

# Solution Properties of Gas-Phase-Polymerized Sodium Acrylate Microparticles. II. Sizing and Thickening Efficiencies

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**ABSTRACT:** The application testing of sodium polyacrylate prepared by spray polymerization as a textile sizer was carried out. Six monomer samples of sodium acrylate, with concentrations ranging from 30 to 45%, were prepared, polymerized, and used on textile yarns to test the sizing and thickening efficiencies of the polymer. Of the six textile yarns treated with the size, only samples 5 and 6, which had the lowest monomer concentration of 30%, had an adequate sizing efficiency comparable to that of the commercial sodium polyacrylate. A Duplan breaking figure of  $3 \times$  blank (unsized) yarn (312 in this instance) or more is satisfactory for successful weaving on an industrial high-speed loom. The two satisfactory samples had Duplan figures of 1067 and 1151, whereas the remaining four samples tested had Duplan values ranging from 393 to 769. The commercially available sodium polyacrylate size had a Duplan figure of 1146. For good sizing efficiency, therefore, a low monomer concentration of 30% or more in the preparation of sodium polyacrylate seemed desirable. Although the Duplan values

for the two samples prepared with a monomer concentration of 45% (samples 1 and 2) were similar (419 and 398, respectively), the Duplan values of the samples prepared with a monomer concentration of 40% (samples 3 and 4) varied markedly (769 and 393, respectively). Samples 5 and 6, prepared with a lower monomer concentration (30%), exhibited similar Duplan values (1067 and 1151, respectively), which made them commercially acceptable as sizing agents. The thickening efficiency of the gas-phase-polymerized sodium polyacrylate was satisfactory when the polymer concentration was less than 0.2%. Above this concentration, the gas-phase-polymerized sodium polyacrylate had a low viscosity in comparison with that of the commercially available thickener. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1044–1050, 2003

**Key words:** gas-phase polymerization; sodium polyacrylate; solution properties

## INTRODUCTION

For many years, sodium polyacrylate has been used in the chemical industry for a variety of purposes. It has been used as a dispersant for calcium carbonate, kaolin, titanium dioxide, and other pigments and fillers in such diverse applications as paints, paper coatings, and carpet backings. It has also been used as a textile size for the protection of the warp yarns in commercial high-speed looms and as a thickening agent in paints and paper coatings. Textile warp yarns are sized to impart strength to the yarns and to allow them to withstand the weaving processes. The shedding and beating-up of the weft yarns during weaving have been described by several authors.<sup>1–15</sup> Schenk<sup>5</sup> discussed the sizing of cellulosic staple fiber yarns with sizes containing starch derivatives, water-soluble alkaline earth salts, (meth)acrylic acid, meth(acrylam-

ide), and/or (meth)acrylate polymers. A polyester-cotton yarn sized with a solution of an acrylic acid/acrylonitrile copolymer Ca salt, potato starch, and ammonium peroxydisulfate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  resulted in a yarn with a residual moisture content of 5% and a size content of 16%. Sizing, the type of salt compound in the size and properties of the polyacrylate size for staple fibers, desizing, and the properties and uses of moisture-insensitive and thermostable Mg and Ca salts of acrylic acid/acrylonitrile copolymer sizes were discussed by Schenk and Wuerz.<sup>6</sup> They described the use of Mg and Ca salts in conjunction with starch sizes to improve weaving efficiencies and to ease the reclamation of sizing compounds from synthetic fiber filaments. Naik<sup>7</sup> discussed practical considerations in sizing, such as equipment, changing requirements for synthetic fibers and high-speed weaving, differences in gray and dyed yarns, and additives for the improved sizing of dyed yarns.

Schenk et al.<sup>8</sup> reported the preparation of powdered polyacid copolymers, such as (meth)acrylic acid, (meth)acrylonitrile, and (meth)acrylamide, with potassium peroxydisulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as initiators. Poly(meth)acrylic acid was mixed with a

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TABLE I  
Sources of Raw Materials (and Their Purity or Concentration)  
Used in the Experiments

Raw material	% Purity/% concentration	Supplier
Acrylic acid	98.5	Catalytic Chemical Co., Japan
NaOH solution	43–50	AECI Ltd., South Africa
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	98.0	Protea Industrial Chemicals, South Africa
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	98.0	Protea Industrial Chemicals, South Africa
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	98.0	Protea Industrial Chemicals, South Africa
ZnAc dihydride	99.5	Merck (South Africa agent)
Acrylamide	98.0	Cyanamid (Pty) Ltd., South Africa

ZnAc = zinc acetate.

stoichiometric quantity of MgO and dissolved in water at 90°C to yield a 15% polymer with a solution pH of 8.0 and a viscosity of 120 cP at 85°C. A cotton fiber was sized with the resulting solution to a 12.7% pickup (with respect to the dry fiber weight) after 24 h of storage at 20°C and 65% relative humidity. The sized cotton yarn showed pendulum hardnesses of 116 at 65% humidity and 27 at 85% humidity, as opposed to 20 and 7, respectively, for the same fiber when it was sized with poly(vinyl alcohol) (degree of polymerization = 1400). The sizing compositions for the synthetic warp for weaving fabrics by a water jet loom were discussed by Taniguchi et al.<sup>9</sup> They reported the use of emulsions of a polymer containing 55–97 mol % vinyl ester units and 3–15 mol % ethylenic unsaturated carboxylic acid units and optionally containing an ester or alcohol, for sizing the polyester and nylon warp, which gave good adhesion of the size to the warp. However, the adhesion of the size to the warp was poor for filaments sized with an aqueous crotonic acid/vinyl acetate copolymer in an ammonium salt.<sup>9</sup>

In this paper, we discuss the use and sizing efficiency of gas-phase-polymerized sodium polyacrylate as a warp yarn sizer on polyester yarns and compare its efficiency with that of commercially available sodium polyacrylate size.

## EXPERIMENTAL

Sodium acrylate was prepared from acrylic acid with sodium peroxydisulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as ini-

tiators. The solution was neutralized with sodium hydroxide (NaOH) to obtain the sodium acrylate monomer, which was polymerized in the gas phase.<sup>16–19</sup> The resulting polymer was used as a yarn sizer, and its sizing efficiency was determined with a Duplan tester. The viscosity, pH, and degree of conversion of the resulting polymers were also determined.

### Monomer solution preparation

Six monomer solutions with three different concentrations of sodium acrylate—45% (sample numbers 1 and 2), 40% (sample numbers 3 and 4), and 30% (sample numbers 5 and 6)—were prepared for the experiments. The reagents were all used as received, without any further purification (as would be the case in an industrial situation). The purities or concentrations of the acrylic acid, NaOH solution, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, zinc acetate dihydrate, and acrylamide raw materials are shown in Table I. The formulations of the acrylic acid monomers are shown in Table II. During the neutralization step, the mix temperature was maintained below 50°C to eliminate any chance of premature polymerization (unlikely, however, in the absence of an initiator).

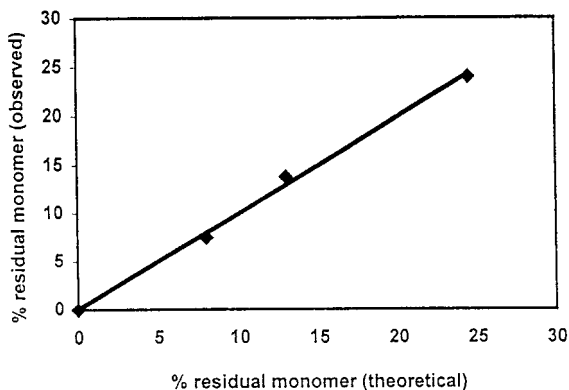
### Sodium polyacrylate preparation

The sodium acrylate monomer was polymerized in the gas phase at reaction temperatures between 110 and 140°C, during which time it was sprayed on the polyester textile yarn. The air-inlet and air-outlet flow

TABLE II  
Formulations of the Acrylic Acid Monomer Solutions

Solution	Amount of acrylic acid (kg)	46% NaOH solution (kg)	Water (kg)	% Theoretical concentration of monomer	% Neutralization of acrylic acid
1	9.8	5.8	9.4	45	49.0
2	8.7	5.2	11.1	40	49.5
3	6.5	3.9	14.6	30	49.7

Two samples from each of these formulations were used for the preparation of the sodium polyacrylate size used for the experiments.



**Figure 1** Residual monomer concentration of sodium acrylate determined experimentally by a bromination titration technique and compared with theoretical values.

rates were  $0.15$  and  $0.134 \text{ m}^3 \text{ s}^{-1}$ , respectively. The monomer solution feed rate was between  $10$  and  $12 \text{ dm}^3 \text{ h}^{-1}$ .

#### Determination of the degree of conversion

The residual unsaturation in the final product of sodium polyacrylate was a measure of the unconverted sodium acrylate monomer remaining in the polymer. The unsaturation was determined by a bromination titration technique, which has been described elsewhere.<sup>19</sup> This test method was evaluated by the addition of the sodium acrylate monomer to a commercial sodium acrylate solution. The results are shown in Figure 1.

#### Solution viscosity measurements

The solution viscosity of sodium polyacrylate was measured by the dissolution of the prepared polymer in water, with the application of heat when it was necessary, to give a solution of a known concentration. This solution was then cooled to a predetermined temperature, usually  $20^\circ\text{C}$ , and the viscosity was measured with a Brookfield model LVT viscometer (Lasec, South Africa).

#### pH measurements

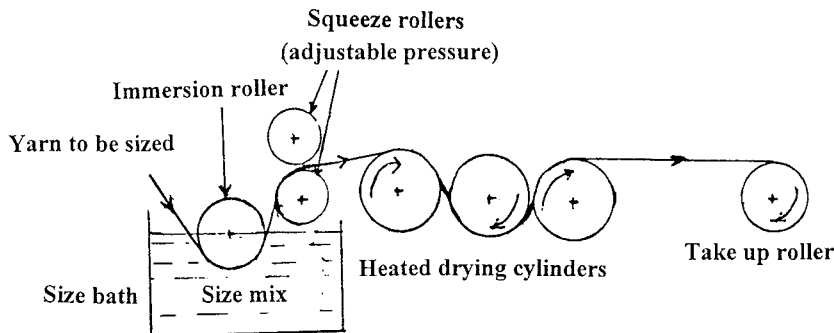
An aqueous polymer solution of a known concentration was prepared, and the pH measured at  $20^\circ\text{C}$ .

#### Determination of the degree of neutralization

A 1% solution of sodium polyacrylate was prepared in distilled water. A known volume of the solution was taken and titrated with a  $1\text{M}$  NaOH solution. A plot of the pH of the solution versus the volume of the NaOH solution titrated was obtained. An inflection point was reached on the titration curve, which was an indication of the number of moles of the unneutralized product. A similar volume of a prepared solution of the product had a reduced pH with the addition of concentrated hydrochloric acid. This was again titrated with a  $1\text{M}$  NaOH solution to the same inflection point. Another inflection point was reached before the initial point. The difference between the two inflection points was a measure of the total number of moles of acid in the product. From the two titrations, the degree of neutralization was calculated.<sup>16,18</sup>

#### Polymerization of partially neutralized sodium acrylate in a spray drier

The feasibility of polymerizing partially neutralized sodium acrylate monomer in a spray drier to give a dried powder product was studied. A partially neutralized sodium acrylate monomer was used (as opposed to a fully neutralized sodium acrylate) to match a sodium polyacrylate product commercially available from Bevaloid SA, Ltd. (Durban, South Africa) albeit as a 25% solution. A formulation of acrylic acid and water (1.5:1) was prepared, giving a 49.6% neutralized solution of acrylic acid with a concentration of 50%. The initiator was prepared from 1 kg of water and 91 g of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Mixing the monomer and initiator solutions gave a level of 0.182% initiator with respect to the monomer. The mixture was sprayed into a spray drier through a brass Jet T type SX 1 nozzle from Spray Systems, Inc. (South Africa) at a pressure between 1.5



**Figure 2** Schematic representation of the textile yarn-sizing machine.

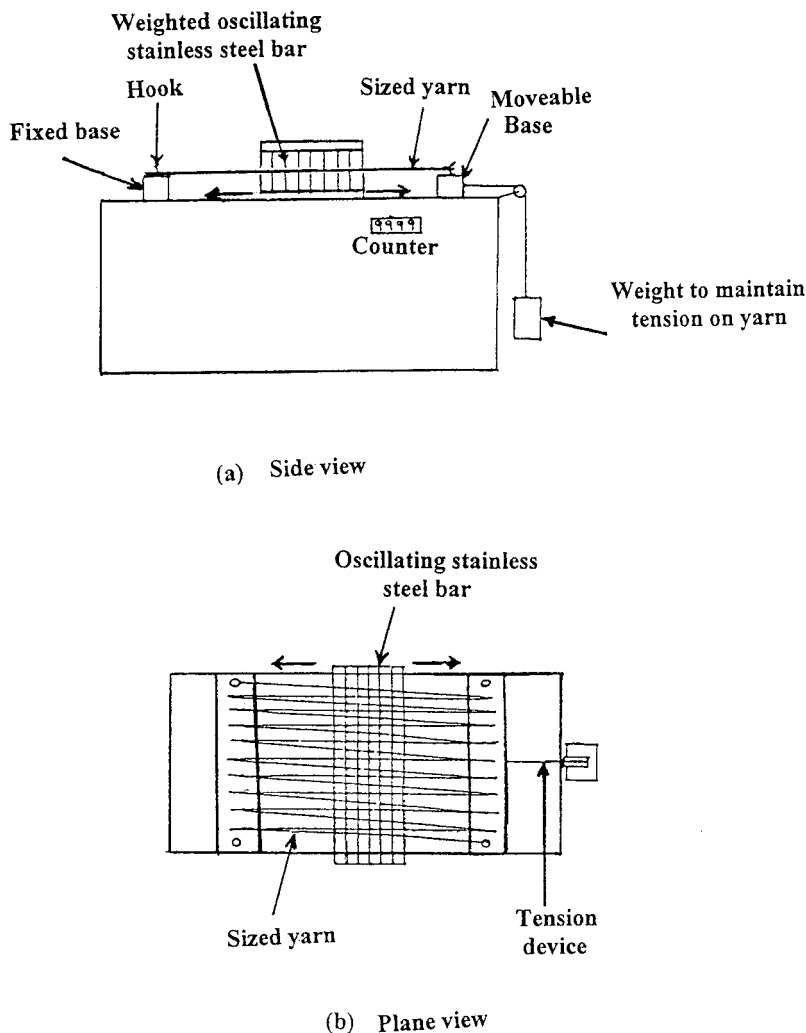


Figure 3 Schematic representation of the Duplan abrasion tester: (a) side view and (b) plane view.

and 3.0 MPa and at a feed rate between 10 and 12 dm<sup>3</sup> h<sup>-1</sup>. The feed rate was governed by the viscosity of the solution being sprayed and the pressure required to achieve a good spray pattern.

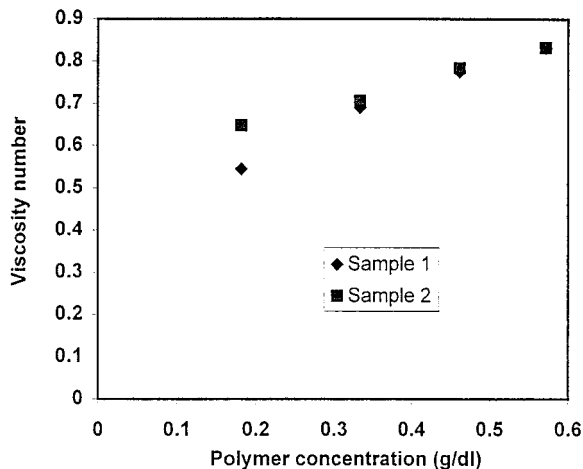
**Determination of the sizing efficiency**

The textile sizing efficiency of the materials prepared as described was evaluated as follows. A size mix was prepared from the product from one of the spray-drier trials and starch, a solution of a known concentration of approximately 10%. It was first boiled for 40 min to cook the starch. The size was

then applied to yarns on a laboratory-scale sizing machine, as shown in Figure 2. After drying and conditioning, the yarn was tested for abrasion resistance (the most important property with respect to yarn protection in weaving). Abrasion testing was carried out on a Duplan tester, as shown in Figure 3. The abrasion on the yarn corresponded to the friction experienced by the yarn between the eyes of the heads and to the friction of the reed when the woven cloth was beaten into place. The number of cycles required to break the yarn was recorded. The higher the number was of Duplan cycles, the better the size efficiency was of the yarn.

**TABLE III**  
**Properties of Two Samples of Sodium Polyacrylate Prepared by the Gas-Phase Polymerization Technique**

Sample	% Volatile content	Viscosity of 10% aqueous solution at 20°C (10 <sup>3</sup> mPa.s)	M <sub>v</sub>	pH of aqueous solution	% Conversion
1	1.8	0.72	52012	7.4	97.4
2	0.8	5.40	74026	7.4	96.6



**Figure 4** Viscosity number (specific viscosity/concentration) of sodium polyacrylate samples 1 and 2 as functions of concentration. Samples 1 and 2 had  $[\eta]$  values of 0.440 and 0.552, respectively. With  $K = 42.2 \times 10^{-5}$  and  $\alpha = 0.64$ , the two samples had  $M_v$  values of 52,012 and 74,026, respectively.

#### Determination of the thickening efficiency

For the determination of the thickening efficiency of sodium polyacrylate, the increase in viscosity achieved with incremental additions of it to a styrene-acrylate copolymer emulsion was investigated. Such emulsions are commonly used as binders in paints, paper coatings, and carpet backing systems (situations in which a thickening agent is required). The thickening efficiency was compared to that of a commercially available material.

#### Molecular mass determination

The molecular masses of sodium polyacrylate were determined by high-pressure liquid chromatography (HPLC) and solution viscometry. A Micromeritics 7500 HPLC system, incorporating a refractive-index detector, was used. DuPont SE 100, 1000, and 4000 gel permeation chromatography columns were used to cover a molecular mass range of  $10^3$  to  $10^7$ . The calibration for the molecular masses was carried out with dextran standards.

Dilute solution viscometry experiments were carried out with an Ubbelohde viscometer suspended in a constant-temperature bath.<sup>19</sup>

The viscosity-average molecular mass ( $M_v$ ) was determined from the intrinsic viscosity,  $[\eta]$ , with the Mark-Houwink equation,<sup>20</sup>  $[\eta] = KM^\alpha$ , where  $K$  and  $\alpha$  are constants for a particular polymer/solvent system at a given temperature. From the literature<sup>21</sup> and for the polymer/solvent system under consideration,  $K$  and  $\alpha$  were  $42.2 \times 10^{-5}$  and 0.64, respectively.

## RESULTS AND DISCUSSION

#### Molecular masses of sodium polyacrylate prepared by spray polymerization

The molecular masses of two sodium polyacrylate samples, the properties of which are shown in Table III, were determined. The viscosity numbers of samples 1 and 2 as functions of the polymer concentration are shown in Figure 4. The viscosity numbers of the two samples did not vary significantly at polymer concentrations greater than 0.3 g/dL. Below this concentration there were variations in the viscosity numbers of the two samples, resulting in different values of  $[\eta]$  and, therefore,  $M_v$ . These variations resulted in sample 2 being greater than sample 1 by approximately 20 and 30% for  $[\eta]$  and  $M_v$ , respectively.

The properties of the products formed during the polymerization of the partially neutralized sodium acrylate monomer in the gas phase are shown in Table IV. The conversion percentage of sodium acrylate to its polymer was very high ( $\approx 98\%$ ). The products formed at different reaction temperatures (130 and 140°C) had the same viscosity and pH of 10% solutions of the polymer at 20°C (i.e., 50 mPa.s and 5.25, respectively).

#### Sizing efficiency of spray-polymerized sodium polyacrylate

With the laboratory sizing machine used in this study, some variations in the dry size percentage on yarn were always likely. However, experience has shown that a comparison of Duplan results is possible if the size uptake varies by only  $\pm 1\%$ . From Table V, there

**TABLE IV**  
Properties of the Products Formed During the Polymerization of Partially Neutralized Sodium Acrylate Monomer in the Gas-Phase at 110, 130, and 140°C

Reaction temperature (°C)	Product				
	% Volatile content	% Conversion	% Neutralization	Viscosity at 20°C (mPa.s)	pH of 10% solution
110	1.6	98.32	—	—	—
130	1.6	97.80	78	50	5.25
140	4.4	98.82	75	50	5.25

TABLE V  
Textile Sizing Efficiencies of Different Sodium Polyacrylates Prepared by the Gas-Phase Polymerization Technique

Sample	Monomer solution concentration (%)	Viscosity of 10% aqueous solution 20°C (mPa.s)	% Conversion	% Dry size on yarn	pH of 10% aqueous solution	Duplan cycles to breaking of yarn
1	45	260	91.5	9.6	6.7	419
2	45	2080	95.3	8.2	6.8	398
3	40	3900	96.9	10.0	6.8	769
4	40	726	98.2	8.2	7.3	393
5	30	720	97.4	9.6	7.4	1067
6	30	5400	96.6	9.9	7.4	1151
BY	—	—	—	—	—	104
CSPAS	—	—	100	8.5	5.8	1146

BY = blank (unsized) yarn; CSPAS = commercial sodium polyacrylate size.

does not seem to be any correlation between the conversion percentage, viscosity, and pH of the aqueous solution and the sizing efficiency (as measured by the number of Duplan cycles to the breaking of yarn). Although the sizing efficiency of only two samples (numbers 5 and 6) approached that of the commercial product, experience has shown that a Duplan breaking figure of  $3 \times$  blank (i.e.,  $3 \times 104 = 312$  in this instance) is satisfactory for successful weaving on an industrial high-speed loom.<sup>18</sup> Therefore, all six samples prepared in this study could be considered suitable for use as sizing agents because they all had Duplan values above 312. Figure 5 shows the variation in the Duplan values with the monomer concentration; as the concentration increased, the Duplan values decreased. Therefore, for sodium polyacrylate to be useful as an effective sizing agent, the sodium acrylate monomer should be present in a low concentration.

The pH values of the aqueous solutions of the polymer samples remained similar, ranging from 6.7 for a

sample with a monomer concentration of 45% to 7.4 for samples with a monomer concentration of 30%. The effect of the pH of the sizing solution on the sizing efficiency, therefore, is not well defined. Also, as shown in Table V, the effect of the solution viscosity of the sizing material on its sizing efficiency does not give a clear insight into what viscosity gives a better size.

#### Thickening efficiency of spray-polymerized sodium polyacrylate

A comparison of the viscosities of the gas-phase-polymerized products and commercial products is shown in Figure 6. At low thickener percentages, the viscosities of the gas-phase-polymerized product were comparable to those of the commercial material.

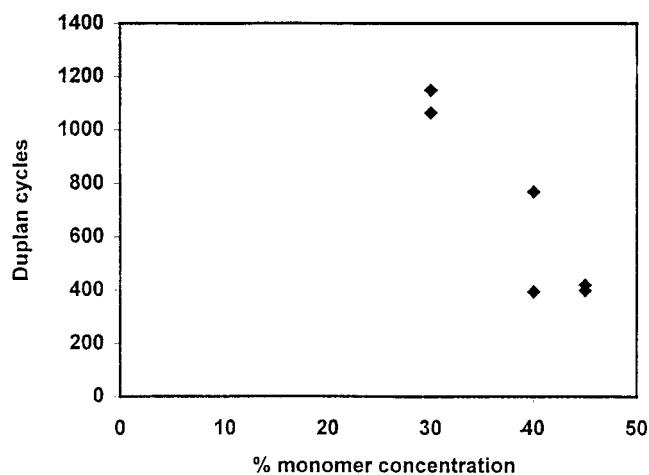


Figure 5 Duplan values of the sodium polyacrylate size on the polyester yarn as a function of the monomer concentration. The concentration of the commercially available sodium polyacrylate solution was not known. The polyester yarn sized with it, however, had a Duplan value of 1146, whereas the blank (unsized) yarn had a Duplan value of 104.

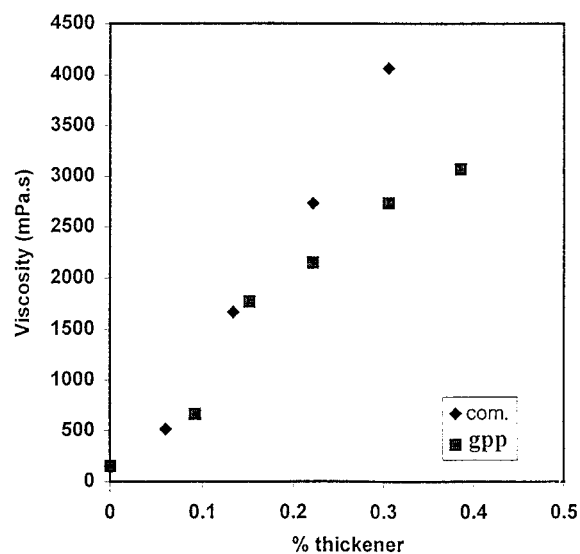


Figure 6 Viscosities of commercial sodium polyacrylate and spray-polymerized sodium polyacrylate as a function of the dry thickener percentage. com = commercial sodium polyacrylate; gpp = gas-phase-polymerized sodium polyacrylate.

## CONCLUSIONS

The pH, conversion percentage, and viscosity of gas-phase-polymerized sodium polyacrylate did not have a significant effect on the sizing efficiency of sodium polyacrylate. The samples with the lowest monomer concentration (30%) produced sizing agents that were commercially acceptable according to the Duplan testing criterion. The sizing efficiency increased as an inverse function of the monomer concentration. As a thickener, the gas-phase-polymerized product had a viscosity comparable to that of the commercially available sodium polyacrylate at a low percentage ( $\leq 0.2\%$ ). Beyond the 0.2% thickener level, a marked deviation in the viscosities of the gas-phase-polymerized and commercially available products existed.

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