 ± 1.6	79.8 ± 1.2	290.6 ± 1.7	9.6 ± 2.3
A8	155.2 ± 1.2	90.7 ± 1.5	269.3 ± 1.4	10.3 ± 2.5
A9	153.6 ± 1.6	55.1 ± 1.6	258.8 ± 1.8	1.8 ± 0.9
A10	154.9 ± 1.5	36.5 ± 1.3	209.8 ± 1.3	9.4 ± 2.3
A11	157.4 ± 1.7	70.3 ± 5.4	267.9 ± 1.5	17.6 ± 3.1
A12	158.4 ± 1.2	116.5 ± 3.5	213.7 ± 1.4	36.4 ± 3.2
A13	159.6 ± 1.5	33.9 ± 3.4	269.9 ± 1.7	28.9 ± 3.5
A14	160.0 ± 1.4	78.9 ± 4.1	267.2 ± 1.3	17.6 ± 2.8
A15	159.7 ± 1.0	49.4 ± 4.2	231.1 ± 1.3	18.9 ± 2.9
A16	153.8 ± 1.8	70.1 ± 3.5	243.2 ± 1.2	26.4 ± 3.4
A17	160.8 ± 1.2	70.9 ± 3.4	256.1 ± 1.4	19.3 ± 2.8
A18	160.5 ± 1.2	57.8 ± 3.5	311.8 ± 1.1	9.9 ± 2.4
A19	159.4 ± 1.1	70.7 ± 3.2	256.8 ± 1.4	9.7 ± 2.3
A20	149.8 ± 1.1	72.3 ± 3.1	222.7 ± 1.7	9.7 ± 2.6
A21	158.8 ± 1.0	64.6 ± 4.1	209.6 ± 1.2	9.7 ± 1.9
A22	156.9 ± 1.5	70.3 ± 2.9	267.2 ± 1.5	15.2 ± 1.9
A23	158.4 ± 1.2	63.8 ± 2.8	211.3 ± 1.8	18.2 ± 1.6
A24	160 ± 2.1	112.2 ± 2.7	288.6 ± 1.8	33.8 ± 3.6
A25	147 ± 1.4	80.8 ± 2.6	278.9 ± 1.9	29.4 ± 3.2
A26	148.4 ± 1.5	81.5 ± 2.4	274.9 ± 1.9	28.9 ± 3.6
A27	145.8 ± 1.6	84.9 ± 2.6	275.6 ± 1.8	29.4 ± 3.1
NS	161.3 ± 1.3	148.9 ± 2.7	—	—

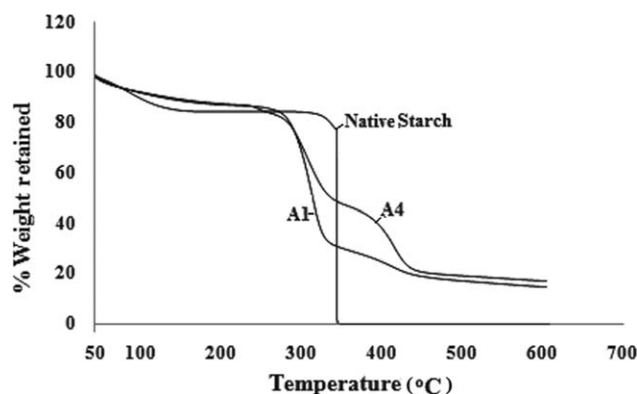All measurements were taken in triplicate.

Figure 5. Thermograms of the native cassava starch and starch-*g*-PMAM.

methacrylamide portions in the graft copolymer. During the last stage, at a temperature higher than 400°C, a rapid decomposition into carbon dioxide and volatile hydrocarbons occurred. Both the grafted starches exhibited higher thermal

stabilities than the native cassava starch. Our results were in agreement with those of most earlier reports.[15,19,25,28]

Viscometry

According to the RVA viscosity data, the grafted starches showed significantly higher peaks and final viscosities than those of the NS (Table IV). The peak and final viscosities were 2238 and 1517 cP, respectively, for the NS, whereas, sample A4 exhibited the highest peak and final viscosities of 6466 and 7094 cP, respectively. This could have been due to the higher amount of hydrophilic segments in the copolymer, which resulted in increased swelling because of better dispersion of the hydrophilic fraction of the polymer chains in the aqueous phase.[19] The final viscosity of the NS was lower than its peak viscosity because of the viscosity breakdown at high temperature. However, all of the graft copolymers showed higher final viscosities in comparison to the peak viscosity and exhibited better paste stability. The breakdown ratio of the grafted starches ranged from 0.09 to 0.14, whereas it was 0.44 for the NS. The pasting temperature of NS was 73.8°C, and for the different grafted

Table IV. RVA Viscosity Parameters of the NS and Starch-*g*-PMAM

Sample	Peak viscosity (cP)	Final viscosity	Pasting temperature (°C)	Breakdown ratio
A1	2566 ± 41	2766 ± 21	72.9 ± 1.5	0.142 ± 0.008
A2	2899 ± 36	2956 ± 23	72.7 ± 1.3	0.123 ± 0.004
A3	3490 ± 32	3623 ± 31	70.2 ± 1.6	0.134 ± 0.003
A4	6466 ± 24	7094 ± 25	60.2 ± 1.4	0.125 ± 0.005
A5	3009 ± 12	3452 ± 24	70.8 ± 1.3	0.126 ± 0.003
A6	3300 ± 32	3897 ± 21	72.9 ± 1.2	0.113 ± 0.008
A7	5090 ± 34	5934 ± 16	63.5 ± 1.8	0.139 ± 0.001
A8	5389 ± 23	5678 ± 12	61.1 ± 1.5	0.098 ± 0.009
A9	2871 ± 26	2989 ± 13	72.5 ± 1.3	0.115 ± 0.004
A10	2890 ± 21	3062 ± 14	71.7 ± 1.2	0.124 ± 0.006
A11	4321 ± 34	4738 ± 13	69.7 ± 1.4	0.116 ± 0.005
A12	4900 ± 32	4919 ± 12	62.5 ± 1.5	0.099 ± 0.007
A13	3078 ± 16	3091 ± 11	73.0 ± 1.6	0.138 ± 0.004
A14	3984 ± 18	3956 ± 18	68.6 ± 1.4	0.095 ± 0.008
A15	3273 ± 17	3398 ± 12	69.0 ± 1.7	0.104 ± 0.003
A16	4234 ± 12	4987 ± 14	67.1 ± 1.3	0.099 ± 0.002
A17	2668 ± 21	2867 ± 12	74.7 ± 1.2	0.125 ± 0.005
A18	3188 ± 25	3266 ± 13	70.9 ± 1.4	0.098 ± 0.004
A19	2859 ± 24	2987 ± 12	75.0 ± 1.5	0.098 ± 0.009
A20	4777 ± 21	4978 ± 31	63.2 ± 1.6	0.092 ± 0.001
A21	2555 ± 23	2750 ± 12	74.3 ± 1.3	0.102 ± 0.003
A22	2535 ± 26	2765 ± 12	74.0 ± 1.8	0.129 ± 0.005
A23	3800 ± 25	3976 ± 11	69.0 ± 1.2	0.104 ± 0.006
A24	4509 ± 24	4690 ± 14	65.9 ± 1.6	0.126 ± 0.003
A25	5490 ± 28	5978 ± 13	62.5 ± 1.4	0.099 ± 0.001
A26	5318 ± 24	5464 ± 12	63.8 ± 1.3	0.099 ± 0.001
A27	5290 ± 29	5590 ± 12	62.9 ± 1.4	0.101 ± 0.002
NS	2238 ± 31	1517 ± 11	73.9 ± 1.2	0.445 ± 0.006

All measurements were taken in triplicate.

Table V. Dynamical Mechanical Spectra of Hydrogels of Starch-*g*-PMAM at a Frequency of 10 Hz

Sample	G'	G''
A1	4312 ± 45	1111 ± 31
A2	6789 ± 23	2132 ± 34
A3	4512 ± 41	1423 ± 32
A4	17,900 ± 35	2210 ± 29
A5	3212 ± 37	1211 ± 28
A6	3680 ± 38	1005 ± 26
A7	5641 ± 41	1907 ± 35
A8	7990 ± 23	2312 ± 37
A9	5182 ± 28	1173 ± 38
A10	8901 ± 34	2983 ± 41
A11	6123 ± 25	1211 ± 32
A12	8990 ± 27	2657 ± 51
A13	5385 ± 26	1298 ± 32
A14	5123 ± 21	1765 ± 41
A15	3211 ± 25	1011 ± 32
A16	9888 ± 21	2134 ± 23
A17	7865 ± 22	2568 ± 28
A18	5678 ± 35	1456 ± 27
A19	4567 ± 34	1214 ± 24
A20	10,123 ± 37	3123 ± 26
A21	2345 ± 34	543 ± 19
A22	5790 ± 33	1567 ± 18
A23	5432 ± 29	1212 ± 24
A24	7689 ± 28	2134 ± 29
A25	9012 ± 27	1230 ± 28
A26	8890 ± 34	1223 ± 31
A27	8990 ± 35	1221 ± 38

All measurements were taken in triplicate.

starches, it ranged from 60.2 to 75.0°C (Table IV). Except for a few samples, most of the graft copolymers exhibited lower pasting temperatures than NS. The graft copolymers with higher %*G* values showed a greater decrease in pasting temperature, and it was the lowest for sample A4. The results of this study show that the grafting reaction resulted in an increase in the paste stability and viscosity with a decrease in the pasting temperature of cassava starch; these are desirable features in many end uses of this product.

Dynamic Mechanical Properties

The dynamic moduli (G' and G'') are functions of the frequency and sensitive probes of polymer solutions or gels. For the gels of grafted starches obtained by swelling in cold water, G' (2345–17,900 Pa) was significantly higher than G'' (543–3123 Pa), and hence, these gels were more solid in nature (Table V). For the sample A4, G' and G'' were 17,900 and 2210 Pa, respectively. Both the moduli showed frequency-independent behavior (Figure 6), and the hydrogels were found to be shear-stable and could withstand drastic deformation. Because the rheological properties often link material formulation and processing stages

with the ultimate end use and product performance, the measurement of these properties of starch-grafted copolymers are very important for developing a better product.

Flocculation Studies

The effect of the flocculant dose on the flocculation efficiency of the cassava starch, PMAM, and the grafted samples A1, A4, and A25 at different pH values, namely, 4.0, 7.0, and 10.0, was studied. Figure 7 illustrates the effect of the flocculant dose on the transmission percentage of the filtrate after flocculation at pH 10.0. We found that all of the grafted starches showed better flocculant ability than native cassava starch and PMAM. Under alkaline conditions, native cassava starch almost had no flocculation ability.

Regardless of the pH of the flocculation medium, we found that the transmission percentage increased with increasing flocculant dose, reached a maximum, and then decreased. Here, the bridging mode of flocculation was operated because the grafted copolymers were uncharged. Under the optimal conditions of flocculant dose, the grafted PMAM side chains could fully contact and strongly combine with the clay particles in the aqueous suspension through bridging to form flocs.[24] With a further increase in the flocculant dose, the clay particles were occluded and enveloped by the PMAM chain, and bridging became negligible. In addition, at higher dosages of the graft copolymer, there was insufficient particle surface for the attachment of the polymer segments; this led to destabilization, and the effect of the flocculant decreased.

The kaolin suspension treated with sample A4 settled more rapidly than those treated with A1 and A25 under different pH conditions. This could have been due to the fact that the graft copolymer with a higher grafting percentage was in favor of bridging among the kaolin-suspended colloids and could efficiently aggregate the dispersed particles in aqueous solution forming denser and larger kaolin floccules. We also found that the optimal dose decreased with decreasing molecular weight and increasing N_{f}, and it followed the order A1 (0.30 g/dL) > A25 (0.16 g/dL) > A4 (0.06 g/dL).

Textile Sizing Studies

The MAM-grafted starches exhibited excellent viscosity, viscosity stability, thermal stability, and gel strength and could be exploited in applications such as textile and paper industries as sizing agents or thickening agents. The effectiveness of the graft copolymer as a textile sizing agent was tested with NS as a control. Figure 8 shows the properties of cotton yarns sized with the NS and three of the grafted starches, A1, A4, and A25. The sizing with grafted starches showed a significant improvement in the mechanical properties of the yarns; this indicated their better sizing performance when compared to the native cassava starch. The tensile strength of the yarns sized with starch-*g*-PMAM was significantly higher (39–104 MPa) than those sized with NS (35 MPa). The elongation at break of the yarns sized with the graft copolymers were also significantly higher (6.8–7.8%) in comparison to those sized with native cassava starch (5.7%). The cotton yarns sized with A4 showed the highest tensile strength (104 MPa), whereas the elongation at break was
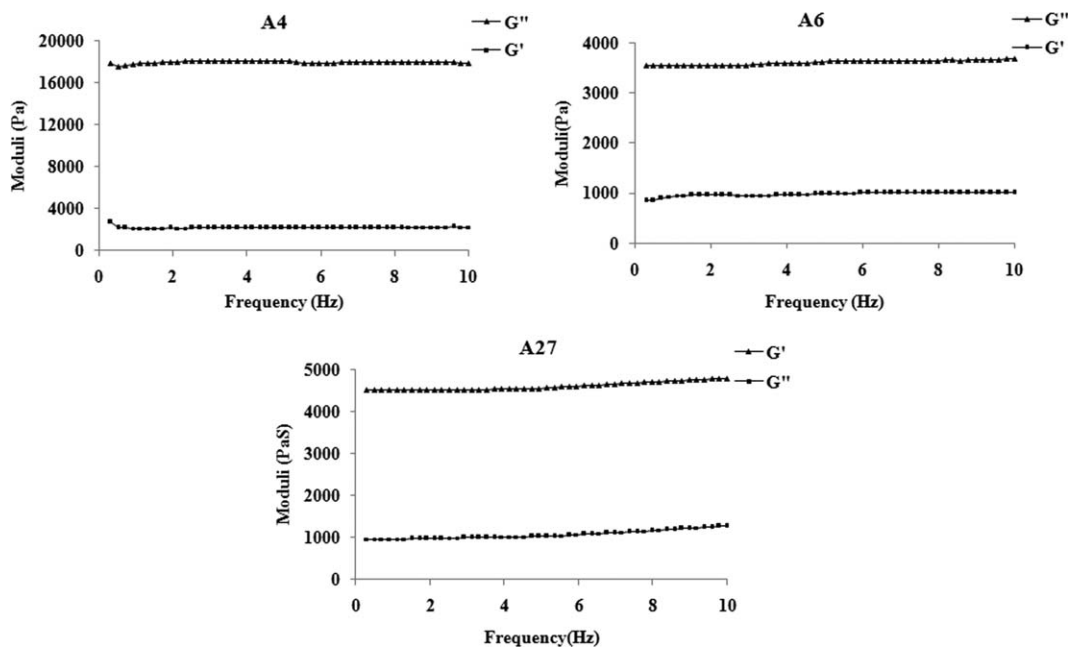
Figure 6. Dynamic moduli (G' and G'') versus the frequency of the hydrogels of the grafted starches.

higher when the yarns were sized with the copolymer A1 (7.8%).

CONCLUSIONS

Cassava-starch-grafted copolymers with different grafting levels were synthesized by the ceric-ion-initiated polymerization of methacrylamide onto cassava starch. Response surface methodology was used for the optimization of the reaction time, temperature, and monomer and initiator concentrations in terms of various grafting parameters. The grafting of MAM onto the starch backbone was confirmed by FTIR spectral analysis. XRD and SEM analyses showed that grafting of MAM onto starch reduced the crystalline region of cassava starch and resulted in the alteration of its surface morphology. The thermal stability and viscosity stability of cassava starch were enhanced by grafting. The hydrogels of the grafted samples were highly shear-stable and could withstand drastic deformation compared to that of cassava starch. The grafted copolymer showed excellent

flocculant ability in acidic, neutral, and alkaline media. The tensile strength of the cotton yarns sized with the graft copolymer was significantly improved compared to NS and could therefore be exploited as an efficient textile sizing agent.
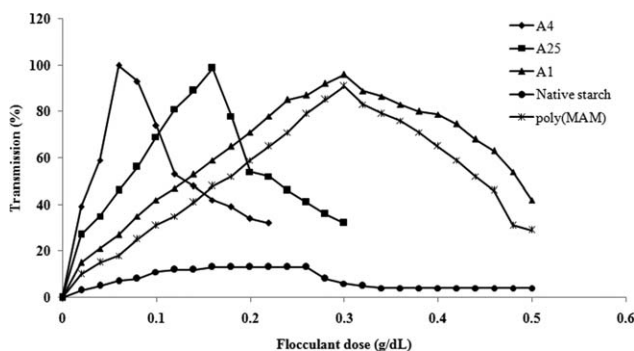

Figure 7. Relationship between the flocculant dose and the transmission percentage of the kaolin filtrate at pH 7.0.
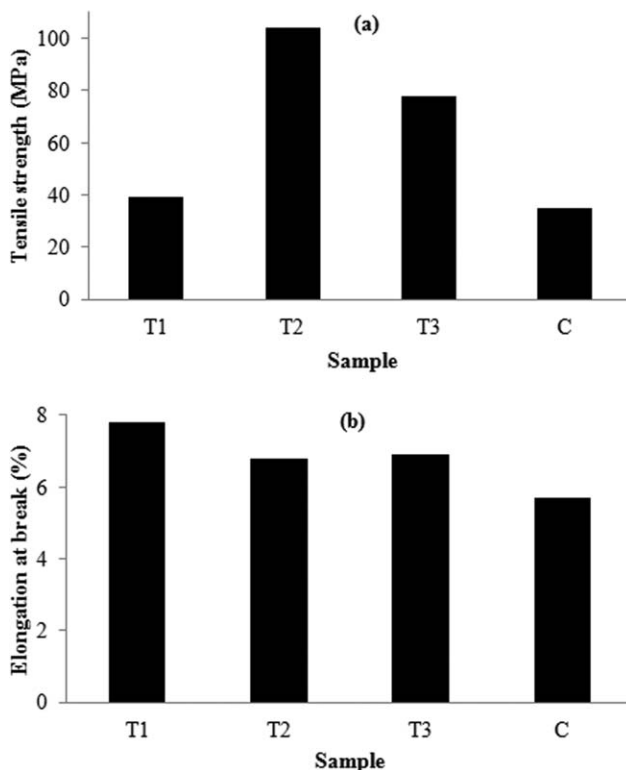
Figure 8. Tensile strength and elongation at break of the cotton yarns sized with starch-grafted copolymers: (T1) sized with A1, (T2) sized with A4, (T3) sized with A25, and (C) NS.

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