

Polymerization Products of Acrylic Acid with *Gleditsia triacanthos* Gum as Thickeners for Reactive Printing

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ABSTRACT: Glactomannan gum was isolated from *Gleditsia triacanthos* seeds. It was then subjected to polymerization with acrylic acid using potassium persulfate initiation system. Products of the polymerization reactions are referred to as composites. Technical evaluation of the latter as thickening agent in reactive printing using cotton fabric was studied. The use of composite in printing cotton fabric with natural dye was also studied. It was found that the composite pastes are characterized by a non-Newtonian pseudoplastic behavior, and their apparent viscosity increases on increasing the concentration of acrylic acid. The composite can be diluted by water and its viscosity increases by neutralization. Printing pastes of the composite are very stable for storing, in contrast with those of natural gum which exhibit no stability for storing. It was also found that reactive prints thickened with the composite display rela-

tively higher K/S than those thickened with native gum do. Meanwhile, K/S values of prints thickened with the composite are comparable with the values of those thickened with sodium alginate. Printed fabrics using the composite as a thickener exhibit soft handle, and their overall fastness properties are almost equal to, if not higher than, the properties of those printed using sodium alginate. On the other hand, printing of cotton fabric with a natural dye using the composite as a thickener results in prints with K/S values lower than those obtained using commercial synthetic thickener; but the overall fastness properties are nearly the same. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 931–943, 2006

Key words: *Gleditsia triacanthos*; acrylic acid; polymerization; thickeners; reactive printing

INTRODUCTION

Alginates are regarded as the only natural thickener suitable for use in printing with reactive dyes.^{1–7} All other carbohydrates react with the reactive dyes, resulting in low color yield.

Unsatisfactory fabric handle may also occur because of insolubilization of the thickener through reaction of the latter with the dye. Although sodium alginate contains hydroxyl groups similar to other carbohydrates, it reacts very little,⁸ presumably because the ionized carboxyl groups on every ring of the alginate polymeric chain repel the dye anions. Since the last 30 years, efforts are continuing for finding alternatives for sodium alginate because of its high cost and limited supply.

Synthetic thickeners with anionic charges show great potential. Poly(acrylic acid) does not react at all with typical reactive dyes, and color yields are higher than those with alginates. Washing off is difficult, however, and the handle may be impaired.⁸

Mention should also be made to previous reports¹ emphasizing that glactomannan gums are more environmentally suitable than sodium alginate.¹

Gleditsia triacanthos is α dicot of the family leguminosae, subfamily caes-alipinideae; their seeds are composed of three components namely, testa (27%), endosperm (34%), and embryo (39%).⁹

The walls of the endosperm cells of *G. triacanthos* contain 81.5% of water-extractable carbohydrates, mainly glactomannan.^{10–12} The latter consists of β -(1–4) linked D-mannosyl backbone with α -(1–6) linked stubs of D-glactose.¹² The molar ratio of mannose to glactose is 2.9 : 1. The separation of the embryo from the endosperm is easy, but that of the testa from the endosperm is difficult.

The present work is undertaken with a view to synthesize a novel thickener for reactive printing on cotton. The synthesis involves polymerization reactions of acrylic acid with glactomannan gum isolated from the seeds of *G. triacanthos*.

Potassium persulfate is used as initiator. The polymerization reactions give rise to several polymeric products such as poly(acrylic acid)–glactomannan graft copolymer, homopoly(acrylic acid), oxidized glactomannan (which is formed by the oxidation action of persulfate on glactomannan) and unattached glactomannan. These polymeric products will be referred to as composites.

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Factors affecting synthesis of the composites along with their application in reactive printing on cotton and the overall fastness properties of the prints are studied. Printing using a natural dye is also studied.

EXPERIMENTAL

Materials

Substrate

Cotton poplin fabric (140 g/m²) supplied by Misr/Helwan Spinning and Weaving Company, (Cairo, Egypt) was used throughout this work.

Plant material

Dry, clean seeds of *G. triacanthos* L. were obtained from ripe pods, collected at National Research Centre Agriculture station. The seeds are composed of three components namely: testa (27%), endosperm (34%), and embryo (39%).¹³ The morphology of the endosperm cells of *G. triacanthos* L. is similar to the carob seeds. The gum is collected in the endosperm and composed mainly from glactomannan; the molar ratio of mannose to galactose is 2.9 : 1.^{10,11}

Thickening agents

Sodium alginate. Dial gin LV 100, low viscosity sodium alginate, was kindly supplied by BF Godlich Diamalt GmbH, Munich, Germany.

Synthetic thickener. Ciba Alco print DICS synthetic thickener is acrylic polymer dispersion, compatible with all anionic and nonanionic auxiliaries that are normally used in printing. This synthetic thickener was kindly supplied by Ciba speciality chemicals, Cairo.

Reactive dyes

Cibacron Brown 6R-P was kindly supplied by Ciba-Geigy, Switzerland; its reactive center is monochlorotriazine.

Remazol Brilliant Red GG was kindly supplied by Dyestar; its reactive center is vinyl sulfone.

Natural dye

Lawsonia intermis Linn, lythraceae (Henna) was used without further purification. It was purchased in a powder form from local market in Egypt.

Binder

Printofix Binder MTB was kindly supplied by Clariant.

Other chemicals

Acrylic acid, sodium carbonate, sodium bicarbonate, ammonium persulfate, hydroquinone, ferrous chloride, and urea were of laboratory grade chemicals. Mild oxidizing agent (Medoxy T) was kindly supplied by El-Nasr Company for Spinning, Weaving and Dyeing Mehalla El-Kobra.

Methods

Separation of the gum from the seeds

Glactomannan gum was separated from *G. triacanthos* seeds by crushing the seeds mechanically followed by sieving to separate the embryo from the other components of the seeds, i.e., the testa and endosperm. The testa and endosperm were soaked in cold water overnight to dissolve the gum. The swelled gum was isolated by filtration through mucline cloth. The gum was precipitated from the aqueous viscous extract by commercial ethyl alcohol, filtered, and finally air dried.

Polymerization procedure

The polymerization of acrylic acid monomers onto glactomannan's gum was conducted as follows.

Dry gum powder (24 g) was added to ammonium persulfate solution (7.5 g dissolved in 1200 mL of distilled water) and mixed well. After complete dissolution of the gum, the mixture is divided into three parts and the temperature adjusted at 65°C. Different amounts of acrylic acid (50, 75, and 100 mL) were added gradually with continuous agitation. The polymerization reaction was kept at 65°C for 30 min. At this end, the polymerization was terminated by addition of 1 mL of 1% aqueous hydroquinone.

The rheological properties of the obtained composite was thoroughly measured before and after neutralization, and the neutralized composite samples were used in the preparation of the printing pastes.

Preparation of the printing pastes

The printing pastes of the reactive dyes were prepared according to the following recipe:

Reactive dye	40 g
Urea	100 g
Thickener ^a	X g
Sodium bicarbonate	30 g
Resist salt	10 g
Water Y	Y g
Total	1000 g

^a The thickener used was either sodium alginate (50 g/kg printing paste) or 400 g/kg neutralized poly(acrylic acid)/glactomannan gum composites.

Printing pastes for application of henna

The pastes used for application of Henna powder as pigment color in printing were prepared as follows:

Henna	100 g
Thickener ^a	X g
Binder ^b	100 g
Diammonium Phosphate	12.5 g
Urea	40 g
Water	Y g
<i>Total</i>	1000 g

^a The thickeners used were either synthetic thickener namely Ciba Alco Print (25 g/kg) or the aforementioned neutralized and diluted poly(acrylic acid)/glactomannan gum composites.

^b The binder used was Printofix MTB.

Printing technique

All the printing pastes were applied to cotton fabric using screen printing.

Fixation

Fixation of the printed goods was effected either by steaming or thermofixation in an automatic thermostatic oven (Wenner Mathis Co., Switzerland).

Steaming. This was carried out at 100–103°C for 15 min for reactive dyes or at 125°C for 25 min for the Henna dye.

Thermofixation. The time and temperature of fixation were varied according to the kind of the dye used as follows:

1. Goods printed with Cibacron Brown 6R-P were fixed at 150°C for 3.5 min.
2. Goods printed with Remazol Brilliant Red GG were fixed at 145°C for 4 min.
3. Goods printed with Henna were fixed at 160°C for 4 min.

Washing

Washing of the printed goods with reactive dyes was carried out through five stages as follows:

1. Rinsing thoroughly with cold water.
2. Treatment with hot water.
3. Treatment near the boiling temperature (90–95°C) with a solution containing 5 g/L Hostapal CV and 2 g/L sodium carbonate.
4. Washing with hot water.
5. Rinsing with cold water.

Finally, the samples were dried and assessed for *K/S* and overall fastness properties.

Washing of the printed goods with Henna was carried out as follows.

1. The printed goods were rinsed thoroughly with cold water.
2. Soaped for 15 min at 45°C in a solution containing 5 g/L Hostapal CV and 2 g/L sodium carbonate, followed by washing with hot water.

Finally the goods were washed with cold water, then air dried and assessed for color strength (*K/S*) and overall color fastness properties.

Analysis and measurement

Determination of rheological properties¹⁴

The rheological properties of the printing pastes were measured using Rheomat-15 (Zurick, Switzerland) at 25°C, and the apparent viscosity (η) at various rates of shear was calculated from the shearing stress (*Z*) and rates of shear (*D*) as follows:

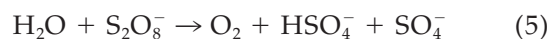
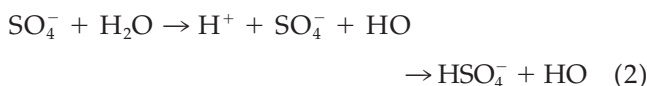
$$\eta = \frac{Z}{D}$$

Color measurements^{15,16}

The color strength, expressed as *K/S* and the overall fastness properties (washing, perspiration, and crocking), were assessed according to the standard techniques.

RESULTS AND DISCUSSION

Previous reports^{17,18} have shown that when an aqueous solution of potassium persulfate is heated, it decomposes to produce sulfate ion radicals along with other radical species, as shown in the reactions suggested by eqs. (1)–(5).



Vinyl polymerization may thus be initiated by either SO_4^- or HO radicals. In the presence of glactomannan gum, these free radicals (R) may also attack the glactomannan macromolecules thereby producing gla-

ctomannan macroradical capable of initiating grafting. Thus, beside homopolmerization, grafting of glactomannan may occur during polymerization of acrylic acid. Oxidation of the gum under the influence of potassium persulfate may also take place. That is, the ultimate result of polymerization of *G. triacanthos* gum with acrylic acid monomer in presence of $K_2S_2O_8$ as initiator is a composite consisting of: (a) glactomannan gum, (b) oxidized gum, and (c) grafted gum and homopoly(acrylic acid). It is anticipated that the properties of the obtained composite would rely on the concentration of monomer, i.e., acrylic acid. Hence three different poly(acrylic acid)/glactomannan gum composite samples were prepared via changing the amount of acrylic acid monomer as previously mentioned in the Experimental section.

The obtained composite products were found to acquire very high viscosity depending on the amount of acrylic acid monomer used. Hence it was diluted by distilled water to different ratios depending on the original viscosity of the obtained composite, as it will be shown later. The rheological properties before and after dilution and neutralization of the obtained composites were thoroughly investigated. Furthermore, the suitability of the neutralized composite as thickening agent in printing on cotton either using reactive dyes or natural color was also investigated. Given below are the results obtained along with the appropriate discussion.

Rheological properties

The rheological properties of the three composite samples prepared using different amounts of acrylic acid viz. 50, 75, and 100 mL acrylic acid monomer/400 g of 2% gum before and after storing for 0, 1, 2, and 7 days are represented in Figures 1–4, respectively.

It is clear from Figures 1–4 that, irrespective of the concentration of acrylic acid used or the time elapsed before commencing the measurement, the relation between the shearing stress and rate of shear is not linear, indicating that these pastes are non-Newtonian. It is also clear that the up- and down-flow curves are coincident, indicating that these pastes are characterized by pseudoplastic behavior.

Current data reveal that if the viscosity (resistance to flow) of these pastes is measured using a large applied force (shearing stress), the apparent viscosity is less than that of the same paste determined with a smaller force and a slower rate of shear. The rheograms depict further that, as the concentration of acrylic acid monomer increases, the rheograms are shifted far from the rate of shear axis, indicating an increase in the apparent viscosity. A clearer picture about the influence of the concentration of the monomer and the storing time on the apparent viscosity of

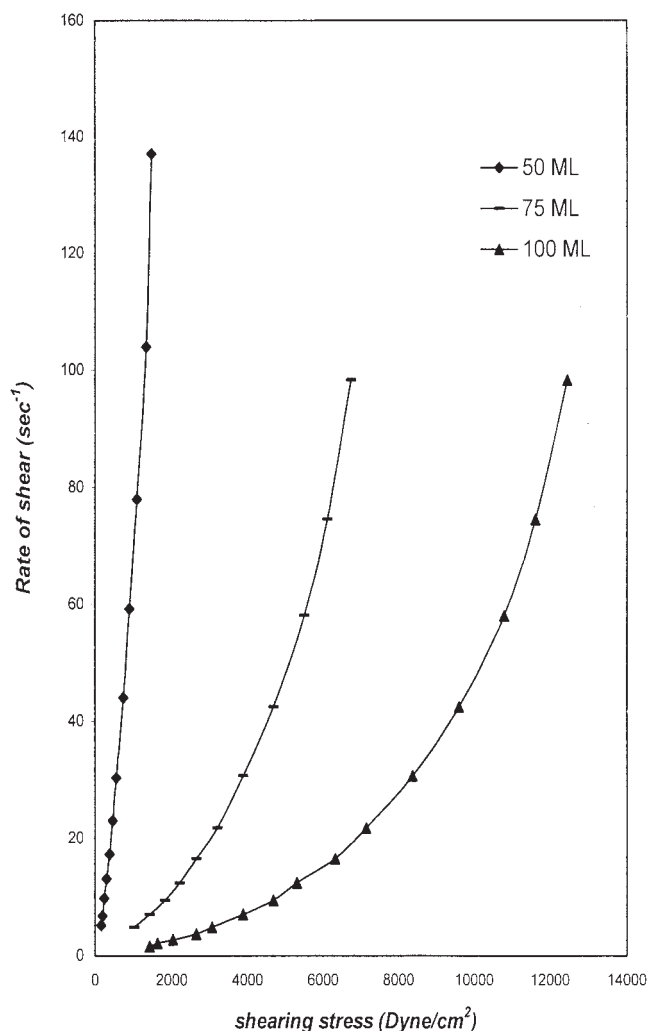


Figure 1 Rheograms of *Gleditsia triacanthos* glactomannan gum/poly(acrylic acid) composites freshly prepared using different amounts of acrylic acid.

the obtained composite at various rates of shear is shown in Table I.

Results of Table I show that, for a given rate of shear, the apparent viscosity of the composite increases on increasing the amount of acrylic acid monomer. For example, at a rate of shear ranging between 9.402 and 9.771, the apparent viscosity increases from 25.2195 to 195.373 to 499.287 on increasing the amount of monomer from 50 to 75 to 100 mL acrylic acid/400 g of 2% gum, respectively.

The increase in the apparent viscosity of the composite on increasing the amount of acrylic acid monomer is expected, since, as the concentration of the latter increases, the length of the side chains in the composite also increases. The increase in the side chains in the composite causes an increase in the molecular weight, and hence an increase in the resistance of the polymer to flow, i.e., an increase in the apparent viscosity.

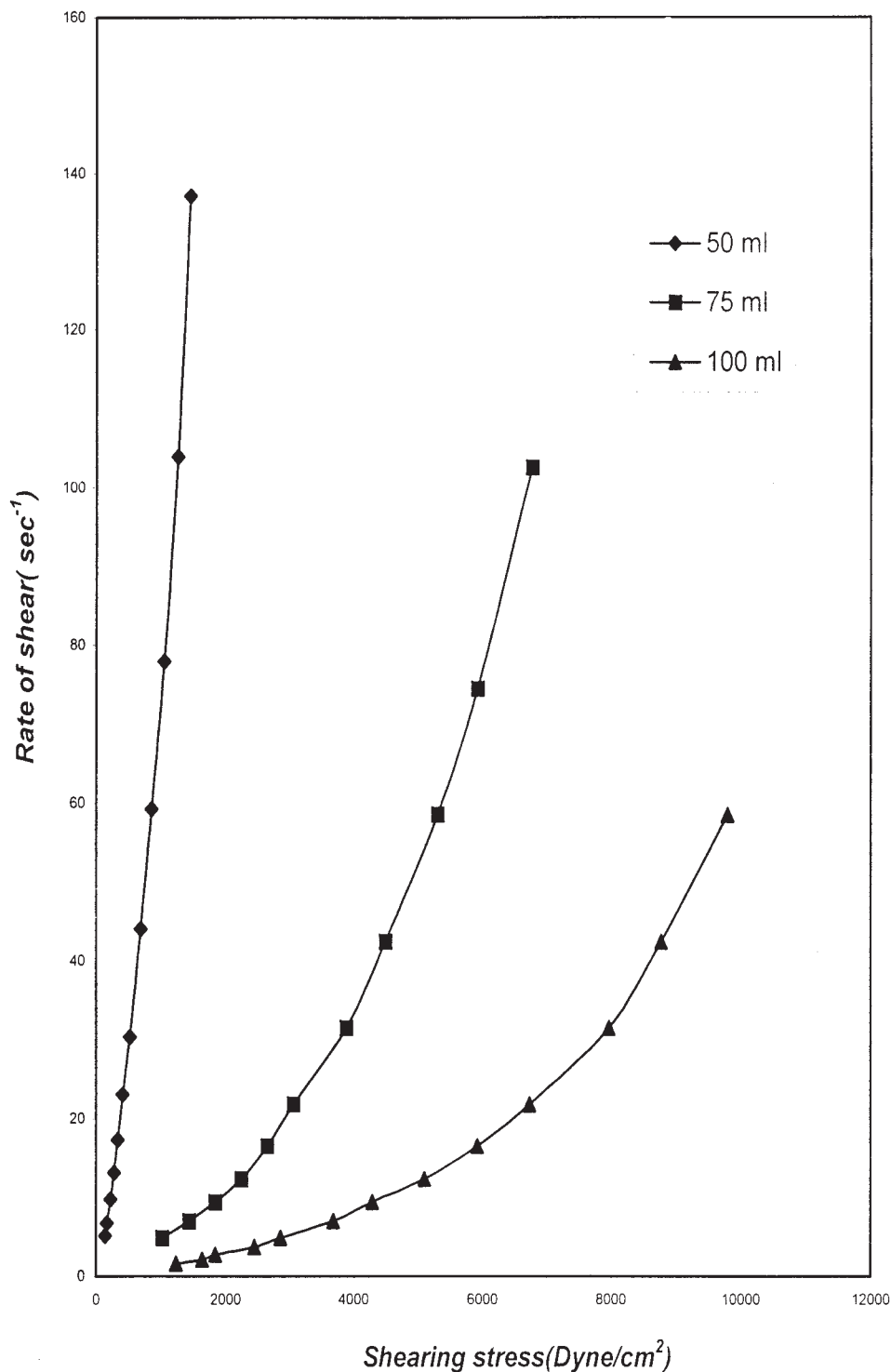


Figure 2 Rheograms of *G. triacanthos* glactomannan gum/poly(acrylic acid) composites prepared using different amounts of acrylic acid after storing for 24 h.

Table II represents the effect of storing of the composite prepared using 75 mL acrylic acid/400 g of 2% gum solution for 1, 3, and 7 days on the apparent viscosity at different rates of shear. It is clear that the composite is very stable to storing, since the change in the values of their apparent viscosity after storing is very marginal.

Effect of dilution and neutralization

It is to be noted that the composites under investigation can be diluted by water to any ratio to obtain the desired viscosity. Figure 5 and Table III represent the rheograms and apparent viscosity, respectively, for composite prepared using 100 mL acrylic acid after

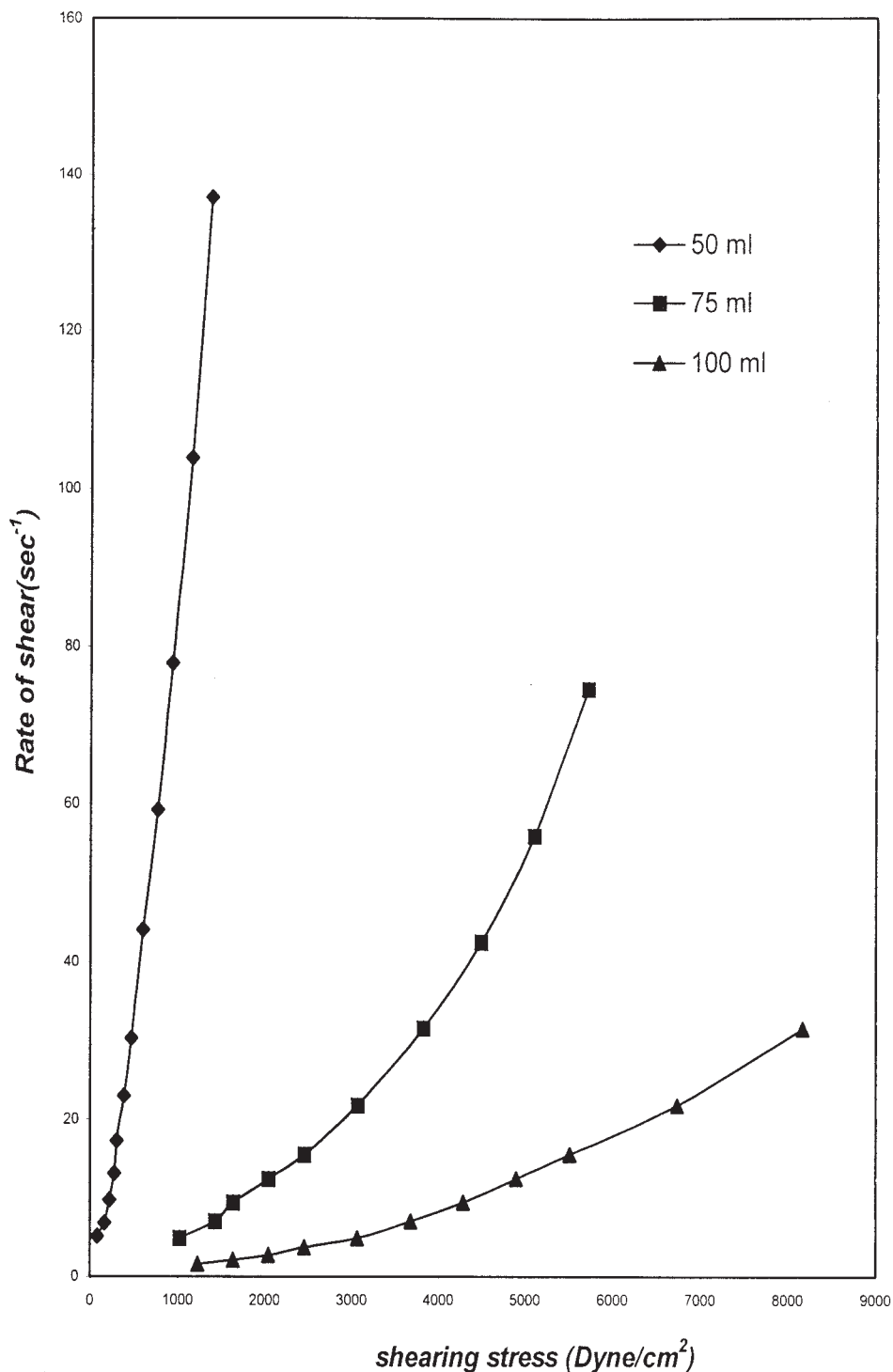


Figure 3 Rheograms of *G. triacanthos* glactomannan gum/poly(acrylic acid) composites prepared using different amounts of acrylic acid after storing for 48 h.

dilution with water at a ratio of 1 : 1 and after neutralization of the diluted sample.

It is clear (Fig. 5) that, neither dilution nor neutralization of the diluted composite has an effect on the rheological characteristic of the composite. In all cases, i.e., before and after dilution and neutralization, the composites exhibit non-Newtonian pseudoplastic be-

havior. However, the location of the rheogram is shifted, indicating a variation in the apparent viscosity, as clarified in Table III.

Results of Table III make it evident that although the apparent viscosity decreases by dilution, neutralization causes an increase in the apparent viscosity. For example, at a rate of shear between 9.402 and 9.771

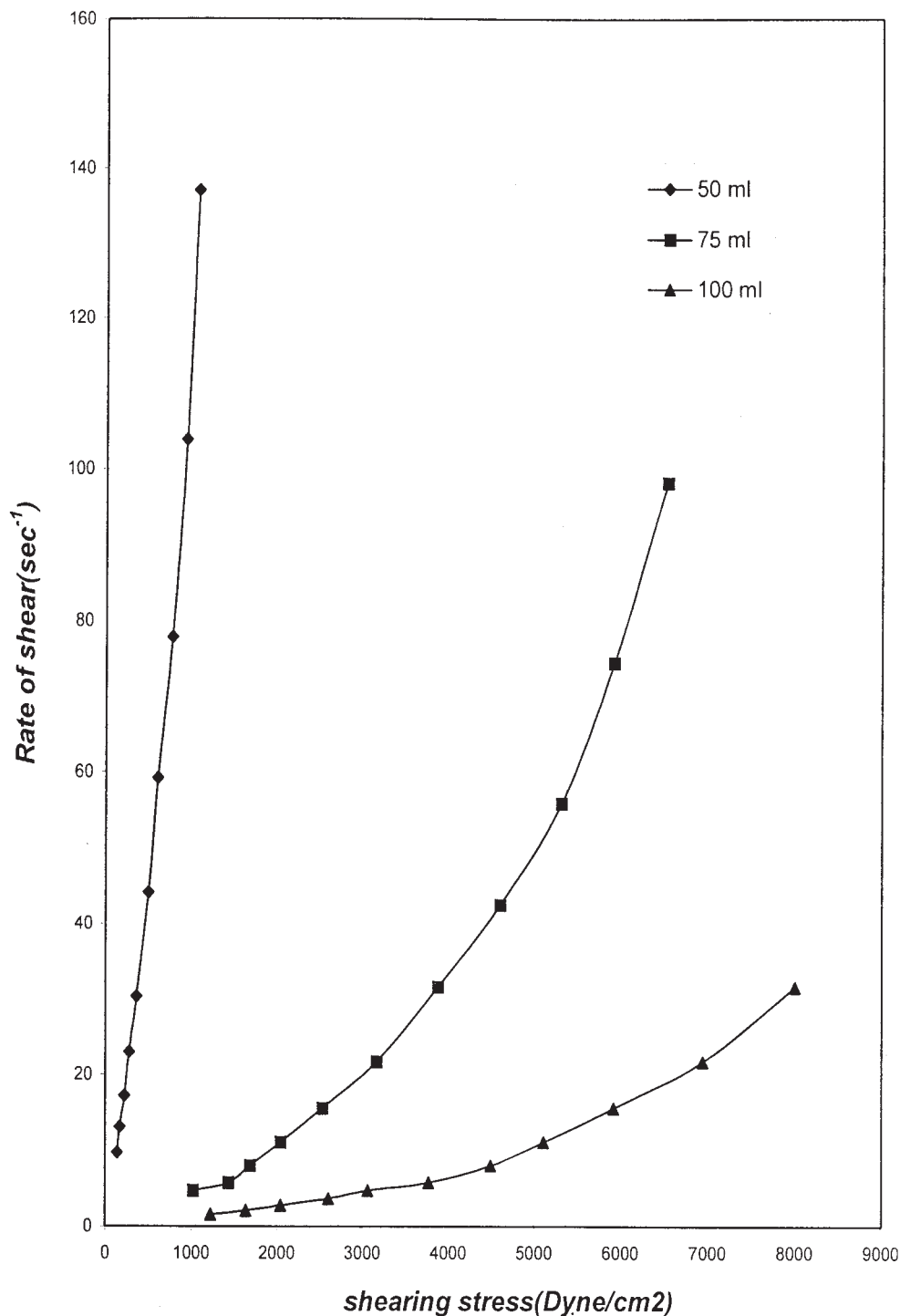


Figure 4 Rheograms of *G. triacanthos* glactomannan gum/poly(acrylic acid) composites prepared using different amounts of acrylic acid after storing for 1 week.

s⁻¹, the apparent viscosity decreases from 455.87 to 22.42 poise. While, after neutralization, the apparent viscosity increases from 22.42 to 117.69 poise.

The decrease in the apparent viscosity by dilution is expected; but the increase in the apparent viscosity after neutralization is surprising and may be due to one or more of the following: (1) an increase in the

molecular weight of the polymer by replacing H (atomic wt = 1) with Na (atomic wt = 23), (2) an increase in the adhesive power, or (3) an increase in the degree of ionization of COO⁻Na⁺ group more than that of the COOH group, and hence the repulsion force between the polymer chains increases. As the magnitude of the repulsion increases, the orientation

TABLE I
Effect of Concentration of Acrylic Acid on the Apparent Viscosity of Freshly Prepared Poly(acrylic acid)/*G. triacanthos* Gum Composite

Rate of shear (s^{-1})	Apparent viscosity in poise on using 50 mL acrylic acid	Rate of shear (s^{-1})	Apparent viscosity in poise on using 75 mL Acrylic acid	Apparent viscosity in poise on using 100 mL Acrylic acid
—	—	1.562	—	914.66
—	—	2.098	—	778.27
—	—	2.76	—	739.49
5.139	31.97	3.683	—	720.42
6.779	28.28	4.859	210.02	630.06
9.771	25.22	7.004	203.98	553.67
13.12	22.96	9.402	195.37	499.29
17.26	22.21	12.37	164.99	428.99
23.03	20.21	16.51	160.71	383.23
30.38	18.03	21.78	140.57	327.98
44.1	16.77	31.61	122.68	264.73
59.22	15.26	42.45	110.59	225.98
77.92	14.06	55.85	95.02	190.03
103.9	12.91	74.48	82.21	158.94
137.1	10.79	98.30	68.52	126.65

of the composite molecules along the rotation axis becomes more difficult, and hence the resistance to flow increases.

Printing

Printing using reactive dyes

As previously indicated, the main aim of the present section was to investigate the suitability of sodium salt of poly(acrylic acid)/glactomannan (derived from *G. triacanthos*) gum composite prepared using 50, 75, and 100 mL acrylic acid/400 g of 2% native gum solution as thickener in printing cotton fabrics with reactive or natural dyes. To achieve this goal, a series of printing pastes thickened with the aforementioned composites, after being diluted with water at a ratio of 1 : 1, 1 : 2,

and 1 : 3, from composites prepared using 50, 75, and 100 mL acrylic acid respectively. This was done to obtain printing pastes having nearly the same viscosity. Meanwhile, either Cibacron Brown 6R-P or Remazol Brilliant Red GG was incorporated therein according to the recipe given in the Experimental section. Furthermore, printing pastes containing natural dye namely Henna and thickened with the three aforementioned composites were also prepared. For the sake of comparison, other pastes thickened with sodium alginate in case of reactive dyes, or synthetic thickener in case of natural dye were also prepared.

After printing using the screen printing technique, the printed sample were dried. The colors were fixed by means of steaming. At this end, the samples were washed thoroughly (according to the technique mentioned in the Experimental section), dried and their color strength (K/S) as well as their overall fastness properties were measured. The results obtained are given in Tables IV–VI

Tables IV and V signify that, when reactive dyes were used, the K/S of the printed samples depends on: (a) nature of the thickening agent used, (b) the nature of the reactive dye, and (c) the time elapsed before commencing printing. On the other hand, the K/S of prints obtained using native glactomannan gum as a thickener is less than that obtained when sodium alginate was used. This is observed when reactive dyes were used, irrespective of their mode of reaction with the hydroxyl groups of cellulose, whether substitution or addition reaction takes place, as well as before or after storing of the printing pastes for 24 h. Possible reaction of the reactive dyes with the free hydroxyl groups in the glactomannan polymer may account for this.

TABLE II
Effect of Storing on the Paste of the Composite that has been Prepared using 75 mL Acrylic Acid for 400 g Glactomannan Gum (2%)

Rate of shear (s^{-1})	Apparent viscosity in poise for the composite			
	Freshly prepared	After 24 h	After 48 h	After 1 week
4.859	210.023	210.023	210.023	210.023
7.004	203.983	203.983	203.983	203.983
9.402	195.373	195.373	173.665	173.665
12.37	164.996	181.496	164.996	164.996
16.51	160.709	160.709	148.346	148.346
21.78	140.565	140.565	140.565	140.565
31.61	122.680	122.680	116.223	122.68
42.45	110.584	105.776	105.777	105.776
55.85	95.015	95.015	91.361	95.015
74.48	82.210	79.470	76.730	79.470
98.30	68.518	64.365	—	66.442

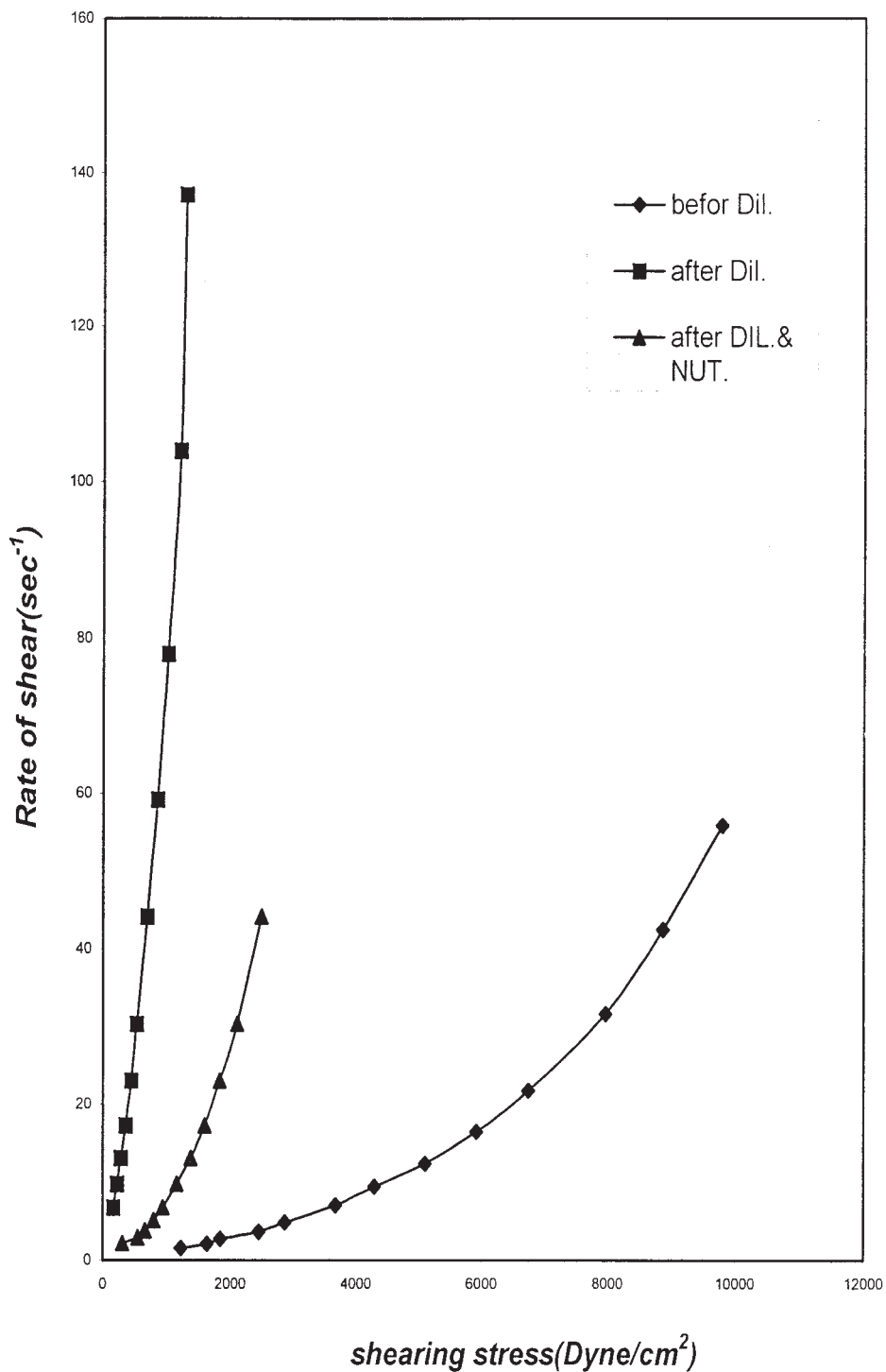


Figure 5 Effect of dilution and neutralization on *G. triacanthos* glactomannan gum/poly(acrylic acid) composite freshly prepared.

Surprisingly, despite the fact that prints obtained with native gum as a thickener exhibit lower K/S values than those obtained with sodium alginate, the prints are soft and acquire no harsh feeling, in contrast with samples printed using native starches¹⁹ or low-substituted starch or cellulose derivatives.²⁰⁻²³ Current results suggest that the reaction products of the

native gum with the reactive dyes are soluble in water and are removed during washing, thereby not causing any adverse effect on handling of the prints. It is emphasized, however, that native *G. triacanthos* gum pastes are not suitable for storing and are highly affected by fermentation; bad odor evolves on storing these pastes for more than 24 h and they lose most of

TABLE III
Effect of Dilution and Neutralization on the Apparent Viscosity of the Synthesized Composite

Rate of shear (s ⁻¹)	Apparent viscosity in poise before dilution	Rate of shear (s ⁻¹)	Apparent viscosity after dilution	Apparent viscosity after dilution and neutralization
1.562	783.99	2.180	—	138.16
2.098	778.27	2.927	—	187.09
2.760	665.54	3.851	—	170.64
3.683	665.00	5.139	—	154.51
4.859	588.06	6.779	24.23	137.32
7.004	524.53	9.771	22.42	117.69
9.402	455.87	13.12	20.87	104.34
12.37	412.49	17.26	20.62	92.00
16.51	358.50	23.03	19.02	79.66
21.78	309.24	30.38	17.12	69.40
31.61	251.82	44.10	15.52	56.50
42.45	206.74	59.22	14.33	—
55.85	175.41	77.92	13.00	—
—	—	103.9	11.59	—
—	—	137.1	9.39	—

The composite was diluted by the same weight of water, i.e. 1 : 1.

the resistance to flow (i.e. viscosity). Fermentation seems to be accompanied by hydrolysis, and therefore, depolymerization. The latter may be aggravated during steaming for dye fixation. Once this is the case, the colorant (dye molecule) is attached to a loosely degraded molecule which can be easily washed off during the washing process.

Tables IV and V show also that the values of the *K/S* obtained with poly(acrylic acid)/*G. triacanthos* gum

composites are almost relatively higher than those obtained with native gum; meanwhile, they are comparable with those obtained with sodium alginate. This is observed in all cases regardless of the amount of acrylic acid monomer used in the composite preparation, nature of the reactive dye used, and the time elapsed before printing.

The superiority of poly(acrylic acid)/*G. triacanthos* gum composite suggests that polymerization of

TABLE IV
Comparison between the Fastness Properties of Cotton Fabric Samples Printed with Different Composite Thickeners along with those Printed using Sodium Alginate and/or *G. triacanthos* Native Gum when Cibacron Brown 6R-P was Used as a Dye

Thickening agent used	Storing time	<i>K/S</i>	Fastness properties to								Handle
			Rubbing		Washing		Perspiration				
			Dry	Wet	St.	Alt.	Acidic	Alkaline			
						St.	Alt.	St.	Alt.		
Sodium alginate	Fresh	6.93	3	3	4	4	3-4	4	4	4-5	Soft
Native <i>G. triacanthos</i> gum	Fresh	5.14	3-4	3-4	4	4-5	3	3-4	4	4	Soft
	24 h	5.14	3-4	3-4	4	4-5	3	3-4	4	4	Soft
Composite I	Fresh	6.28	3-4	3-4	4-5	4-5	4	4	4-5	4-5	Soft
	24 h	6.18	3-4	3-4	4-5	4-5	4	4	4	4-5	Soft
Composite II	Fresh	6.97	4	4	4	4-5	4	4	4-5	4-5	Soft
	24 h	6.61	3-4	3-4	4-5	4-5	3-4	4	4	4-5	Soft
Composite III	Fresh	6.84	4	4	4-5	4-5	4	4	4	4-5	Soft
	24 h	6.61	3-4	3-4	4-5	4-5	3-4	4	4	4-5	Soft

St., Staining; Alt., Alteration. Composite I, II, and III are sodium salt of poly(acrylic acid)/*G. triacanthos* gum composite prepared using 50, 75, 100 mL of acrylic acid/400 mL of 2% native gum after neutralization and dilution at a ratio of 1 : 1, 1 : 2, and 1 : 3, respectively.

TABLE V
Comparison between the Fastness Properties of Cotton Fabric Samples Printed with Different Composite Thickeners along with those Printed Using Sodium Alginate and *G. triacanthos* Gum when Remazol Brilliant Red GG was Used as the Dye

Thickening agent used	Storing time	K/S	Fastness properties to:								Handle
			Rubbing		Washing		Perspiration				
			Dry	Wet	St.	Alt.	Acidic		Alkaline		
St.	Alt.	St.	Alt.	St.	Alt.	St.	Alt.	St.	Alt.		
Sodium alginate	Fresh	1.727	3-4	3-4	4-5	4-5	4	4	4	4-5	Soft
Native <i>G. triacanthos</i> gum	Fresh	1.443	4	4	4-5	4-5	3-4	4	4	4-5	Soft
	24 h	1.373	3-4	3-4	4-5	4-5	4	4	4	4-5	Soft
Composite I	Fresh	2.01	4	3-4	4-5	4-5	4	4	4	4-5	Soft
	24 h	1.929	4	4	4-5	4-5	4	4	4	4-5	Soft
Composite II	Fresh	1.993	3-4	3-4	4-5	4-5	3	3-4	4	4-5	Soft
	24 h	1.987	4	4	4-5	4-5	3-4	4	4	4-5	Soft
Composite III	Fresh	2.22	3-4	4	4-5	4-5	3-4	4	4	4-5	Soft
	24 h	1.60	4	4	4-5	4-5	3-4	4	4	4-5	Soft

St., Staining; Alt., Alteration. Fixation was carried out by steaming. Composite I, II, and III are sodium salt of poly(acrylic acid)/*G. triacanthos* gum composite prepared using 50, 75, 100 mL of acrylic acid/400 mL of 2% native gum after neutralization and dilution at a ratio of 1 : 1, 1 : 2, and 1 : 3, respectively.

acrylic acid on native glactomannan gum converts the gum into a thickening agent capable of swelling, dispersion, and jumping in aqueous medium without complete elimination of intermolecular forces between themselves and water. At the same time, the composites carry carboxyl groups greater than that of sodium alginate, which cannot react with the reactive dyes

and play a dominant role in repelling the similarly charged reactive dye ions, in full conformation with previous reports which stated that poly(acrylic acid) does not react at all with typical reactive dyes and the color yield is higher than that with the alginate.

A comparison among the said three composites prepared using different amounts of acrylic acid mono-

TABLE VI
Comparison between the Fastness Properties of Cotton Fabric Samples Printed with Different Composite Thickeners along with those Printed Using Sodium Alginate and *G. triacanthos* Native Gum when Natural Dye Henna was Used

Thickening agent used	Storing time	K/S	Fastness properties to:								
			Rubbing		Washing		Perspiration				
			Dry	Wet	St.	Alt.	Acidic		Alkaline		
St.	Alt.	St.	Alt.	St.	Alt.	St.	Alt.	St.	Alt.		
Synthetic thickener	Fresh	0.886	4	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Native <i>G. triacanthos</i> gum	Fresh	1.096	4	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	24 h	1.423	4	4	4-5	4-5	4	4	4	4-5	4-5
Composite I	Fresh	0.469	4	4	4-5	4-5	4	4	4	4-5	4-5
	24 h	0.723	4	3-4	4-5	4-5	4	4	4-5	4-5	4-5
Composite II	Fresh	0.723	4	4	4-5	4-5	4-5	4-5	4	4	4
	24 h	0.873	3-4	3-4	4-5	4-5	4	4	4-5	4-5	4-5
Composite III	Fresh	0.596	4	4	4-5	4-5	4	4	4	4-5	4-5
	24 h	0.908	4	4	4-5	4-5	4	4	4-5	4-5	4-5

St., Staining; Alt., Alteration. Composite I, II, and III are sodium salt of poly(acrylic acid)/*G. triacanthos* gum composite prepared using 50, 75, 100 mL of acrylic acid/400 mL of 2% native gum after neutralization and dilution at a ratio 1 : 1, 1 : 2, and 1 : 3, respectively.

mers viz. 50, 75, and 100 mL/400 g of 2% gum would indicate no substantial difference in the values of the K/S of the printed samples. The fact that different amounts of the composites were used during the preparation of the printing pastes as a means to control obtaining equal viscosity of the three pastes may account for this.

Tables IV and V show further that irrespective of nature of both the reactive dye and the thickening agent, storing of the pastes of reactive dyes causes a slight decrease in the K/S of the printed goods. This suggests that some of the dye molecules undergo alkaline hydrolysis during storing.

On the basis of the results of Tables IV and V, it is clear that all the samples printed using the three composites before and after storing acquire soft handle, similar to their corresponding samples printed using sodium alginate. This reflects the ease of removal of poly(acrylic acid)/*G. triacanthos* gum composite by washing.

Tables IV and V contain the overall fastness properties of the aforementioned printed samples, i.e., fastness to rubbing, to washing, and to perspiration. As is evident, the overall fastness properties of the cotton fabrics printed using poly(acrylic acid)/*G. triacanthos* gum composites before and after storing are nearly identical, if not higher, to their corresponding samples printed using sodium alginate.

Printing using natural dye

Table VI shows the values of K/S and overall fastness properties obtained when the aforementioned composites were used for printing with a natural dye, namely, Henna as a pigment. It is obvious that there is no remarkable difference between the overall fastness properties when the commercial synthetic thickener, or natural gum or the said three synthesized composites were used. On the other hand, the K/S values are dependent on the nature of thickening agent used and follows the order native glactomannan gum > synthetic thickener > the three composites.

The failure of the sodium salt of poly(acrylic acid)/glactomannan gum can be explained as follows. The main constituent of the color in Henna is lawsone. The structure of lawsone is 2-hydroxy-1,4-naphthoquinone. Lawsone has a very small molecule and exhibits a remarkable substantivity for wool, silk, and also polyester. It apparently behaves like a disperse dye. In the present work, the pigment printing technique was carried out to fix Henna color on cotton. The fixation of the color depends on the polymerization of the binder, which occurs at slightly acidic pH. The presence of great numbers of $-\text{COONa}$ groups in the current composite may affect the pH of the printed film, and hence affect the magnitude of the binder polymerization, where $-\text{COONa}$ groups ionized to

$-\text{COO}^-$ and Na^+ ions. The presence of Na^+ ions shifts the pH to the alkaline side.

CONCLUSIONS

Glactomannan gum is isolated from *G. triacanthos* seeds and subjected to polymerization with acrylic acid using potassium persulfate initiation system. The obtained composite is evaluated as thickening agents in printing. The results obtained highlight the following features:

- The composite pastes are characterized by a non-Newtonian pseudoplastic behavior, and their apparent viscosity increases on increasing the concentration of acrylic acid used.
- The composite can be diluted by water and its viscosity increases by neutralization.
- Printing pastes of natural gum is not stable for storing, in contrast with those containing composite which are very stable.
- When reactive dyes are used, the K/S of cotton samples thickened and printed using the composite are relatively higher than those obtained with printing paste thickened with native gum. Meanwhile, K/S values of prints obtained with the composite as a thickener are comparable with those obtained using sodium alginate.
- Cotton fabric samples printed using the composite exhibit soft handle, and their overall fastness properties are almost equal to, if not higher than, the properties of those printed using sodium alginate.
- When the synthesized composite in question is used in printing cotton with a natural dye, the K/S is lower when compared with those obtained using commercial synthetic thickener, but the overall fastness properties are nearly the same.

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