

Effect of Grafting with Acrylic Monomers on the Viscosity, Gelatinization Temperature, and Granule Swelling Characteristics of Starch

P. ARAVINDAKSHAN, V. G. KUMAR

Polymers Section, Hindustan Lever Research Centre, I.C.T. Link Road, Chakala, Andheri (E), Mumbai 400 099, India

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ABSTRACT: Amylography and scanning electron microscopy (SEM) studies on grafted copolymers of starch with methacrylic acid and methyl methacrylate demonstrated significant changes in the viscosity and granule disintegration characteristics, depending on the extent of grafting and the nature of the monomer. Marked viscosity changes were observed when the carboxyl groups of the starch-graft-poly(methacrylic acid) (SPMAA) were neutralized with sodium hydroxide. The viscosity modification was found to be dependent on the extent of neutralization, and a maximum was observed at 10–25% neutralization. With an increase in extent of neutralization, there was a decrease in gelatinization temperature. For a sample of SPMAA with a percentage grafting of 14.1, the gelatinization temperature decreased from 64°C for the acid form to 42°C for the fully neutralized form. The gelatinization temperature of the fully neutralized samples of SPMAA showed a linear relationship with the percentage grafting. SEM was used to elucidate the effect of grafting on the granule swelling characteristics of starch at various temperatures. In the case of starch-graft-polymethyl methacrylate (SPMMA), granule disruption on heating with water was observed. However, this did not lead to the build-up of viscosity on gelatinization. This was explained to be caused by the hydrophobic nature of SPMMA. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 528–534, 2002; DOI 10.1002/app.10266

Key words: graft copolymers; viscosity; gelatinization temperature; granule swelling; extent of neutralization

INTRODUCTION

Knowledge about the structural changes of starch granules caused by chemical modification can be of importance, not only for understanding the altered functional properties but also to provide better control of the modification process and to develop chemically modified starches with de-

sired properties. Microscopy and amylography have played an important role in the improvement of the understanding of the granular structure of starches.^{1–4}

Electron microscopic investigation of grafted nitrocellulose was reported recently.¹ These studies demonstrated that homogeneous grafting changed not only the morphological structure of the surface layer but also the internal character. The grafted polymer was shown to be uniformly distributed over the whole mass of nitrocellulose substrate.

The structural changes of potato starch granules, caused by hydroxypropylation, were re-

Correspondence to: P. Aravindakshan (perncheery.aravindakshan@unilever.com).

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ported recently by Kim et al.² They observed that both the rate of viscosity development and the shapes of the pasting curves differed markedly, depending on the degree of molar substitution. Microscopic studies revealed that the hydroxypropylation reaction occurred mainly at the center of the granule.

Effects of cationization on the physicochemical and functional properties of pea and corn starches were investigated by amylography, scanning electron microscopy (SEM), differential scanning calorimetry, and X-ray analysis. Vihervaara et al.³ showed that in aqueous/solvent medium, the cationization reaction was uniform, whereas cationic potato starch prepared by a gas reaction had cationic groups deposited mainly on the outer region of the starch granule. Studies by Yook et al.⁴ indicated that cationization not only decreased the pasting temperature but also promoted complete dispersibility of amylose and amylopectin molecules from the granule at a relatively low temperature. Changes in morphology and other functional properties such as granule swelling, viscosity, and gelatinization temperature due to chemical modification has been the subject of many recent studies.⁵⁻¹⁰

The effect of physically blending starch with an ionizable synthetic polymer such as poly(ethylene-*co*-acrylic acid) was investigated by Fanta et al.¹¹ They studied the influence of pH on the solubilization and complex formation of poly(ethylene-*co*-acrylic acid) with starches. It was observed that the viscosity of the starch-poly(ethylene-*co*-acrylic acid) complex increased with pH, that is, with an increase in the neutralization of carboxyl groups. It was proposed that this may have been due to an increased complexation of ethylene-*co*-acrylic acid with swollen amylopectin molecules.

The previous results demonstrated the dependence on the solution viscosity of the blend in the ratio of starch with an ionizable polymer. The solution properties of starch graft copolymers with ionizable groups are not extensively reported in literature. We undertook a study to quantify the effect of ionization on the viscosity and gelatinization behavior of starch-graft-poly(methacrylic acid) (SPMAA) and to compare the results with those of unmodified starch and starch-graft-poly(methyl methacrylate) (SPMMA). In addition, the variations of granular swelling characteristics shown by the graft copolymers were studied by SEM.

EXPERIMENTAL

Materials

Materials included commercial-grade tapioca starch (Hinustan Lever Ltd., Mumbai, India), laboratory reagent-grade methacrylic acid (MAA; Fluka), laboratory reagent-grade methyl methacrylate (MMA; Fluka), and laboratory reagent grade sodium hydroxide (S.D. Fine-Chem Ltd., Mumbai, India).

Methods

Preparation of Grafted Starches

Tapioca starch was graft copolymerized with varying amounts of MAA and MMA as per a procedure reported elsewhere.¹²⁻¹⁴ The samples were prepared with MAA (5, 10, and 20% treatment levels; % with respect to wt of starch) and MMA (5, 10, and 15% treatment levels).

In the case of MMA graft copolymers, poly(methyl methacrylate (PMMA) homopolymer was removed by extraction with boiling methylene chloride. In the case of MAA graft copolymers, poly(methacrylic acid) (PMAA) homopolymer was removed by repeated water washing.

Preparation of Neutralized SPMAA

Fully ionized sodium salt of SPMAA was prepared by the reaction of SPMAA with one equivalent (based on carboxyl groups) of sodium hydroxide. Sodium hydroxide solution (3%) was added dropwise to a 40% slurry of SPMAA at 30°C in water under stirring, and the stirring was continued for 30 min. The slurry was filtered and dried. Partially neutralized SPMAA samples with 12.5, 25, 37.5, and 50% neutralization were prepared by treatment of SPMAA with 0.125, 0.25, 0.375, and 0.5 equivalents of sodium hydroxide (equivalence based on moles of carboxyl groups present in SPMAA), respectively.

Measurement of Brabender Viscosity

The gelatinization characteristics of the modified starch samples were studied by heating a 5.6% starch (dry basis) suspension in a Brabender viscosograph (Duisburg, Germany) (model PT-100, mounted with 350 cm g cartridge) at a rotating speed of 75 rpm. The starch suspension was heated to 40°C at a fast rate of 4.5°C/min and from 40 to 90°C at a rate of 1.5°C/min. The tem-

Table I Grafting Yield, Gelatinization Temperature, Peak Viscosity (Brabender), and the Temperature at Which Peak Viscosity Was Achieved for Starch and Starch Graft Copolymers

Grafted Starch	% Grafting	Initial Gelatinization Temperature (°C)	Peak Viscosity (BU) ^b	Stable Viscosity (BU) ^b	Peak Viscosity Temperature (°C) ^a
Tapioca	0.0	64	570	430	76
SPMAA					
SPMAA-I	3.9	64	675	430	76
SPMAA-II	7.2	64	630	360	76
SPMAA-III	14.1	64	400	220	76
SPMMA					
SPMMA-I	4.5	—	10	—	—
SPMMA-II	9.2	—	10	—	—
SPMMA-III	14.8	—	10	—	—

^a The temperature at which peak viscosity was attained.

^b BU = Brabender units.

perature was thereafter maintained at 90°C for 20 min.

Sample Preparation for SEM Analysis

Starch samples (1 g of starch/modified starch and 4 g of water) were equilibrated at 30, 55, 75, and 95°C for 30 min and freeze-dried. The dried powder was sprinkled on a Vistanex-coated glass slide and fixed on an aluminum stub. The sample was then sputter-coated with silver under a reduced argon atmosphere. The SEM examination was carried out at 25 kV accelerating voltage with beam current of 60i A in secondary emissive mode with a Hitachi S570 instrument (Japan).

RESULTS AND DISCUSSION

Pasting Characteristics of Starch Graft Copolymers

SPMAA and SPMMA were prepared by a procedure discussed elsewhere.^{12–14} The graft copolymers with varying grafting levels were prepared by variation of the monomer treatment levels. In all these cases, the grafting efficiencies were above 70%. The percentage grafting was estimated gravimetrically in the case of SPMMA and by alkali titration in the case of SPMAA after removal of the homopolymers. The homopolymer from SPMAA was removed by water washing. In the case of SPMMA, the poly(methyl methacrylate) (PMMA) homopolymer

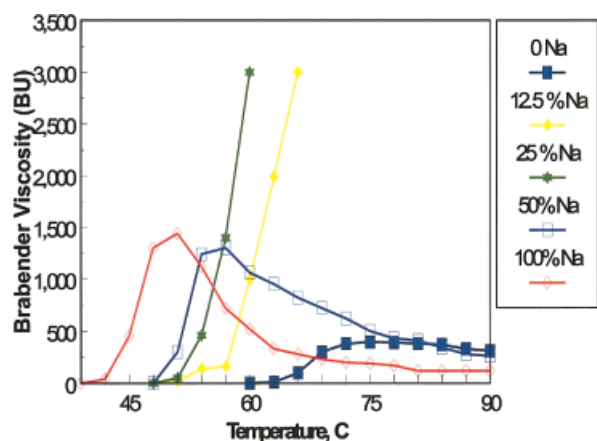


Figure 1 Effect of alkali neutralization of carboxyl groups of SPMAA-II on viscosity.

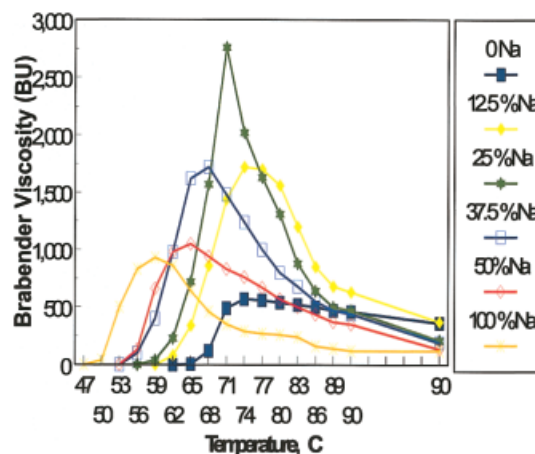


Figure 2 Effect of alkali neutralization of carboxyl groups of SPMAA-III on viscosity.

Table II Viscosity Characteristics of SPMAA Samples: Effect of Percentage Grafting and Extent of Neutralization

Sample	% Neutralization of COOH	Initial Gelatinization Temperature (°C)	Peak Viscosity (BU)	Stable Viscosity (BU) ^a	Peak Viscosity Temperature (°C) ^b
SPMAA-I	0	64	675	430	76
	12.5	63	1000	570	74
	25	62	1150	570	71
	37.5	61	655	240	69
	50	60	625	230	68
	100	59	215	40	64
SPMAA-II	0	64	560	360	76
	12.5	61	1720	370	74
	25	58	2760	210	71
	37.5	55	1780	135	66
	50	54	1050	135	63
	100	51	960	120	59
SPMAA-III	0	64	395	220	7
	12.5	54	>3000	440	69
	25	51	>3000	440	60
	37.5	50	1500	300	58
	50	49	1300	260	57
	100	42	1510	220	49

^a Brabender viscosity after 10 min hold at 90°C, in brabender units.

^b Temperature at which peak viscosity was attained.

was removed by extraction with methylene chloride.

Three samples each of SPMAA and SPMMA differing in PMAA and PMMA levels, respectively (PMAA contents: SPMAA-I = 3.9%, SPMAA-II = 7.2%, and SPMAA-III = 14.1%; PMMA contents: SPMMA-I = 4.5%, SPMMA-II = 9.2%, and SPMMA-III = 14.8%) were used for pasting/viscosity studies. The results are given in Table I. The amylograph curves of SPMAA samples were similar to that of tapioca starch. They showed a rapid increase in slurry viscosity during pasting and a slight decline during 90°C hold. This suggested that there was no significant variation in the extent of granule swelling, intermolecular interactions, and conformation of molecules in solution between starch and SPMAA. In contrast, the three SPMMA samples did not increase the viscosity due to gelatinization. The very low viscosities for gelatinized SPMMA were reflective of the lower granule swelling and insignificant levels of amylose leaching due to grafting with a hydrophobic monomer like MMA. However, granule disruption of these samples on heating with water was shown to occur, which is described later in the section on SEM Studies.

Variation of Viscosity Due to Neutralization of the Carboxyl Groups of SPMAA

The carboxyl groups of the SPMAA samples (I, II, and III) were neutralized to varying degrees (0, 12.5, 25, 37.5, 50, and 100 mol %) with sodium hydroxide. The Brabender viscosity plots for SPMAA-II and SPMAA-III are given in Figures 1 and 2, and the summary of the results is given in Table II. Increased ionization as a result of neutralization of carboxyl groups altered the pasting properties. A major decrease in initial pasting temperature with increase in percentage of grafting and extent of ionization was observed. The effect of neutralization on gelatinization temperature for the three samples with varying percentage grafting is given in Figure 3. In all three samples, a uniform trend was observed wherein the maximum viscosity was achieved at a 12.5–25% neutralization level, beyond which a drop in viscosity with respect to neutralization was noticed.

Leach et al.¹⁵ described the behavior of starch granules during heating. Water was described to penetrate into the more accessible amorphous region of the starch granule, resulting in hydration

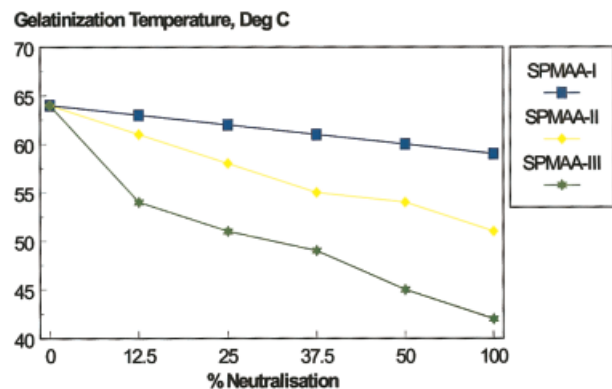


Figure 3 Effect of neutralization on gelatinization temperature.

and limited swelling. As the temperature increased to the point of gelatinization, the swelling of the amorphous phase accelerated the disruption of the crystalline region. The viscosity development during this process was believed to be

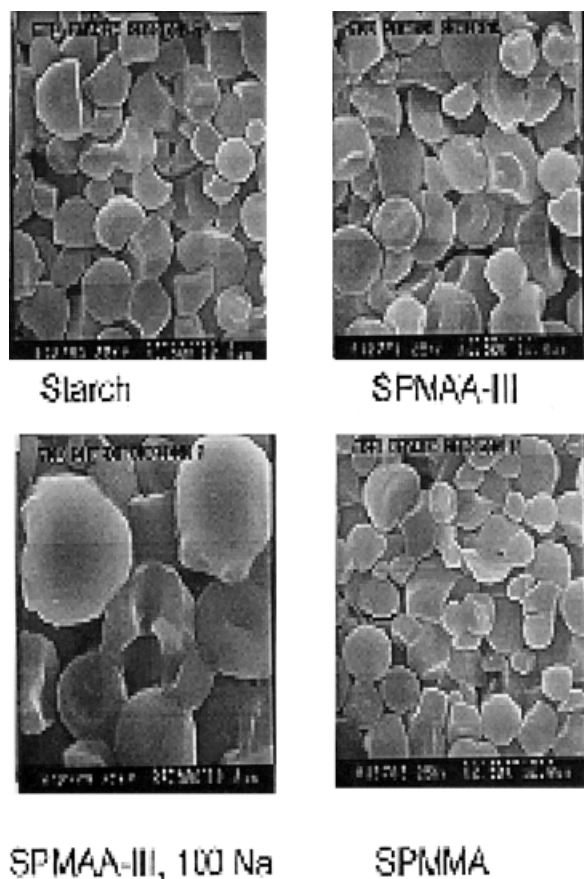


Figure 4 SEM of native starch, SPMAA-III, SPMAA-III, 100 Na, and SPMAA at 30°C.

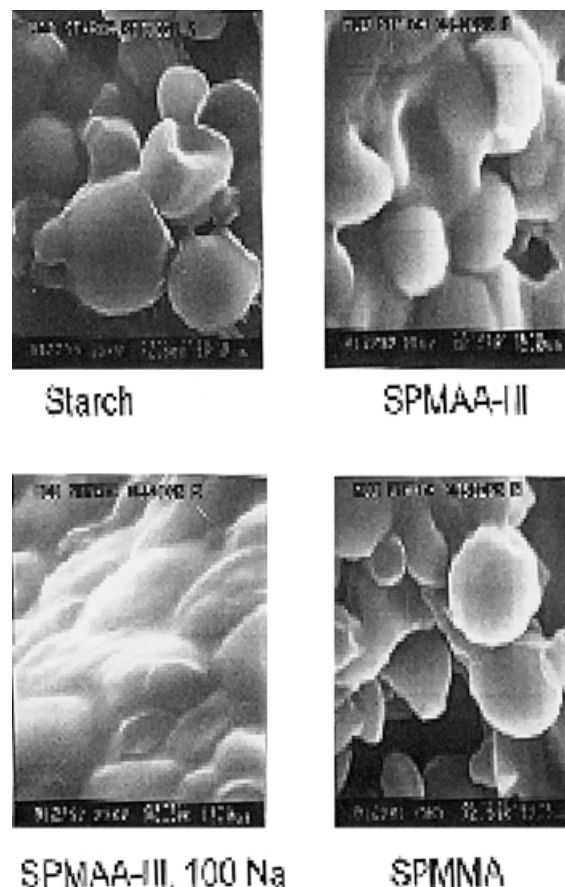


Figure 5 SEM of native starch, SPMAA-III, SPMAA-III, 100 Na, and SPMAA at 55°C.

related to the swelling properties of the starch granule.² The region of peak viscosity was reported to be where granules were fully swollen. Beyond this point, the granules disrupted under shear, resulting in a breakdown in viscosity. An increase in viscosity from partial neutralization of SPMAA samples could thus be explained by the increased swelling of the SPMAA granules, arising out of the neutralization of the carboxyl groups. At very high levels of neutralization of the carboxyl groups, the chances of granule disruption (prior to achievement of complete swelling) were high, thus explaining the reduction in peak viscosity beyond 25% neutralization. However, with an increase in the percentage grafting, there was a significant increase in the peak viscosity.

Although the peak viscosities of the alkali-neutralized SPMAA samples were significantly higher than that of corresponding unneutralized SPMAA, the final viscosity, (i.e., after shear in the Brabender viscosgraph for 10 min at 90°C), was either equal or close to that of unneutralized SP-

MAA (except in the case of the 100% neutralized sample, which was much lower). This once again indicated that neutralization affected mostly the extent and rate of granule swelling, and at moderate neutralization levels (12–25%), granule swelling might be maximal and cause the high viscosity. On continued stirring, granule breakdown took place, and finally, the solution viscosity leveled off to that of unmodified SPMAA. At increased neutralization levels, the extent and rate of granule swelling increased to such an extent that the granules disrupted before achieving peak viscosity. This behavior was observed by SEM studies of aqueous slurries of samples with varying extents of neutralization.

SEM Studies

Granule swelling and disintegration characteristics of starch graft copolymers were further investigated by SEM. Starch samples (1 g of starch and 4 g of water) were equilibrated at 30, 55, and 75°C. The freeze-dried samples of tapioca starch, SPMAA-III, and SPMAA-III sodium salt, and SPMAA were examined by SEM.

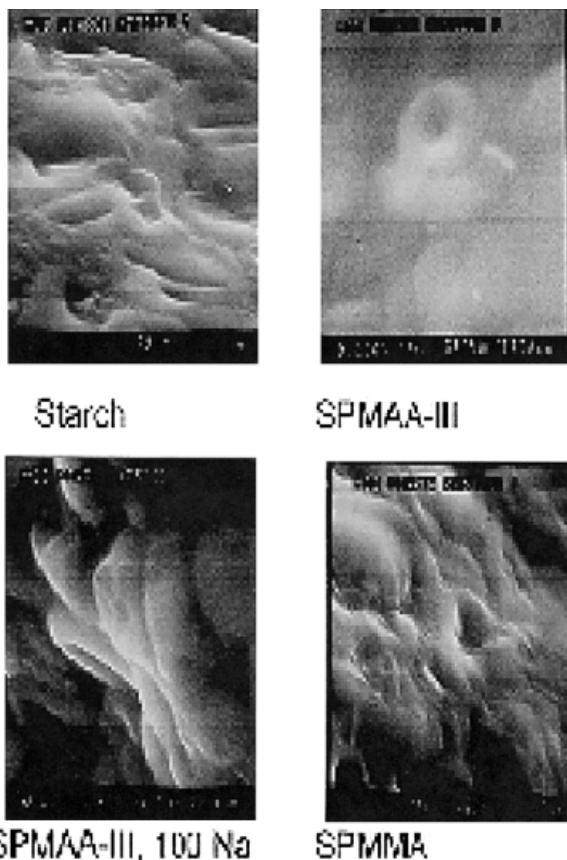


Figure 6 SEM of native starch, SPMAA-III, SPMAA-III, 100 Na, and SPMAA at 75°C.

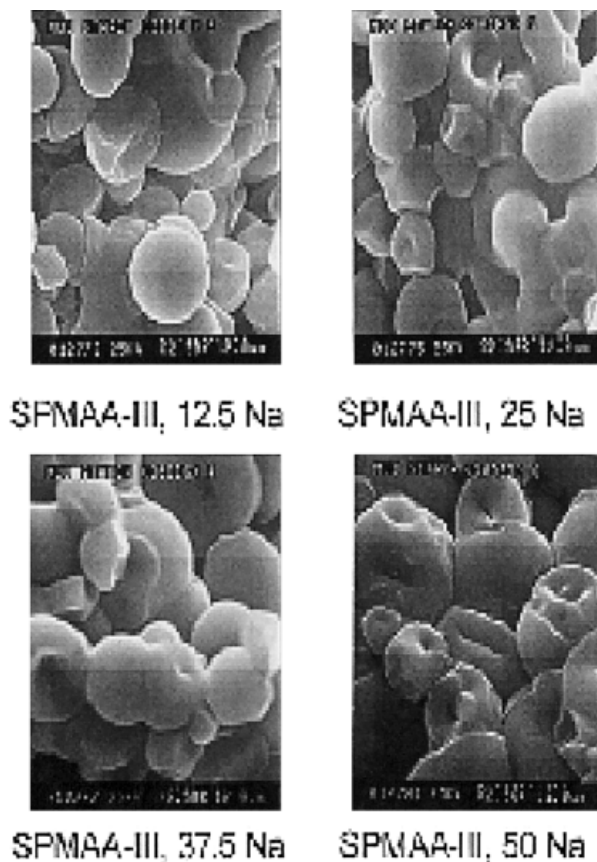


Figure 7 SEM of SPMAA-III and 12.5, 25, 37.5, and 50% Na at 30°C.

SPMAA-III sodium salt, and SPMAA were examined by SEM.

Figures 4, 5, and 6 give the scanning electron micrographs of the samples equilibrated at 30, 55, and 75°C, respectively. Native tapioca starch, SPMAA, and SPMAA showed no difference in their external morphology at 30°C, whereas SPMAA sodium salt showed some extent of surface erosion. The granules of tapioca starch, SPMAA, and SPMAA were intact at 55°C (except that SPMAA showed a slightly higher level of swelling), whereas SPMAA sodium salt showed a partial disintegration of granules, indicating amylose leaching. At 75°C, all of the starches showed granular disintegration.

The scanning electron micrographs of SPMAA-III samples, neutralized to 12.5, 25, 37.5, and 50% and heated to 30 and 55°C are given in Figures 7 and 8, respectively. These studies demonstrated that even at a lower temperature of 30°C and lower neutralization levels, the granules were highly swollen with minimal granule disintegration. At 55°C, the swelling and granule disinte-

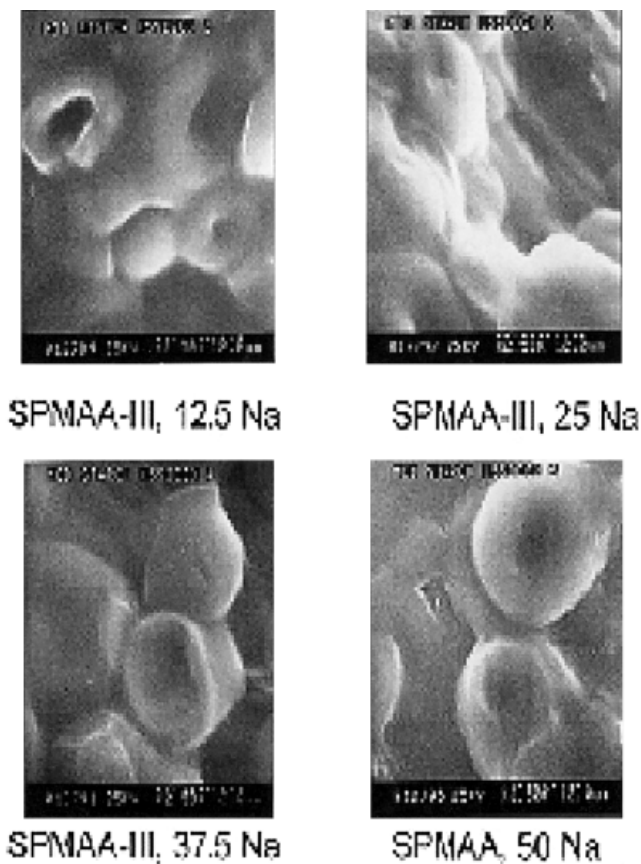


Figure 8 SEM of SPMAA-III and 12.5, 25, 37.5, and 50% Na at 55°C.

gration was at a maximum without dispersion into the medium, between 12.5 and 37.5% neutralization, leading to the maximum in viscosity.

SEM studies revealed that there was gelatinization and granule disruption on heating of aqueous SPMAA slurries above 75°C. There were no significant differences in granule swelling characteristics between native tapioca starch and SPMAA. Increased swelling and easier granule disruption were, however, noticed for the alkali-neutralized SPMAA.

CONCLUSIONS

Major differences in viscosity and granule swelling characteristics of starches grafted with MAA and MMA were observed. Partial neutralization

of the carboxyl groups of SPMAA led to a significant increase in peak viscosity. This was explained to be caused by the increased granule swelling resulting from the increased ionization of carboxyl groups. SEM investigations demonstrated that even at temperatures as low as 55°C, the fully neutralized SPMAA granules were highly swollen and were partially disintegrated. Peak viscosity was achieved at the higher swollen state of the granules, and it was at 55°C for SPMAA-III (SPMAA with 14% PMAA add-on) between 12.5 and 37.5% neutralization.

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