

STUDY OF POLYMETHACRYLIC ACID /SESBANIA GUM COMPOSITE AS THICKENING AGENT IN PRINTING WITH REACTIVE DYES

I. ABD EL-THALOUTH¹, M. REKABY^{1*}, A. A. H. RAHMAN² and SH.A.EL-KHABERY¹

1. Textile Research Division, National Research Center, Cairo, Egypt

2. Faculty of science, Menoufia University, Menoufia, Egypt

Abstract

Galactomannan gum was isolated from Sesbania seeds and subjected to chemical modification via grafting with methacrylic acid monomers using potassium persulphate as initiator. The rheological properties of the prepared composites before and after storing for three and seven dyes were thoroughly investigated. Furthermore; the obtained composite was evaluated as thickening agent in reactive dye printing pastes of cotton fabrics.

It was found that poly methacrylic acid / Sesbania seeds gum composites could be used as a substitute for sodium alginate in printing cotton fabrics with reactive dyes, where samples acquire soft handle, K/S and overall fastness properties were obtained, nearly equal to those printed using sodium alginate. These composites are compatible with sodium alginate and their mixture at a ratio of 1:1 (wt/wt), improving the K/S than that of pure sodium alginate.

Introduction

Galactomannan gum is a rigid, non-ionic, neutral carbohydrate polymer. It is one of the few carbohydrate natural polymers which have been used extensively in industry^(1, 2). It has been used in industries such as mining⁽³⁾, food⁽⁴⁾ pharmaceuticals⁽⁵⁾, and paper⁽⁶⁾, etc. However, it has been reported that galactomannan especially that of Guar gum suffers from biodegradability, which limits its application. But this drawback can be improved through grafting of synthetic polymer viz. grafting of poly acrylamide onto guar galactomannan gum which gives stability towards biodegradation⁽⁷⁾ and drag – reducing properties can also be enhanced⁽⁸⁾. Acrylic acid, which is vinyl monomer, possesses some unique characteristics and the polymer derived from it finds commercial applications^(2, 9).

Furthermore grafting of acrylic acid onto different types of natural polymers is reported to have wide range of application in various fields^(10, 11, and 12).

In our laboratory, polyacrylic acid – galactomannan gum was prepared by polymerization of acrylic acid on Leucaena gum and / or Gleditsia triacanthos galactomannan gums using potassium persulphate as initiator. The products were used successfully as thickener in printing cotton fabrics with reactive dyes.

In the present work galactomannan gum was isolated from the seeds of *Sesbania*. The gum obtained was subjected to polymerization using methacrylic acid monomers. The rheological properties as well as the suitability of the obtained products, as thickener in printing cotton fabric with reactive dyes were thoroughly investigated.

Experimental

Substrate

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

Materials

Plant seeds

Sesbania seeds were supplied from Faculty of agriculture, Menoufia University, Egypt.

Thickening agents

Sodium alginate of high viscosity type manufactured by Ceca Kolloid Chemie, Paris, France, was kindly supplied under the commercial name Cecalginat HV/KL 600.

Reactive dye:

Cibacron Blue 3 R Supplied by Ciba Speciality Chemicals, Cairo. The reactive moiety is monochlorotriazine.

Chemicals:

Methacrylic acid, sodium hydroxide, potassium persulphate, hydroquinone, urea, sodium bicarbonate, were of laboratory grade chemicals.

Methods:

The experimental methods used for the separation of galactomannan gum from the *Sesbania* seeds, along with its chemical modification via grafting as well as the method used for its application as thickening agent in textile printing are briefly described below:

Separation of the gum from the seeds⁽¹³⁾:

To separate the endosperm, the seeds were soaked overnight in water so that they become swollen, and then blended thoroughly using a warring blender to form slurry. The slurry was washed on a sieve (1mm) under tap so that all the cotyledon

portions were washed away through the sieve. The seed coat and endosperm fractions remaining on the sieve were collected in a beaker and a boiling 2M KOH solution was added. The contents were stirred thoroughly for 30 sec. and immediately washed thoroughly for 10 min. on a sieve using forced water jet to remove the seed coats and KOH. The endosperm was then soaked in 80% ethanol on a flat glass plate and any remaining seed coat or cotyledon particles were separated by hand. The separated endosperm was again thoroughly blended with water and the blend was neutralized using acetic acid. The endosperm from the blend was precipitated by addition 80% ethanol, Washed with tap water, dried and ground into powder.

Polymerization procedure:

The polymerization of methacrylic acid monomers onto Sesbania galactomannan gum was conducted as follows ⁽¹⁴⁾:

42g of the dry gum powder was added to potassium persulphate solution (10g dissolved in 1200 ml distilled water) and mixed well. After complete dissolution of the gum, the mixture is divided into 3 parts and the temperature was adjusted at 65°C .Different amounts of methacrylic acid (100, 125 and 150 ml) were added gradually with continuous agitation .The polymerization reaction was kept at 65°C for 30 minutes. At this end, the polymerization was terminated by addition of 1 ml of 1% aqueous hydroquinone.

The rheological properties of the obtained composites were thoroughly measured after neutralization, and the neutralized composite samples were evaluated as thickener in printing cotton fabrics with reactive dye.

Preparation of printing paste:

The printing paste was prepared according to the following recipe:

Reactive dye	40g
Urea	100g
Thickener*	X
Sodium bicarbonate	30g
Resist salt (Iyoprint)	10g
Distilled water	Y
<hr/>	
Total	1000g

The thickener* used were either sodium alginate (50g / Kg. printing paste) or Sesbania gum (400g / Kg. printing paste) , neutralized poly methacrylic acid /

galactomannan gum composites, which were prepared using 100,125,150 ml methacrylic acid .

Printing technique

All the printing pastes were applied to cotton fabric according to the conventional screen printing technique.

Fixation

All the printed goods were subjected to fixation via either:

- Steaming at 102°C for 10 minutes
- Thermofixation at 150°C for 5 minutes.

Washing

After fixation the printed goods were subjected to washing, which 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 solution containing 2g/L Hostapal CV.ET (non – ionic detergent).
- 4- Washing with hot water.
- 5-Rinsing with cold water.

Finally the samples were air dried and assessed for colour strength and overall fastness properties.

Analysis and Measurements:

Measurement of the rheological properties

The reological properties of the printing pastes were measured using a Rheomat-15 at 25°C. ⁽¹⁵⁾ and the apparent viscosity (η) at various rates of shear was calculated from the shearing stress (τ) and rates of shear (D) as follows:

$$\eta = \frac{\tau}{D} \quad (1)$$

Colour strength measurements

The colour strength of the printed samples expressed as K/S was evaluated by high reflectance technique ⁽¹⁶⁾.

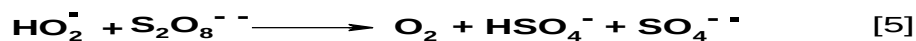
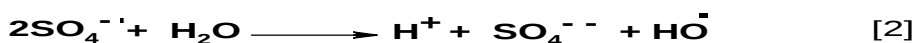
Fastness properties

The colour fastness properties to washing ⁽¹⁷⁾ to rubbing ⁽¹⁸⁾ and to perspiration ⁽¹⁹⁾ were carried out according to standard methods.

Results and Discussion

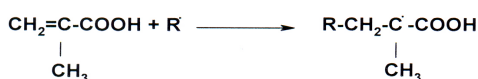
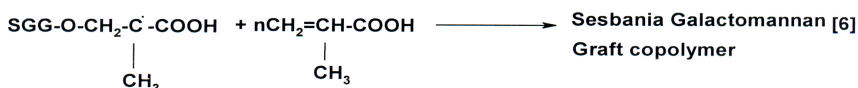
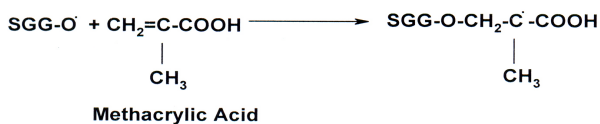
In the present work galactomannan gum was isolated from the seeds of Sesbania according to the procedure described in the experimental section. The Sesbania gum obtained was polymerized with methacrylic acid monomers under the initiation action of potassium persulphate.

Previous reports ^(20, 21) have shown that when an aqueous solution of potassium persulphate is heated, it decomposes to produce sulphate ion radicals along with other radical species as shown in the reactions suggested by equations 1-5.



Vinyl polymerization may be initiated by either ($\text{SO}_4^{\cdot -}$) or HO^{\cdot} radicals. In presence of galactomannan Sesbania gum these free radicals may also attack the galactomannan macromolecules by there producing galactomannan macro- radicals capable of initiating grafting. Thus beside the homopolymerization of methacrylic acid, grafting of methacrylic acid monomers on galactomannan may take place during polymerization of methacrylic acid. Oxidation of the gum under the influence of potassium per sulphate may also take place.

That is, the ultimate result of polymerization of Sesbania galactomannan gum with methacrylic acid monomers in presence of potassium persulphate as initiator is a composite consist of a mixture of galactomannan ,oxidized galactomannan, grafted galactomannan and homomethacrylic acid .To grafting, polymerization and oxidation reactions can be represented as follows:



R = Free Radical



It is anticipated that the properties of the obtained composite would rely on the concentration of monomers, i.e. methacrylic acid. Hence three different poly-methacrylic acid / Sesbania gum composite samples were prepared via changing the amount of methacrylic acid monomers as previously mentioned in the experimental section.

Rheological properties:

The rheological properties of the three composite samples prepared using different amounts of methacrylic acid viz. 100, 125 and 150ml methacrylic acid monomer/400g of 2% gum solution before and after storing for 3 and 7 days are represented in figures (1-3) respectively.

It is clear from figures (1-3) that, irrespective of the concentration of methacrylic acid used and / or the time elapsed before commence measuring, the relation between the shearing stress and rate of shear is not linear indicating that these pastes are non-Newtonian. Beside that, it is 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 pastes determined with a smaller force and a slower rate of shear.

Furthermore, it is clear from the rheograms that as the concentration of acrylic 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 methacrylic acid monomer on the apparent viscosity of the obtained composite samples at various rates of shear is shown in tables (I-III).

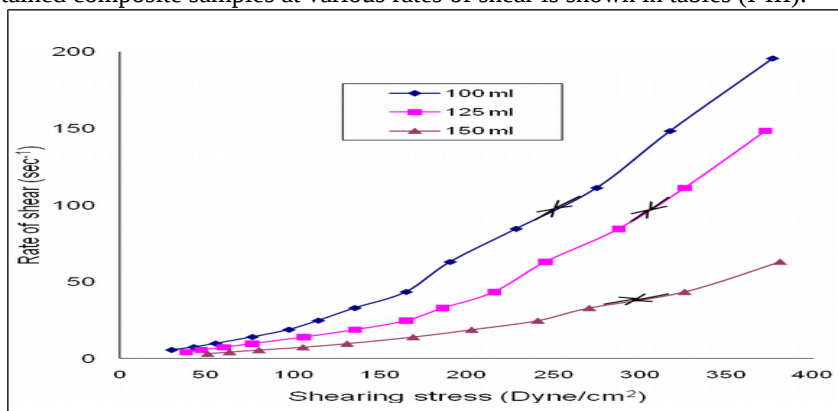


Fig. 1: Rheograms of Sesbania galactomannan gum polymethacrylic acid composites freshly prepared using different amounts of methacrylic acid

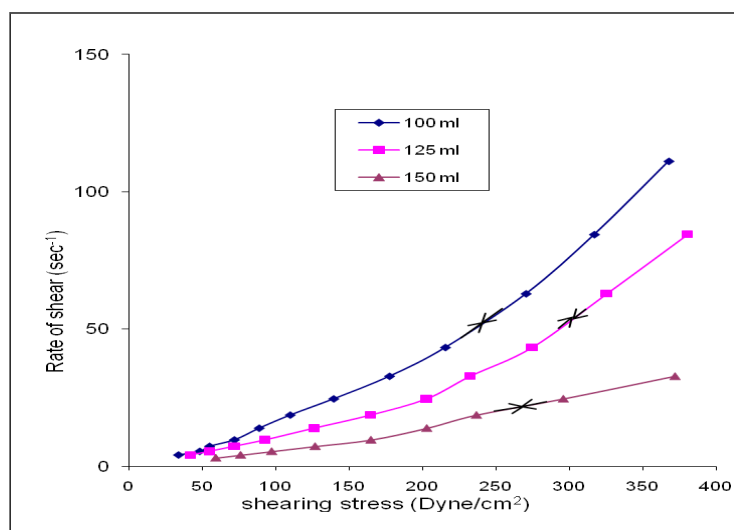


Fig. 2: Rheograms of Sesbania galactomannan gum polymethacrylic acid composites .freshly prepared using different amounts of methacrylic acid after storing for 3 days

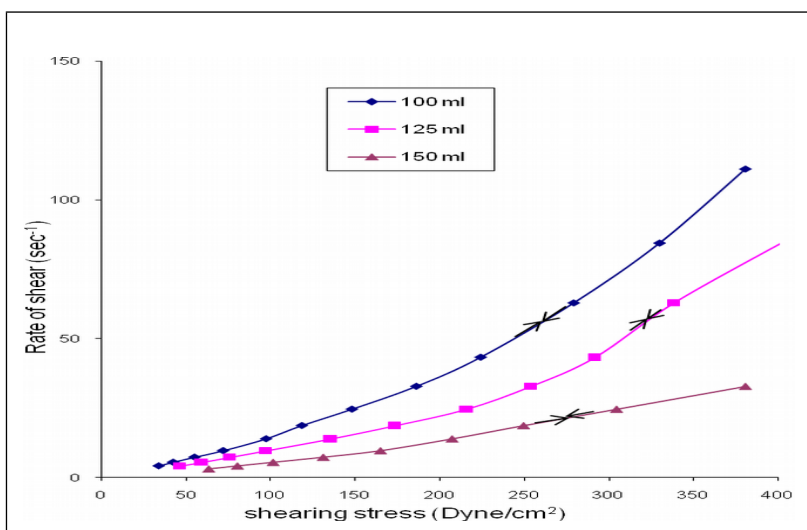


Fig. 3: Rheograms of Sesbania galactomannan gum polymethacrylic acid composites .freshly prepared using different amounts of methacrylic acid after storing for 7 days

Table I: Effect of concentration of methacrylic acid on the apparent viscosity of freshly prepared polymethacrylic acid / Sesbania gum composite.

Rate of shear (sec.-1)	Apparent viscosity in poise		
	on using 100 ml methacrylic	on using 125 ml methacrylic	on using 150 ml methacrylic
3.111	-	-	16.312
4.177	-	9.112	15.186
5.495	5.387	8.465	14.622
7.333	5.767	8.073	14.417
9.573	5.683	7.869	13.553
13.94	5.460	7.584	12.134
18.72	4.969	7.229	10.84
24.63	4.635	6.696	9.786
32.80	4.118	5.662	8.236
43.35	3.804	4.975	7.511
62.30	3.024	3.897	6.048
84.50	2.702	3.403	-
111.2	2.971	2.928	-

148.30	2.138	2.509	-
195.70	1.923	-	-

Apparent Viscosity:

It is clear from the data of Table (I) that as the amount of methacrylic increases the apparent viscosity at any specific rate of shear increases too. For example at a rate of shear of 9.573 sec^{-1} the apparent viscosity increases from 5.683 to 7.869 to 13.553 by increasing the amount of methacrylic monomer from 100 to 125 to 150 ml / 400 g of 2% Sesbania gum solution. The increase in the apparent viscosity may be due to the increase in the molecular weight of the obtained composite as the amount of the added monomer increases.

Table II: Effect of concentration of methacrylic acid on the apparent viscosity of the obtained polymethacrylic acid / Sesbania gum after storing for 3 days.

Rate of shear (sec.-1)	Apparent viscosity in poise		
	on using 100 ml methacrylic	on using 125 ml methacrylic	on using 150 ml methacrylic
3.111	-	-	19.031
4.177	8.099	10.124	18.224
5.495	7.696	10.004	17.701
7.333	7.497	9.804	17.301
9.573	7.432	9.618	17.050
13.94	6.370	9.072	14.561
18.72	5.873	8.810	12.650
24.63	5.666	8.241	12.019
32.80	5.405	7.078	11.325
43.35	4.975	6.341	-
62.30	4.300	5.174	-
84.50	3.753	4.504	-
111.2	3.308	-	-

Table III: Effect of the amount of methacrylic acid on the apparent viscosity of the obtained polymethacrylic acid / Sesbania gum after storing 7 days.

Rate of shear (sec ⁻¹)	Apparent viscosity in poise		
	methacrylic	methacrylic	methacrylic
3.111	-	-	20.390
4.177	8.099	11.136	19.236
5.495	7.696	10.774	18.470
7.333	7.497	10.380	17.877
9.573	7.432	10.055	17.050
13.94	6.977	9.707	14.862
18.72	6.325	9.262	13.328
24.63	6.00	8.756	12.362
32.80	5.662	7.721	11.582
43.35	5.170	6.731	-
62.30	4.435	5.376	-
84.50	3.903	4.754	-
111.2	3.422	-	-

It is worthily to mention that storing of the pastes for 3 and 7 dyes (as it is clear on comparing Tables I with tables II and III) causes an increase in the apparent viscosity of the composite pastes. The increase in the viscosity may be due to one or more of the following:

- 1- An increase in the molecular weight of grafted and polymerized methacrylic acid due to delayed polymerization.
- 2- Formation of cross links between different galactomannan grafted substrates as a result of mutual termination of residual free radicals on different growing polymer chains.
- 3- Formation of additional hydrogen bonds between different molecular chains of the gum constituents.

Printing:

As previously mentioned , in the experimental section , the main aim of the present work was to investigate the suitability of the sodium salt of polymethacrylic acid / galactomannan gum (derived from Sesbania seeds) composites prepared using 100, 125 , or 150 ml methacrylic acid / 400ml of 2 % native gum solution as thickener in printing cotton fabrics with reactive dyes.

Tables IV, V, and VI represent the data of K/S and overall fastness properties obtained on using the aforementioned three composite samples as well as sodium alginate for the freshly prepared pastes and after storing for 3 or 7 days.

It is clear from tables (IV-VI) that the K/S depends on both of the nature of thickening agent and on the time elapsed before commencing printing.

It is clear from the data of Table (IV) that the K/S of the samples printed using polymethacrylic acid / Sesbania seeds gum composites is nearly equal to their corresponding samples printed using sodium alginate. For example the sample printed using composite III acquire K/S of 6.39 against 6.50 for the sample printed using sodium alginate. It is also clear from the data of Table (IV) that the K/S increases regularly as the amount of methacrylic acid in the composite increases. This phenomenon holds true before and after storing of their pastes for 3 or 7 days before commence printing, as it is clear from Tables IV-VI. An example for the sample stored for 7 dyes the K/S increases from 5.79 to 6.08 to 6.50 as the amount of methacrylic acid increases from 100 to 125 to 150 ml respectively.

The increase in the K/S by increasing the amount of methacrylic acid is expected. Since as the amount of the latter increases the number of the carboxylic groups in the obtained composite increases. Increasing, the number of $-\text{COONa}$ in the composite increases the negative charge of the composite. Hence, the composite carry carboxyl groups grater which cannot react with reactive dye and plays dominant role in repelling the similarly charged reactive dye ions; these results is in full conformation with previous reports which stated that poly acrylic acid doesn't react at all with typical reactive dye and the colour yield is higher.

Besides, from the results of Tables (IV-VI) , it clear that all the samples printed using the three composites before and after storing acquire soft handle . Similar to their corresponding sample printed using sodium alginate . This reflects the ease of removal of polymethacrylic acid / Sesbania seeds gum composite by washing. It can be concluded, that polymerization of methacrylic acid on native glactomannan gum (extracted from Sesbania seeds) convert the gum into a thickening agent capable of swelling, dispersing and jumping in aqueous medium without complete elimination of inter molecular forces between themselves and water .At the same time, the composite carry carboxyl groups which cannot react with the reactive dyes and plays a dominant role in repelling the similarly charged reactive dye ions.

Table (IV-VI) 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 methacrylic acid / *Sesbania* seeds gum composite before and after storing are nearly identical if not higher to their corresponding samples printed using sodium alginate.

Table IV: comparison between the K/S and fastness properties of cotton fabric samples printed with different composite thickeners along with those printed using sodium alginate. Freshly prepared

Thickener used	Fixation system	K/S	Washing fastness		Rubbing fastness		Perspiration fastness				Handle
			St.	Alt.	Dry	Wet	Acidic		Alkali		
							St.	Alt.	St.	Alt.	
Sodium alginate	Steaming	5.98	4	4-5	4	3	4	5	4	5	S
Composite(I)	Steaming	5.70	4	4	4	3-4	4	4	4-5	5	S
Composite (II)	Steaming	5.87	4-5	4	4-5	2-3	4	5	4	4	S
Composite(III)	Steaming	5.89	4	4-5	4	2-3	4	3-4	4	4	S

The reactive dye used was Cibacron Blue 3 R.

St: staining

Alt: alteration

S: soft

Composites I, II and III are the sodium salt of polymethacrylic acid / Sesbania seeds gum composites prepared using 100, 125 and 150 ml methacrylic acid /400g of 2% native gum respectively.

Table V: Comparison between the K/S and fastness properties of cotton fabric samples printed with different composite thickeners along with those printed using sodium alginate. After storing 3 days

Thickener used	Fixation system	K/S	Washing fastness		Rubbing fastness		Perspiration fastness				Handle
			St.	Alt.	Dry	Wet	Acidic		Alkali		
							St.	Alt.	St.	Alt.	
Sodium alginate	Steaming	6.50	4	5	4	3-4	4	4	4	4	S
Composite (I)	Steaming	5.79	3-4	4	5	3	4-5	4	4-5	4	S
Composite (II)	Steaming	6.18	4	4	4	3	4	4	4	4-5	S
Composite (III)	Steaming	6.39	4-5	4	4	3-4	4-5	4	4	4-5	S

The reactive dye used was Cibacron Blue 3 R.

St: staining Alt: alteration S: soft

Composites I, II and III are the sodium salt of polymethacrylic acid / Sesbania seeds gum composites prepared using 100, 125 and 150 ml methacrylic acid /400g of 2% native gum respectively.

Table VI: Comparison between the K/S and fastness properties of cotton fabric samples printed with different composite thickeners along with those printed using sodium alginate. After storing 7 days

Thickener used	Fixation system	K/S	Washing fastness		Rubbing fastness		Perspiration fastness				Handle
			St.	Alt.	Dry	Wet	Acidic		Alkali		
							St.	Alt.	St.	Alt.	
Sodium alginate	Steaming	6.61	4	5	5	3-4	4	5	4	4	S
Composite (I)	Steaming	5.79	4-5	4	4	3	4	4	3-4	4	S
Composite (II)	Steaming	6.08	3-4	4	4	2-3	3-4	4	5	4	S
Composite (III)	Steaming	6.50	3-4	4	4	2-3	3-4	4	5	4	S

The reactive dye used was Cibacron Blue 3 R.

St: staining Alt: alteration S: soft

Composites I, II and III are the sodium salt of polymethacrylic acid / Sesbania seeds gum composites prepared using 100, 125 and 150 ml methacrylic acid /400g of 2% native gum respectively.

Table VII: Effect of mixing sodium alginate with poly methacrylic acid/Sesbania galactomannan gum composite. (1:1), freshly prepared.

Thickener used	Fixation system	K/S	Washing fastness		Rubbing fastness		Perspiration fastness				Handle
			St.	Alt.	Dry	Wet	Acidic		Alkali		
							St.	Alt.	St.	Alt.	
Sodium alginate / Composite I mixture (1: 1)	Steaming	5.89	4	4	4-5	4	4	5	4	5	S
Sodium alginate / Composite II mixture (1: 1)	Steaming	6.28	5	3-4	4	3	5	5	3-4	4	S
Sodium alginate / Composite III mixture (1: 1)	Steaming	6.39	4	4	4	3	4	4	5	4	S

The reactive dye used was Cibacron Blue 3 R.

St: staining Alt: alteration S: soft.

Composites I, II and III are the sodium salt of polymethacrylic acid / Sesbania seeds gum composites prepared using 100, 125 and 150 ml methacrylic acid /400g of 2% native gum.

Table VIII: Effect of mixing sodium alginate with composite poly methacrylic acid/ Sesbania galactomannan gum composite (1:1), after storing for 3 days.

Thickener used	Fixation system	K/S	Washing fastness		Rubbing fastness		Perspiration fastness				Handle	
			St.	Alt.	Dry	Wet	Acidic		Alkali			
							St.	Alt.	St.	Alt.		
Sodium alginate / Composite I mixture (1: 1)	Steaming	6.18	5	4	4-5	4	4	4	4	3-4	5	S
Sodium alginate / Composite II mixture (1: 1)	Steaming	6.50	5	4	3	2-3	4	5	3-4	5	S	S
Sodium alginate / Composite III mixture (1: 1)	Steaming	6.97	4	5	4	3	5	4	4	4	5	S

The reactive dye used was Cibacron Blue 3 R.

St: staining

Alt: alteration

S: soft

Composites I, II and III are the sodium salt of polymethacrylic acid / Sesbania seeds gum composites prepared using 100, 125 and 150 ml methacrylic acid /400g of 2% native gum.

Table IX: Effect of mixing sodium alginate with poly methacrylic acid/ Sesbania galactomannan gum composite (1:1), after storing for 7 days.

Thickener used	Fixation system	K/S	Washing fastness		Rubbing fastness		Perspiration fastness				Handle	
			St.	Alt.	Dry	Wet	Acidic		Alkali			
							St.	Alt.	St.	Alt.		
Sodium alginate / Composite I mixture (1: 1)	Steaming	6.28	4	5	5	4	5	5	4	4	4	S
Sodium alginate / Composite II mixture (1: 1)	Steaming	6.39	5	4	3	2-3	4	4	5	4	4	S
Sodium alginate / Composite III mixture (1: 1)	Steaming	7.10	4	5	4	2-3	4	4	4	4	5	S

The reactive dye used was Cibacron Blue 3 R.

St: staining

Alt: alteration

S: soft

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Composites I, II and III are the sodium salt of polymethacrylic acid / Sesbania seeds gum composites prepared using 100, 125 and 150 ml methacrylic acid /400g of 2% native gum.

Conclusion

It can be concluded that polymethacrylic acid / Sesbania seeds gum composites could be used as a substitute for sodium alginate in printing cotton fabrics with reactive dyes .The samples acquire soft handle, K/S and overall fastness properties nearly equal to those printed using sodium alginate.

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