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Technological Evaluation of Acrylic Acid /Cassia Saligna Gum Grafted Products as Thickener in Textile Printing

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GALACTOMANNAN gum extracted from Cassia Saligna seeds was subjected to graft copolymerization using acrylic acid. The graft copolymerization has been performed using potassium persulphate as initiator. The rheological property of the grafted product and it is utilization as a thickening agent in printing cotton fabrics with reactive dyes was thoroughly investigated. The rheological properties and the viscosity at various rates of shear were investigated. Furthermore, the results obtained indicate that grafted product gum could be used safely as a thickener in printing of cotton fabric, using silk screen printing instead of the commercial thickener of sodium alginate.

Keywords: Acrylic Acid, Cassia Saligna, Gum, Grafted products, Thickener, Textile Printing.

Introduction

The most potentially important plant seeds which contain galactomannan gum in their endosperm comprises: Guar[1], Cassia [2], Leucaena [3], Gleditisiatriacnthes [4] Fenugreek seeds [5], fenugreek seed is composed of repeating units of mannose and galactose [6], i.e. galactomannan. The ratio of D-galactose D-mannose in fenugreek (Trigonellafoenum-graecum) is 48: 52 [7] and Cassia Saligna. In the earlier work the gum was isolated from the seeds. Since the gum was not completely soluble in cold water, and its solution undergoes fermentation on storing, it was subjected to chemical modification viacarbamoylethylation [8], Cyanoethylation [9] to render it soluble in cold water; increase their stability for storing and to be used as a substitute for sodium alginate. In the present work, the graft polymerization of acrylic acid monomers on galactomannan gum extracted from Cassia Saligna seeds using potassium persulphate as initiator was thoroughly investigated. The rheological properties and the suitability of the product as a thickening agent in printing cotton fabrics with reactive dyes was also studied.

Materials and Methods

Materials

Cassia Saligna seed

Clean, dry cassia saligna (Acacia saligna) seeds were kindly cultivate in Egypt.

Fabrics

Mill scoured, bleached and mercerized plain weave cotton fabric (135 g/m2) kindly supplied by Miser Co., El-Mahalla Elcobra.

Thickener

Commercial sodium alginate of high viscosity type manufactured by Coca colloid Chemie, Paris, and France.

Graft copolymerization of Acrylic Acid / Cassia Saligna Gum.

Dyestuff

Tulactive Blue P3R, Reactive dye was kindly supplied by Cognis, Japan.

Chemical

Acrylic acid, potassium persulphate, sodium bicarbonate, urea and ethyl alcohol were laboratory grade chemicals.

Methods

Separation of the gum from the seeds

For the separation of the galactomannan gum from cassia saligna seeds the seeds were crushed mechanically followed by the sieving in order to separate the germ from the other components of the seeds, *i.e*., the husk and endosperm. The husk and endosperm were soaked in cold water overnight to dissolve the gum which is the main constituent of

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the endosperm. The viscous mass was separated from the other in soluble components of the husk and endosperm *via* filtration through a mucline cloth. It was precipitated with ethanol (95%), and dried at room temperature.

Polymerization procedure

The polymerization of acrylic acid monomers onto cassia saligna gum was conducted according to a procedure elsewhere [10, 11]. The procedure was modified and carried out as follows:

20 g of dry cassia saligna gum powder was added to potassium persulphate solution (8 g dissolved in 1000 cm^3 distilled water) and mixed well. After complete swelling of the gum, the temperature was adjusted to 70 ^oC and different amounts of acrylic acid (20, 40, 60, and 80 cm^3) were added gradually with agitation. The polymerization reaction was kept at 70 ^oC for 1 h with continuous stirring. Finally, the reaction was stopped by the addition of a few milligrams of hydroquinone, and the product was neutralized by adding concentrated sodium hydroxide solution using phenolphthalein as indicator.

Preparation of printing pastes

The printing pastes for printing cotton fabrics were prepared according to the following recipe:

Reactive dye	40 g
Thickener*	600 g
Urea	100 g
Sodium bicarbonate	20 g
Ludigol	10 g
Water	X g
Total	1000 g

*The thickener used was either commercial sodium alginate (5%) or Acrylic Acid /Cassia Saligna Gum grafted product.

Printing technique

The pastes were applied to the fabric through a screen printing process. After printing and drying the goods were subjected to thermofixation for fixed the color, which was achieved at 150°C for 2 min for printed cotton fabrics using an automatic thermostatic oven (Wemer Mathis Co., Switzer land). After that the printed goods were subjected to washing according to the recommendation of the reactive dye manufacture.

Testing and Analysis

Rheological properties

The rheological properties and apparent viscosity, were measured according to the procedure reported elsewhere [12]. Using a Brookfield Model DV-111, Programm ablerheometer, (USA). The experimental conditions use: rate of shear range between 1.7–34 S^{-1}, the temperature 25°C. The viscosity was calculated from equation (1):

$$\eta = \tau/D \quad (1)$$

Where: -η = apparent viscosity [poise].

τ= shearing stress [dyne/cm^2].

D = rate of shear [S^{-1}]

Color measurements

Color strength expressed as K/S was measured according to a previously reported method [13] by the light reflectance technique. The relative color strength was

calculated from the Kubelka-Munk equation(2).

$$\text{Color strength (K/S)} = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0} \quad (2)$$

where R and R° are the decimal fractions of the reflectance of the colored and uncolored fabrics respectively.

K: is the absorption coefficient and S: is the scattering coefficient.

Fastness properties

Fastness properties to washing, rubbing and perspiration were measured according to the standard method [14].

Results and Discussion

Preparation of poly acrylic acid/ cassia saligna gum grafted product

Cassia saligna gum (galactomannan gum) was isolated from cassia saligna seeds according to the aforementioned procedure. The obtained gum was subjected to the reaction with acrylic acid in the presence of potassium persulphate as initiator. Previous reports [15,16] have shown that grafting was initiated by the thermal decomposition of the persulphate groups to produce sulphate ion radicals along with their radical species. The radicals formed in this way were used as initiators for grafting the cassia saligna gum. The mechanism of the free radical generating reaction is shown by equations 1-5.

$$S_2O_8^{--} \rightarrow 2\,SO_4^{-\cdot} \quad (1)$$

$$SO_4^{-\cdot} + H_2O \rightarrow H^+ + SO_4^{--} + HO^{\cdot} \quad (2)$$

$$2\,HO^{\cdot} \rightarrow H_2O_2 \rightarrow H_2O + 1/2O_2 \quad (3)$$

$$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \quad (4)$$

$$HO_2^{\cdot} + S_2O_8^{--} \rightarrow O_2 + HSO_4^{-} + SO_4^{-\cdot} \quad (5)$$

Thus, vinyl polymerization can either be initiated by the $SO_4^{-\cdot}$ or by $HO^{\cdot}$ Radicals. In the presence of Cassia saligna gum (galactomannan), these free radicals can attack the galactomannan hydroxyls via hydrogen abstraction, thereby giving rise to galactomannan macro radicals capable of initiating grafting. Thus besides the normal polymerization of acrylic acid, grafting of this monomer on galactomannan can take place. It is also possible that the persulphate oxidises the galactomannan in the polymerization system. Thus, the ultimate product of the reaction is a mixture of galactomannan, oxidized galactomannan, grafts galactomannan and homo polyacrylic acid.

The grafting polymerization and oxidation reactions are shown below:

$$CSG\text{-}OH + HO^{\cdot} \rightarrow CSG\text{-}O^{\cdot} + H_2O$$

where CSG = Cassia Saligna (galactomannan) Gum

$$CSG\text{-}O^{\cdot} + CH_2 = CHCOOH \rightarrow CSG\text{-}O\text{-}CH_2\text{-}^{\cdot}CH\text{-}COOH$$

$$CSG\text{-}O\text{-}CH_2\text{-}^{\cdot}CH\text{-}COOH + n\,CH_2 = CHCOOH \rightarrow \text{cassia saligna}$$

saligna galactomannan grafted copolymer. (6)

$$CH_2 = CHCOOH + R^{\cdot} \rightarrow R\text{-}CH_2\text{-}^{\cdot}CH\text{-}COOH \quad (R^{\cdot} = \text{Free radical})$$

$$R\text{-}CH_2\text{-}^{\cdot}CH\text{-}COOH + CH_2 = CHCOOH \rightarrow \text{Poly acrylic acid (Homo polymer)} \quad (7)$$

$$R^{\cdot} + H_2O \rightarrow RH + HO^{\cdot} \quad (8)$$

$$CSG\text{-}O^{\cdot} + HO^{\cdot} \rightarrow CSG\text{-}O\text{-}OH \quad \text{Oxidized galactomannan gum} \quad (9)$$

Four different acrylic acid/ cassia saligna gum samples were prepared by changing the amount of acrylic acid monomer (20, 40, 60, and 80 cm^3/ 20 g cassia saligna gum). The rheological properties were measured at 25 ^0C, and the aforementioned acrylic acid/ cassia saligna gum was measured according to the method mentioned in the experimental section,t he rheological data are given in Table 1. From Table 1 we noticed that, as the rate of shear increases the rheological properties increases this is true irrespective of the concentration of acrylic acid used. Also, at the

TABLE 1. Effect of the concentration of acrylic acid on the rheological properties of grafted product of cassia saligna gum at various rates of shear.

Rate of shear (Sec^{-1})	Rheological properties on using Acrylic acid concentration/ 20 g cassia saligna gum			
	20 g	**40g**	**60g**	**80g**
1.7	2.55	6.8	46.83	92.7
5.1	4.25	10.2	138.6	167
8.5	9.69	17	207.06	230
10.2	10.57	18.7	213.79	237
15.3	11.2	27.1	227.15	252
18.7	12.2	28.1	235.54	276
22.1	14.2	34.8	247.52	305
25.5	15.1	35.2	251.17	320
28.9	15.2	37.1	255	332
30.6	15.4	40.2	260	336
34	18.4	41.1	265	363

same rate of shear as the concentration of acrylic acid used increases the rheological properties increases.

The effects of the concentration of acrylic acid on the apparent viscosity of grafted product of cassia saligna gum at various rates of shear are shown in Table 2 . It is clear from the data in Table 2 that, the apparent viscosity of all the aforementioned acrylic acid/ cassia saligna pastes decreased with increasing rate of shear. At constant rate of shear, the apparent viscosity increased as the amount of acrylic acid monomer increased, as an example, at rate of shear $5.1S^{-1}$ the apparent viscosities increased from 117 to 3238 centipoise by increasing the amount of acrylic acid monomer from 20 to80cm^3/20 g gum. The increase in the apparent viscosity on increasing the amount of acrylic acid monomer may be due to the formation of long side chains in the copolymer, and / or an increase in the amount of homo polymer.

TABLE 2. Effect of the concentration of acrylic acid on the apparent viscosity ofGrafted product of cassia saligna gum at various rates of shear.

Rate of shear (S^{-1})	Apparent viscosity in cent poise on using			
	Acrylic acid concentration/ 20 g cassia saligna gum			
	20 g	**40g**	**60g**	**80g**
1.7	150	350	2755	5600
5.1	117	220	2718	3238
8.5	107	183	2436	2690
10.2	95	175	2096	2252
15.3	73	145	1484	1775
18.7	61	136	1259	1682
22.1	56	123	1120	1352
25.5	47	117	985	1254
28.9	46	113	882	1165
30.6	43	111	849	1128
34	38	103	779	1058

Utilization of the grafted product in printing cotton with reactive dye

The suitability of poly acrylic acid/ cassia saligna gum grafts as thickening agents in printing cotton fabrics with reactive dyes. For this purpose a series of printing paste was made using Tulactive Blue P3R, and thickened with acrylic acid/ cassia saligna gum graft, prepared using 60 and 80 cm^{3}acrylic acid/ 20 g of cassia saligna gum. For comparison the other printing pastes containing commercial sodium alginate was prepared the printing pastes were used for printing cotton fabric freshly and after storing for seven days. After printing and dried,the cotton samples were thermo fixed at different fixing temperature (140, 160 and 180 °C for 3 min.), the printed goods were assessed for color strength as shown in Fig. 1 and 2 respectively. It is clear from the figures that, the color strength depends on both and either the nature of the thickening agent used or the fixing temperature. The highest color strength was obtained upon using either freshly prepared or storing pastes for seven days and thickened with acrylic acid/ cassia saligna gum grafted product, prepared using 60 cm^3 acrylic acid/ 20 g of cassia saligna gumand fixed at 180 °C for 3 min.

The higher values of K/S obtained upon using either freshly prepared or storing pastes for seven days and thickened with acrylic acid/ cassia saligna gum grafted product, prepared using 60 cm^3 acrylic acid/ 20 g of cassia saligna gumas thickeners than commercial alginates is probably due to that sodium alginate physically its shape is homogenous structure but the acrylic acid/ cassia saligna gum grafted product is heterogeneous in its structure [9].

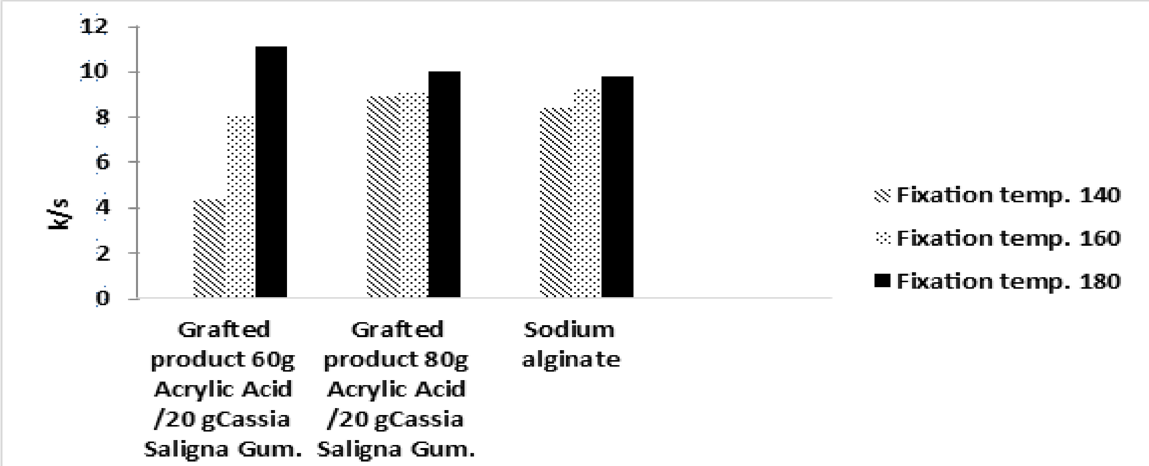

Fig.1.Color strength of printed cotton fabrics with Tulactive Blue P3R using prepared acrylic acid/cassia saligna gum and commercial sodium alginate as thickeners, freshly prepared paste, at different fixation temperature.

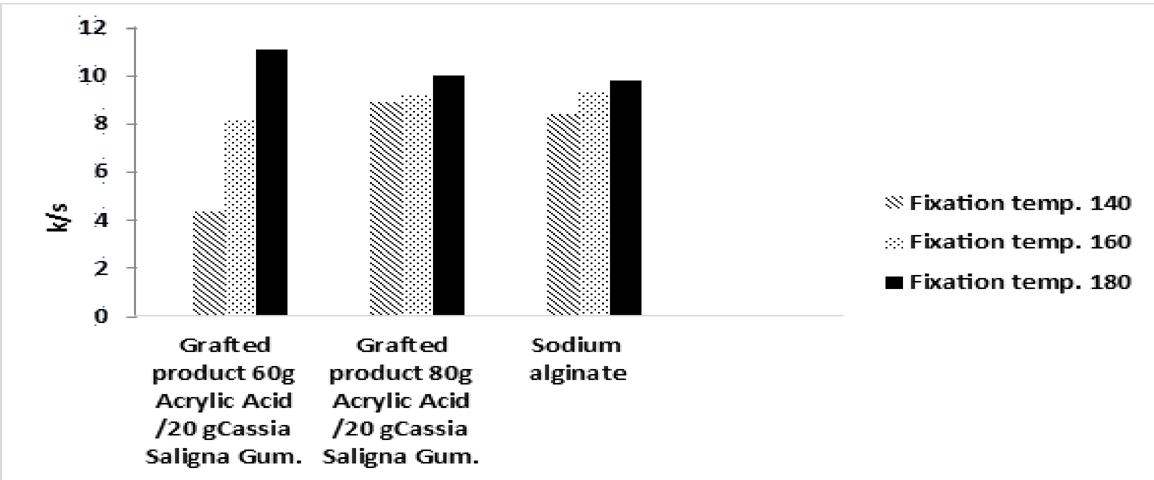

Fig. 2. Color strength of printed cotton fabrics with Tulactive Blue P3R using prepared acrylic acid/cassia saligna gum and commercial sodium alginate as thickeners, and the printing paste stored for 7 days at different fixation temperature.

The overall fastness properties

Tables 3 and 4 show results of the overall fastness properties of cotton sample, printed using either a sodium alginate, and/or prepared acrylic acid/cassia saligna gum before and after storing for seven days respectively. It is clear from the Tables 3 and 4 that, the rubbing fastness which an important property in the field of textile printing for the color to wet and dry of cotton fabric samples printed with the aforementioned printing pastes, that the samples printed using the acrylic acid/ cassia saligna gum grafted sample is nearly equal to their corresponding samples printed using commercial sodium alginate and their values ranging from very good to excellent.

The washing fastness properties of printed cotton samples, as shown from the data Tables 3 and 4 that, the fastness properties to washing are nearly comparable, and range from very good to excellent in case of staining and excellent in case of alteration. This statement holds true for all the aforementioned series of thickener used.

Acidic and alkaline perspiration for the goods is nearly equal to their corresponding samples printed using commercialalginate. Generally, the values of the color fastness to perspiration is ranging from very good to excellent in both cases i.e. for acidic and alkaline perspiration.

TABLE 3. Color strength and overall fastness properties of printed* cotton fabrics with Tulactive Blue P3R using prepared acrylic acid/cassia saligna gum and commercial sodium alginate as a thickener, freshly prepared pastes.

Thickener used	Fixation Temp.	K/S	Fastness to rubbing		Wash fastness Alkaline			Fastness to Perspiration					
								Acidic					
			Dry	Wet	Alt	SC	SW	Alt	SC	SW	Alt	SC	SW
Grafted product prepared using 60 cm^3 /20 gcassia saligna gum.	140°C	4.12	4-5	4	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5
	160°C	7.2	4-5	4	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5
	180°C	10	4-5	4	5	5	5	5	5	5	5	5	5
Grafted product prepared using 80 cm^3 /20 gcassia saligna gum	140°C	7.13	4-5	4	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5
	160°C	10.03	4-5	4	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5
	180°C	9.1	4-5	4	5	5	5	5	5	5	5	5	5
sodium alginate	140°C	3.43	4-5	4	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5
	160°C	9.5	4-5	4	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5
	180°C	9.33	4-5	4	5	5	5	5	5	5	5	5	5

* The washing fastness at 95°C. Thermo fixation for 3 min.
.Alt: Color change of dyed sample; SC: staining on cotton; SW: staining on wool.

TABLE 4. Color strength and overall fastness properties of printed* cotton fabrics with Tulactive Blue P3R using prepared acrylic acid/cassia saligna gum and commercial sodium alginate as a thickener, stored for seven days.

Thickener used	Fixation Temp.	K/S	Fastness to rubbing		Wash fastness Alkaline			Fastness to Perspiration					
								Acidic					
			Dry	Wet	Alt	SC	SW	Alt	SC	SW	Alt	SC	SW
Grafted product prepared using 60 cm^3 /20 gcassia saligna gum.	140°C	4.39	4-5	4	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5
	160°C	8.14	4-5	4	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5
	180°C	11.1	4-5	4	5	5	5	5	5	5	5	5	5
Grafted product prepared using 80 cm^3 /20 gcassia saligna gum	140°C	7.33	4-5	4	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5
	160°C	9.16	4-5	4	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5
	180°C	10	4-5	4	5	5	5	5	5	5	5	5	5
sodium alginate	140°C	4.43	4-5	4	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5
	160°C	9.28	4-5	4	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5
	180°C	9.79	4-5	4	5	5	5	5	5	5	5	5	5

** The washing fastness at 95°C. Thermo fixation for 3 min .

Alt: Color change of dyed sample; SC: staining on cotton; SW: staining on wool.

It is also clear from the data (Table 4) the storing of the printing pastes for seven days that, in all cases the K/S values are accompanied by a slight increase or slight decrease; this may be due to the increase in the swellability of the thickening agents used which lead to homogeneity of the printing pastes. While the decrease in K/S upon storing of the printing pastes containing reactive dyes may be due to the hydrolysis of reactive dyes under the action of the alkali present in the printing paste. The overall fatness property for freshly or storing paste for seven days are the same.

Conclusion

It can be concluded that poly acrylic acid/ cassia saligna gum grafted product prepared from galactomannan gum extracted from cassia saligna seed using 60 and 80 cm^3 acrylic acid/ 20 g of cassia saligna gum, could be used safely as thickener in printing cotton fabrics with reactive dyes. The color strength values as well as the color fastness properties to rubbing, washing and perspiration for the goods printed using this prepared thickener is either higher or equal to corresponding samples printed using commercial sodium alginate.

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التقييم التكنولوجي لصمغ الكاسيا سليجنا المطعم بحمض الاكريليك واستخدامه كمثخن في طباعة المنسوجات

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تم استخدام صمغ الجلاكتومنان المستخرج من بذور نبات الكاسيا ساليجنا وتطعيمه باستخدام حمض الأكريليك. وقد تمت عمليه البلمرة باستخدام بيرسلفات البوتاسيوم كبادئ للتفاعل فى عمليه البلمرة و استخدام تركيزات مختلفه من حمض الاكريلك. وقد تم التحقيق من المثخن المطعم بقياس الخواص الريولوجية واستخدامه كمثخن في طباعة الأقمشة القطنية باستخدام الصبغات النشطه. تم دراسة الخصائص الريولوجية واللزوجة عند معدلات القص المختلفة. ودراسه خواص الثبات المختلفه للاقمشه المطبوعه وتشير النتائج التي تم الحصول عليها أن االصمغ المستخلص من بذور نبات الكاسيا ساليجنا و المطعم باستخدام حمض الأكريليك. يمكن استخدامه بأمان كمثخن في طباعة الاقمشه القطنيه، وذلك باستخدام الطباعة بطريقه الشابلونة الحريرية كبديل عن المثخن التجاري الجينات الصوديوم المستورد.