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Microstructural Features of Galactomannan Fenugreek Gum Newly Oxidized by Sodium Perborate under Microwave Irradiation for Reactive Printing

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GALACTOMANNAN gum was extracted from fenugreek seeds through seed grinding and sifting, washing and filtering and precipitating by ethyl alcohol and drying. Thus obtained products were submitted to innovative oxidation using microwave irradiation and sodium perborate (SPB) oxidant under a variety of conditions. Variable studied include concentration of SPB and duration of oxidation as well as pH and temperature of the oxidation reaction. Thus oxidized gum samples were subjected to chemical and chemical-microscopically analysis for quantitative determination of carboxyl and carbonyl groups and rheological properties along wilts residual SPB. Microstructural changes in the innovatively oxidized gum vis-à-vis those of conventionally oxidized gum were presented. Results indicate that the innovative oxidation using the microwave for heating the oxidation medium containing SPB consumes less time and energy than the conventional oxidation by SPB using conventional heating. Results indicate further that current oxidation using the microwave or conventional heating brings into focus oxidized galactomannan gums, which induce excellent overall color fastness when applied as thickeners in printing pastes of reactive dyes. These gums may be considered as a real substitute for sodium alginate thickener which is universally accepted thickeners for reactive printing on cotton. In addition, oxidized galactomannan gum creates eco- friendly environment during its preparation.

Keywords: Textile Printing, Color, Dyeing, Chemical modification, Properties.

Introduction

Fenugreek is a leguminous herb cultivated in many countries. Egypt, Iran, France, Turkey, Spain Afghanistan, India and North African countries. India and North Africa are the largest producing countries [1]. It has been reported that each 100 g of fenugreek leaves contains 89% H_2O, 6% carbohydrates, 40% Calcium, 4% protein and less than 1% fat; all of them provide 210 kilojoules ≈49 kcal. It belongs to the Fabaceae family, Binomial name is known as Trigonella foenum-graecum and its scientific classification is shown in Table 1 [2]:

Polysaccharide gums are regarded as one of the most plentiful raw materials. Polysaccharide gums possess many advantages which attract the interest of researchers [3,4]. It is understandable that polysaccharide gums acquire sustainable, biodegradable and bio safe characteristics.

Fenugreek isolated gum is the last addition to the galactomannan fenugreek gums list. It was not used in manufacture until 1990 after that fenugreek acquired the double use by removing the spice and other components and isolating the galactomannan which is also known as fenugreek gum. Now, fenugreek gum display high demand as being of many applications in manufactures. The fenugreek gum is flavorless and scentless. It consists of galactomannan which is a polysaccharide made of galactose incorporated

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TABLE 1. Scientific classification of Fenugreek gum

Kingdom	Plantae
Clade	Angiosperms
Clade	Eudicots
Clade	Rosids
Order	Fabales
Family	Fabaceae
Genus	Trigonella

with mannan. Galactomannan is viscous and it forms gum when dissolved in water [4- 6].

The ratio of galactose to mannose for guar gum 1:2, while this ratio is 1:4 in case of locust bean gum. This is against the ratio 1:1in case of fenugreek. Hence the fenugreek gum powder contains extra galactose, this is why it has excellent solubility and dispersive-ness which leads to form stable colloid for a long period of time. On the other hand, mannan is hydrophobic, it is completely water insoluble. However, the fenugreek gum is the combination of the hydrophilic (galactose) and hydrophobic (mannan), so it has surface active, it means that the fenugreek gum is an emulsifier and it can mix with water as well as oil [6,7].

Time is valuable; this can be said in all daily processes, particularly in the synthetic chemistry field, which consumes a lot of time and energy. Hence, the idea of using microwave irradiation was to see to it as an ecological and economic advance in knowledge technology for chemistry. In the microwave heating, the energy supplied by an electromagnetic field directly to the material leads to rapid heating throughout the material thereby resulting in reducing thermal gradients. The understanding of electromagnetic theory and the dielectric response is major to optimize any material processing through microwave heating. The characteristics of the microwave heating are reducing the reaction time, the energy consumption, and chemical wasting alongside product yields without agglomeration [8-11].

To the author's knowledge, a great deal of research involving microwave in the preparation of binders are published [12-16]. In contrast, no work has been published so far on the synthesis of a thickener from galactomannan polysaccharides extracted from fenugreek seeds for special applications in textile processing

Current work addressed the fabrication of polysaccharides thickener through innovative oxidation of galactomannan gum extracted from fenugreek seeds. The innovation based on oxidation of the galactomannan gum by sodium perborate (SPB) under the influence of heat induced by microwave irradiation. The oxidation was conducted under different conditions and the so obtained oxidized gums alongside gum oxidized with SPB under conventional heating were submitted to characterization for micro molecular change and ability to act as a thickener in the printing paste of reactive printing

Experimental

Materials:

Fenugreek seeds

Clean, dry fenugreek seeds cultivated in Egypt were purchased from local market

Fabrics

Mill scoured, bleached and mercerized plain weave cotton fabric (135 g/m^2) was kindly supplied by Misr Co. for spinning and weaving, El Mahalla ElKOBRA, Egypt.

Microwave equipment:

The oxidation process of galactomannan fenugreek gum was carried out using microwave synthesis systems: Lab station, which is equipped with a magnetic stirrer, and a non-contact infrared continuous feedback temperature system, MILSTON, USA.

Chemicals:

Sodium perborate, sodium thiosulphate, and sodium disulphate, were supplied by Sisco Research Laboratory PVT. Co. Hydroxyl amine hydrochloride was purchased from Oxford Lab Chem, India, Cas No: 5470-11-1. Phenolphthalein and methyl red were supplied by Fisher Scientific, Egypt. Sodium hydroxide, sulfuric acid, hydrochloric acid, and absolute ethanol were all of laboratory grade chemicals.

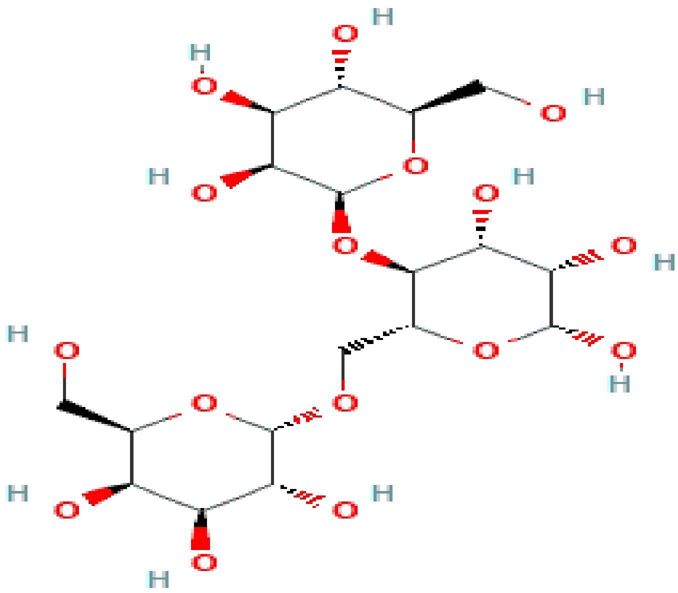


Fig. 1. The structure of galactomannan.

Reactive dyes:

Procion Red PX-88 was kindly supplied by Ciba-Geigy.

Thickeners

a) Commercial sodium alginate of high viscosity type manufactured by ceca colloid Chemie, Paris. France.

b) Oxidized fenugreek gum prepared from galactomannan fenugreek gum extracted from fenugreek seed and oxidized with sodium perborate ($NaBO_3 \cdot 5H_2O$).

Methods:

Separation of gum from seeds:

For the separation of the galactomannan fenugreek gum from fenugreek seeds, followed were the following three steps, in the 1st step the seeds were grinded and sifted to remove nucleus. In the 2nd step, the crunches were performed with tap water and placed in a blender, soaked for approximately 24 h, then filtering it by using nylon net. In the final step, the resultant was precipitated by ethyl alcohol and dried at ambient temperature.

Oxidation of galactomannan fenugreek gum by Sodium Perborate (SPB):

Microwave irradiation:

Galactomannan fenugreek gum was prepared by adding 5 g of gum into 40 mL of tap water, to different amounts of SPB (0.25, 0.5, 0.75 and 1 g) dissolved in 10 ml of tap water under mechanical stirring. The mixture was kept at room temperature for 15 min with moderate stirring. After that, the temperature was raised to 60°C and maintained at this temperature for 5 min under continuous gentle stirring in microwave at 300 watt. At this end, the reaction was stopped by adding 0.1 gm of sodium disulphate. The rheological properties of the oxidized gum were characterized before precipitation. Then the oxidized gum was precipitated by drop wise addition of absolute ethanol under constant moderate mechanical stirring. The obtained gum was filtered. The filtrate was subjected to frequently washing with ethanol to remove the unreacted SPB and dried in an oven for 2 h at 50°C. Then, the dried gum was milled into powder. The resultant oxidized gum was subjected to characterization.

Traditional heating:

The oxidation process was carried out as follows: the fenugreek gum was introduced in a 500 ml Stoppard flask containing a solution of SPB and adjusted at pH 7, material to liquor ratio, and the temperature used. The flask was Stoppard and kept in thermostatic water bath. The contents of the flask were occasionally shaken during the course of the oxidation reaction. At the end of the desired time (30 min), the reaction was stopped by adding sodium bisulphate (0.1g/l) and the product was precipitated in ethyl alcohol. Finally the product was filtered on a sintered glass funnel, and air dried at room temperature.

Preparation of Printing Pastes:

The printing paste was prepared according to the following recipe:

Reactive dye	40 g
Thickener	X g
Urea	100 g
Sodium bicarbonate	30 g
Water	X
distilled water	10 g
Total	1000 g
Species	T. foenum-graecum

Printing technique:

The pastes were applied to the fabric through a screen printing process. Fixation of the color was achieved at 100-103°C for 10 min using an automatic thermostatic oven (Wemer Mathis Co., Switzerland). After that, washing was carried out according to the recommendation of the dye Manufacturer: 1) Rinsing thoroughly with cold water; 2) Treatment with hot water; 3) Soaping near boiling temperature (90- 95°C) with a solution containing 2g/L Aspkon, 4) Washing with hot water; 5) Finally rinsing with cold water.

Characterization of the oxidized galactomannan fenugreek gum:

Determination of carboxyl and carbonyl groups content:

The acidic (carboxyl) [17] and reducing (carbonyl) groups of Galactomannan fenugreek gum before and after oxidation with SPB was determined according to a method of Wing and Willett [17-19].

Rheological measurement:

The rheological properties and apparent viscosity were carried out using Brookfield model DV-111, Programmable Rheometer, U.S.A. at different rates of shear range between, 3.4 - 68 s-1, at 25°C according to a procedure reported elsewhere [19] by dissolving the purified samples in tap water at a concentration of 3%. The apparent viscosity was calculated using the following formula:

Where = apparent viscosity in poise.

= shearing stress (dyne / cm2).

= rate of shear (s^{-1})

Fourier Transform Infrared Spectra:

FTIR spectra were created for selected samples using a Spectrum 65 FTIR spectrometer (PerkinElmer Co., Ltd., MA, USA). Thermal characterizations and the remaining ash content were evaluated using a TA Instruments TGA Q5000 at a heating rate of 10 K/min under air atmosphere. High temperature platinum pans were used and sample mass was approximately 5 mg.

ZEISS LEO 1530 Gemini Optics Lens scanning electron microscopy (SEM) with 30 kV scanning voltages was employed to observe the morphologies of non- oxidized and oxidized galactomannan fenugreek gum. Zeiss LEO 438 VP with Oxford Instruments EDX with INCA software system. EDX measurement conditions, 20 kV accelerating voltage, 21 mm working distance, 1 nA sample

Color measurements:

Color strength expressed as K/S was measured by a previously reported method [19] by the light reflectance technique.

Fastness properties:

Fastness properties to washing, rubbing (dry &wet), perspiration as well as light fastness were measured according to a standard method [19].

Results and Discussion

The present study focusses on improving the synthesis of oxidized galactomannan fenugreek gum extracted from fenugreek seeds by making use of SPB. Although many researchers worked on the synthesis of oxidized galactomannan fenugreek gum yet there are no reports pertaining to fabrication of this oxidized gum in order to accentuate multifunctional action of this gum via microwave irradiation in an oxidized process with sodium perborate. Multifunctional properties, namely, carboxyl and carbonyl groups content, rheological properties, apparent viscosities as well as coloration were successfully created after synthesis of oxidized gum by using microwave as a source of heating. Particularly notable is that the microwave heating is better than the imitative heating (oil bath method). The microwave heating shortens the reaction times and reducing the energy consumption. Variation in the magnitude of each of the said functional properties by changing factors affecting oxidation of the gum under investigation using sodium perborate, microwave irradiation system are given below.

Effect of sodium perborate concentration on Acidic and Reducing properties:

Figures 2 (a, b, c) illustrate the effect of different concentration of SPB on the carboxyl, carbonyl groups as well as the residual of $NaBO_3 \cdot 5H_2O$ which added at the end of oxidized process of galactomannan fenugreek gum to stop the reaction. At the first glance, it is obvious that the oxidized gum samples display variable values of carboxyl content upon using different PSB concentrations. The carboxyl content increases from 39.3 to 48.2 meq/ 5 g galactomannan fenugreek gum by increasing SPB concentration from 0 to 0.75 mg/ 5 g fenugreek gum, then it dramatically decreases. Similar trend is observed with the carbonyl content, SPB content decreases as the SPB concentration increases until 0.75 mg/ 5 g gum then it increases again.

Increasing in the carboxyl content of the oxidized galactomannan fenugreek gum by the increasing SPB concentration could be associated

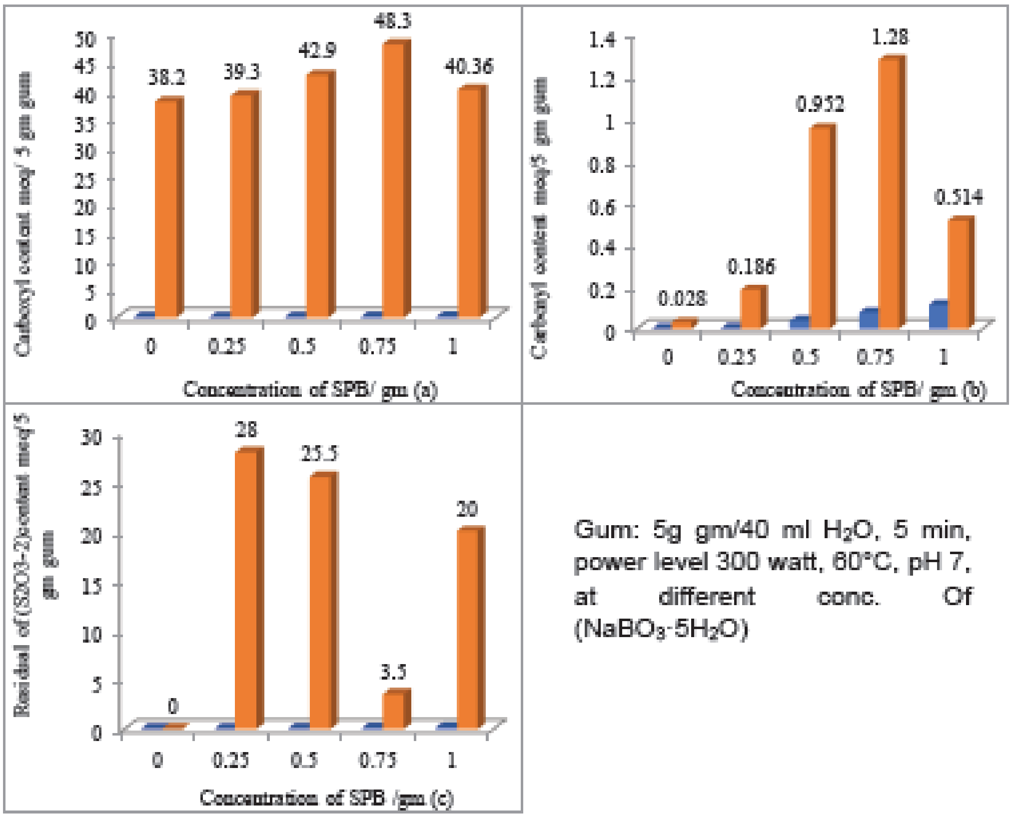
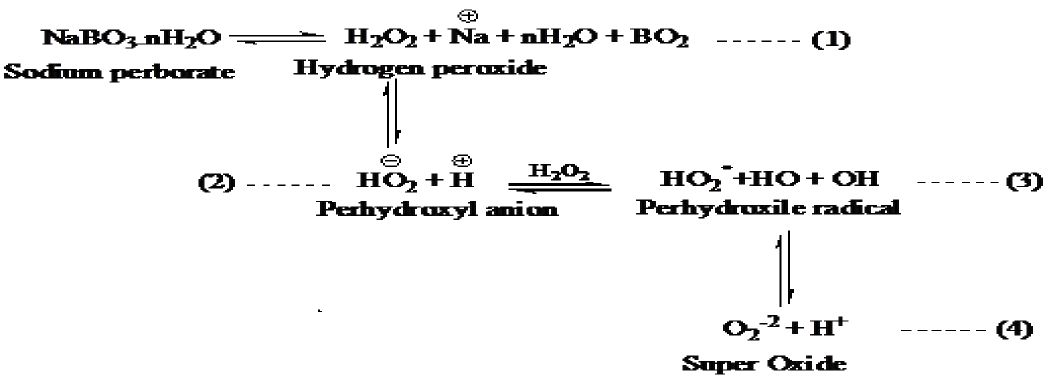


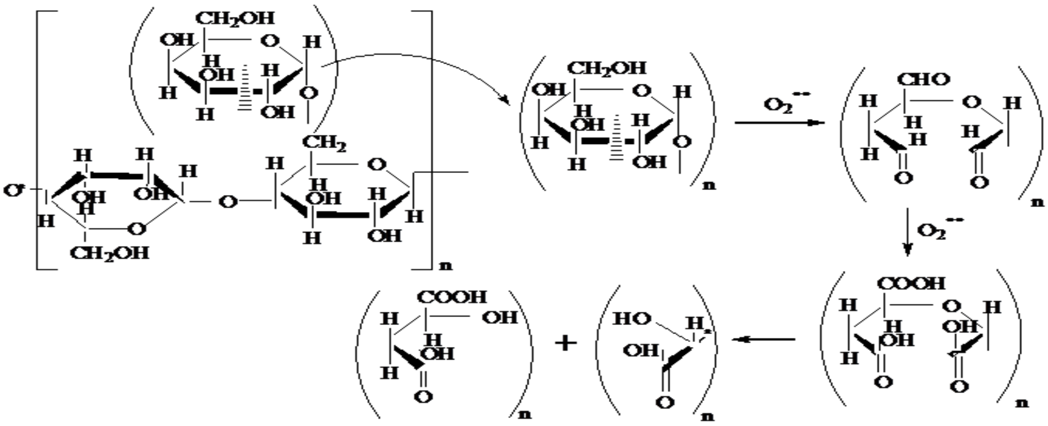
Fig. 2 (a-c). Effect of SPB concentration on the (a) carboxyl content; (b) carbonyl content; (c) the Residual of SPB content of the oxidized gum.



Scheme (1)

with abundance of SPB decomposition products at higher SPB concentrations, leading ultimately to formation of -C=O and/or -COOH groups in the molecular structure of galactomannan fenugreek gum. Stated in other words, the oxidation under investigation yields mixed type of oxidized fenugreek gum by virtue of acquiring acidic (-COOH) and reducing (-C=O) groups. Sodium perborate may decompose in the presence of moist air or water and release hydrogen peroxide (equ.1), which forms per-hydroxyl anions (HO_2^{-}) in aqueous solution (equ.2); the latter may further produce other active species namely per-hydroxyl anion ($HO^{\cdot}$) (equ..3) Which may also dissociate to anion O_2^{-2} (known as super oxide) (equ.4) which very lately was considered as an active oxidizing agent (see Scheme 1):

According to Scheme 2 we can postulate that the galactomannan fenugreek gum undergoes molecular oxidation by SPB thorough active per-hydroxyl radical ($HO_2^{\cdot}$) which is formed during decomposition of SPB. Such oxidation results in formation of carboxyl group (-C=O) that occurs on C_2, C_3, as well as C_6 which is oxidized immediately. Because the presence of



Scheme (2)

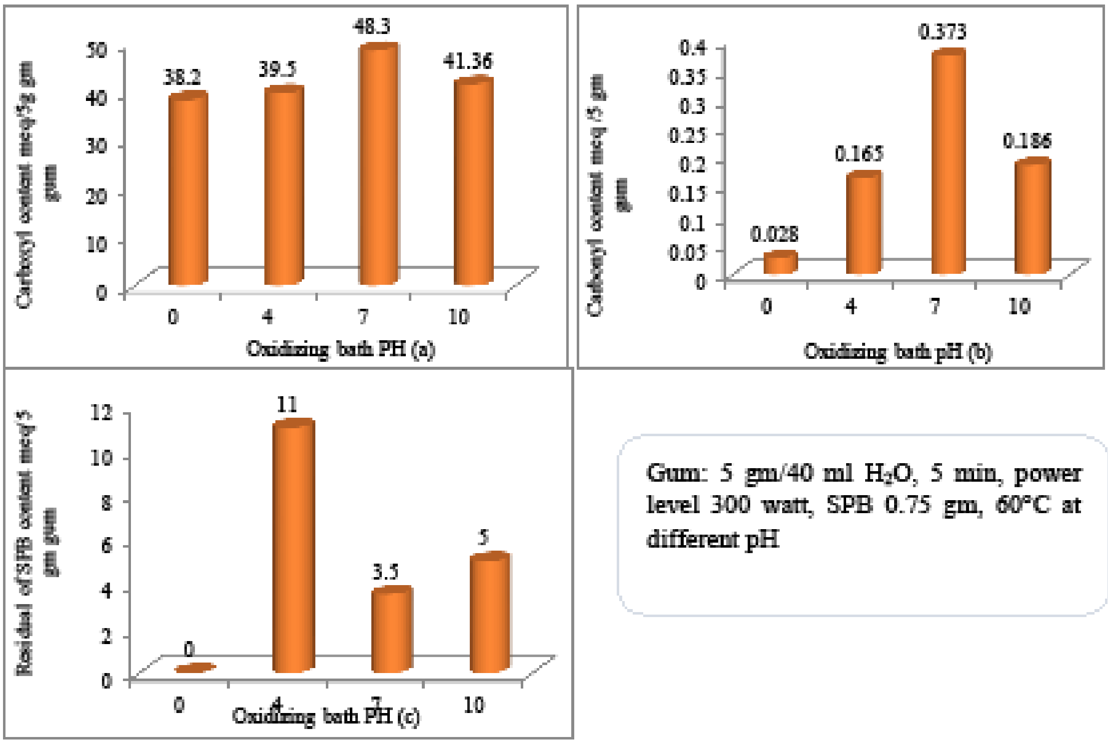


Fig. 3. Effect of oxidizing bath PH on the (a) carboxyl content; (b) carbonyl content; (c) the Residual of SPB content of the oxidized gum.

ketone group at C_2 and C_3 that causes breaking of glucoside bonds and, in turn, the galactomannans chain are broken down at β elimination, this leads to a reduction in molecular weight of fenugreek gum (as shown in equation 1).

Figure 2 (c) depicts the residual amount of SPB. It is seen that as the concentration of SPB increases the residual SPB decreases until o.75 g/ 5g gum, and thereafter increases. This may be attributed to the effect of microwave irradiation which may cause decarboxylation.

Figures 3 (a & b) show the effect of pH of the oxidizing medium on the acidic and reducing properties of galactomannan fenugreek gum. Obviously, the carboxyl and carbonyl contents exhibit the highest values at pH 7. In conformation of this is, the minimum residual of SPB which is also found at pH 7.

Figure 4 illustrates the effect of duration (3-9 min) of oxidation using SPB on the carboxyl and carbonyl contents of galactomannan fenugreek gum. As is evident the carboxyl and carbonyl contents increase as the duration of oxidation increases until 5 min then decreases thereafter. Here also the residual SPB follows the opposite trend until 5 min then it increases again. The microwave interaction with materials is based on microwave energy which is transmitted directly to the molecular structure of the gum with an electromagnetic field. Considering these

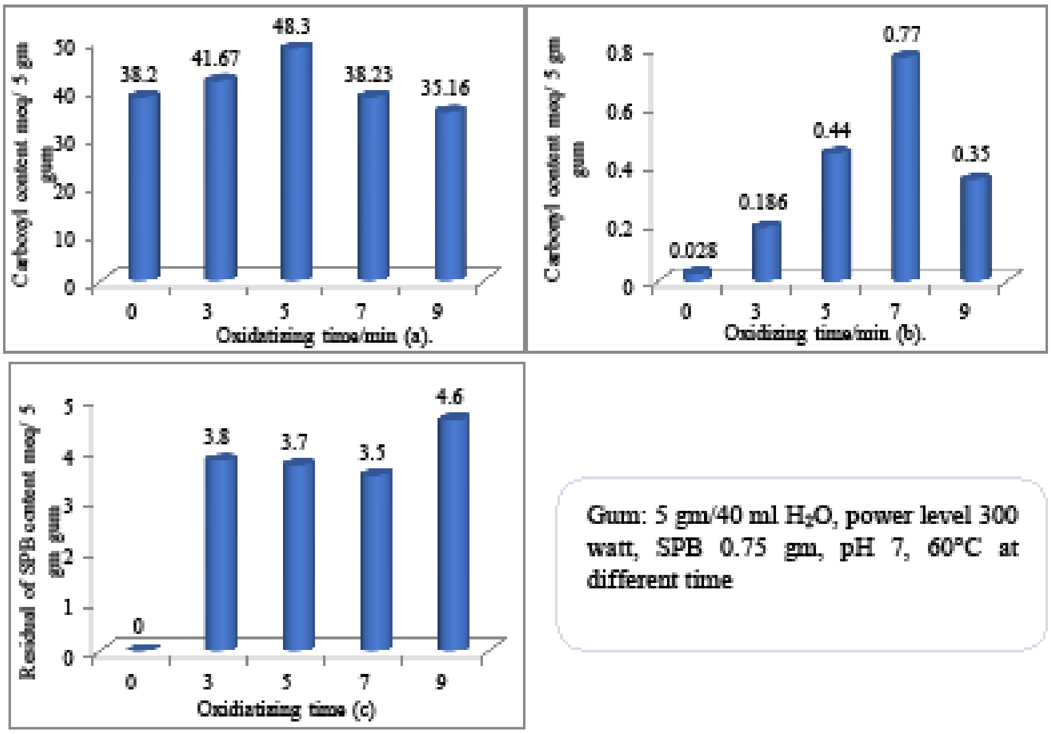
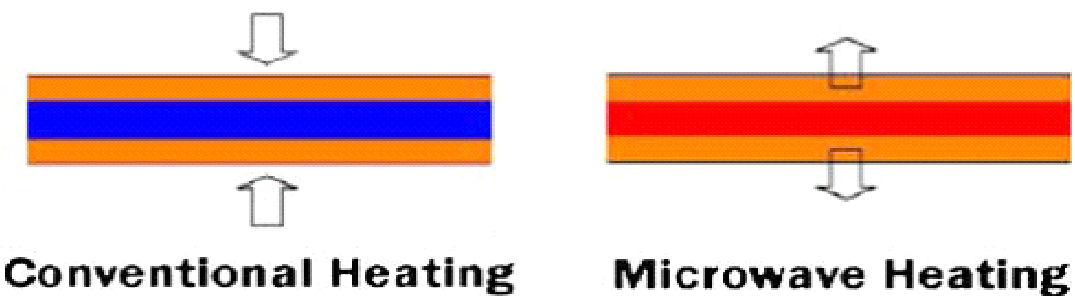


Fig. 4. Effect of oxidizing time on the (a) carboxyl content; (b) carbonyl content; (c) the Residual SPB content of the oxidized gum.



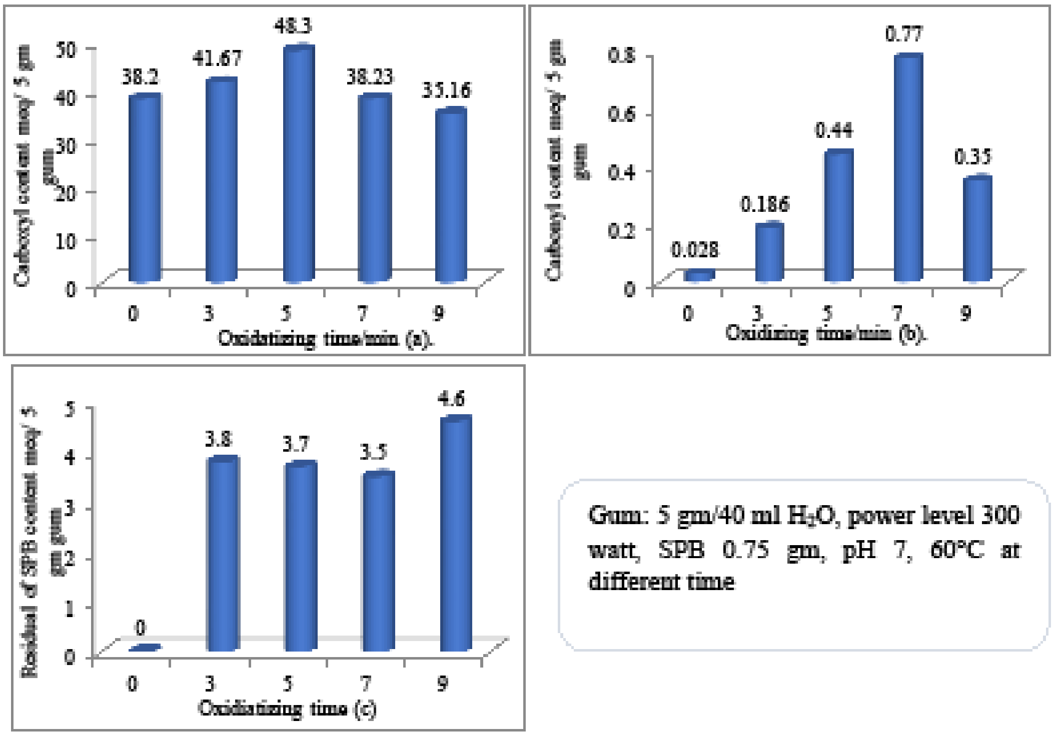


Fig. 5. Effect of oxidizing temperature on the (a) carboxyl content; (b) carbonyl content; (c) the Residual of SPB content of the oxidized gum.

phenomena, the predominance of microwave heating of the material where the latte absorbs microwave irradiation from inside to the outside of the material and change it into heat; this leads to quick, controlled, specific and uniform heating in a short time (Fig. 4).

Figure 5 shows the effect of temperature on the carboxyl and carbonyl content of the gum after oxidation. The results indicate that the oxidizing temperature exerts a considerable effect on the acidic and reducing properties of the oxidized galactomannan fenugreek gum. As the temperature increases the acidic and reducing properties of fenugreek gum increases up to 60ºC. Thereafter no significant change occur in carbonyl, carbonyl and residual SPB.

Based on the above results it can be concluded that the best condition for the oxidizing processes of galactomannan fenugreek gum when using microwave irradiation is (0.75 gm SPB/5 gum, pH 7, for 5 min at 60°C).

Dependence on Rheological properties on SPB concentration:

The expression rheology indicates studying of mechanical properties of concentrated colloidal system such as flux, flexibility, and plasticity. There is also a tentative relationship among flow properties described several thickeners and their use and suitability for printing different designs [20]

Table 2 exhibits the apparent viscosity of oxidized galactomannan fenugreek gum prepared at different concentrations of SPB (0.25, 0.5, 0.75, 1 gm/ 5 gum). The results signify that: (a) increasing SPB concentration is accompanied by significant decrease in the apparent viscosity, (b) increasing SPB concentration up to 0.75 g per 5 g galactomannan fenugreek gum leads to very low apparent viscosity which levels off even at higher rates of shear and finally (c) increasing the rate of shear causes dramatic decrease in apparent viscosity.

The viscosity of the prepared oxidized galactomannan fenugreek gum by using microwave irradiation meaningfully decreases by increasing the oxidizing agent SPB concentration in a short time. This could be ascribed to microwave irradiation which accelerates breaking down of the glucoside linkages as the oxidation proceeds. The decrement in apparent viscosity

TABLE 2. Effect of SPB concentration on the apparent viscosity of oxidized galactomannan fenugreek gum extracted from fenugreek seeds.

Conc. Of $NaBO_3.5H_2O$ RS cm^{-1}	0.25	0.5	0.75	1
	Apparent Viscosity in centipoise			
3.4	5424	4600	800	550
6.8	3940	3600	730	550
10.2	1776	2400	542	330
13.6	1400	1433	380	288
17	1444	1095	250	250
20.4	1360	992	229	220
23.8	1224	731	211	163
27.2	906	717	156	162
30.6	500	700	139	120
34	450	260	125	108

Paste conc. 3%, oxidation condition: 5 g gum/40 ml H_2O, 5 min, power level 300 watt, pH 7, at 60°C.

could be associated with glucoside bond cleavage during oxidation process which leads to a decrease in molecular weight of the prepared gum. SPB oxidation of prepared gum brings about ketone groups at C_2, C_3 and C_6, a situation which facilities cleavage of the glucoside linkages. C_3 position is weakened through monomeric ring (i.e., glucose unit) opening and shortening the gum molecular chain. Hence, the extent of galactomannan fenugreek gum oxidation depends on the concentration of oxidizing agent (SPB).

Figure 6a depicts the experimental rheograms for the oxidized galactomannan fenugreek gum extracted from fenugreek seeds. Figure 5 shows that the pastes under study display a non-Newtonian pseudo plastic behaviour because the relation between the shearing stress and the rate of shear is not linear and the up and down flow curves are coincident. This means that if the viscosity (resistance to flow) of oxidized fenugreek pastes were measured using a large applied force (shearing stress) which generates a high-velocity flow (shear rate), the apparent viscosity is less than that of the same paste determined using a smaller force and a slower rate of flow [21,22]. It is worthy to remark that in pseudo plastic solution no time-dependent effects are detected [22].

Table 3 describes the apparent viscosity of prepared oxidized galactomannan fenugreek gum at different oxidizing bath PH (4, 7, and 10). The results signify that, regardless of the pH values used for preparation of oxidized galactomannan fenugreek gum selection samples, the apparent viscosity decreases as the rate of shear increases, as well as the increment of pH value.

Figure 6b shows the rheograms of the gum after oxidation with SPB at different pH values. It is clear from Figure 5b that all the samples examined are characterized by non-Newtonian pseudo plastic behavior because the relation between the shearing stress and the rate of shear is linear and the up and down flow curves are coincident. The same figure illustrates that the location of rheogram with respect to the rate of shear axis depends on the pH values used, there by elucidating difference in the apparent viscosity.

Table 4 depicts the experimental rheograms for oxidizing gum by using microwave irradiation at different time (3, 5, 7, 9 min.). It is clear that as the rate of shear increases the apparent viscosity of all the above-mentioned oxidized fenugreek pastes decreases. But the magnitude of decrement in the apparent viscosity at the same rate of shear depends on the oxidation time, as an example, at rate of shear 3.4 S-1 the apparent viscosity values are 7950, 800, 725 and 655 centipoises at time of oxidation 3, 5, 7 and 9 minutes, respectively. The decrease in the apparent viscosity at a constant rate of shear by increasing the oxidation time may be attributed to the hydrolysis of fenugreek gum which leads to decrease in molecular weight of the oxidized galactomannan chain under the influence of both: the presence of SPB as well as exposure time to microwave during oxidation.

Figure 6c depicts the experimental rheograms for oxidizing gum by using microwave irradiation at different time (3, 5, 7, 9 min.). It is evident that all samples inspected are characterized by non-Newtonian pseudo plastic behavior. It is also clear

TABLE 3. Effect of oxidizing bath pH on the apparent viscosity of oxidized galactomannan fenugreek gum extracted from fenugreek seeds.

pH	4	7	10
RS cm^{-1}	Apparent Viscosity in centipoise		
3.4	1544	800	770
6.8	1530	730	728
10.2	1504	542	533
13.6	1482	380	332
17	1475	250	227
20.4	1428	229	225
23.8	1387	211	208
27.2	1381	156	146
30.6	1345	139	131
34	1225	125	111

Paste concentration 3%, oxidation condition: gum: 5 gm/40 ml H_2O, 5 min, 300 watt, 0.75 gm SPB, at 60°C

TABLE 4. Effect of oxidizing time on the apparent viscosity of oxidized galactomannan fenugreek gum extracted from fenugreek seeds.

Oxidizing time/min	3	5	7	9
RS cm^{-1}	Apparent Viscosity in centipoise			
3.4	7950	800	725	655
6.8	6550	730	625	624
10.2	4942	542	475	434
13.6	4131	380	313	309
17	4205	250	230	213
20.7	3775	229	224	212
23.8	3912	211	211	107
27.2	3557	156	142	103
30.6	3275	139	120	101
34	3186	125	120	100

Paste concentration 3%, oxidation condition: gum: 5 gm/40 ml H_2O, 300 watt, 0.75 gm SPB, 60°C, at different time

from the rheograms that as the oxidation time increases, the location of the rheograms is shifted towards a rate of shear axis elucidating a decrease in the viscosity of the paste.

Table 5 depicts the experimental rheograms for gum oxidized by using microwave irradiation at different temperature (50, 60, 75°C). It is clear from the data recorded in Table 4 that as the rate of shear increases the apparent viscosity of all the above-mentioned oxidized fenugreek pastes decreases. But the extent of decrement in the apparent viscosity at the same rate of shear depends on the oxidizing temperature, as an example, at rate of shear 3.4 S^{-1} the apparent viscosity are 7950, 800 and 755 centipoises at time of oxidation 3, 5 and 7 minutes, respectively

Figure 6d depicts the experimental rheograms for oxidizing gum by using microwave irradiation at different temperature (50, 60, 75°C.). It is evident that, all samples inspected are characterized by non-Newtonian pseudo plastic behavior. It is also clear from the rheograms that as the oxidation temperature increases, the location of the rheograms is shifted towards a rate of shear axis elucidating a decrease in the viscosity of the paste. From the same figure it is illustrated that the location of rheogram with respect to the rate of shear axis depends on the temperature used, which elucidate difference in the apparent viscosity.

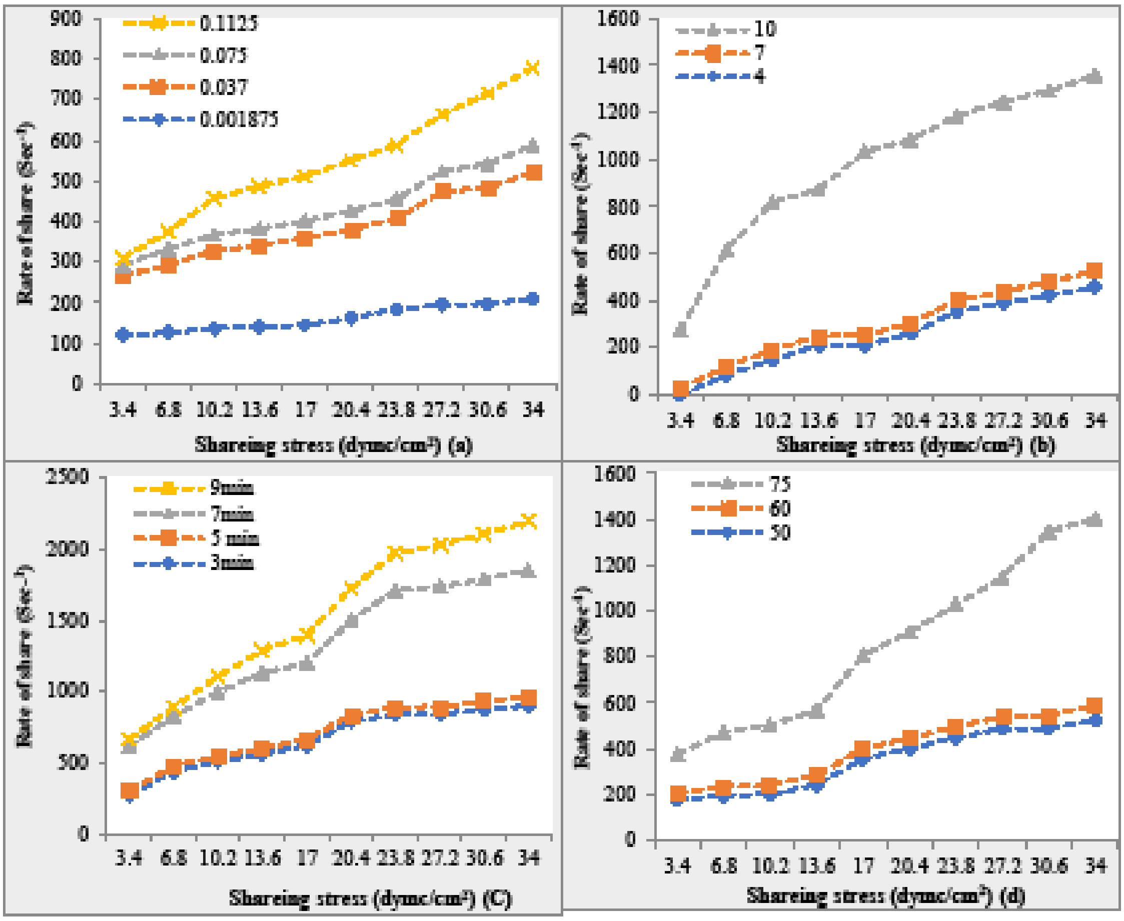


Fig. 6. Effect of (a) SPB concentration, (b) oxidizing bath PH, (c) oxidizing time,(d) oxidizing bath temperature on the rheological properties of prepared oxidized galactomannan fenugreek gum.

TABLE 5. Effect of oxidizing temperature on the apparent viscosity of oxidized galactomannan fenugreek gum extracted from fenugreek seeds.

RS cm^{-1}	Apparent Viscosity in centipoise		
	50°C	60°C	75°C
3.4	---	800	755
6.8	1925	730	720
10.2	1850	542	475
13.6	1781	380	361
17	1765	250	250
20.4	1721	229	227
23.8	1671	211	204
27.2	1659	156	144
30.6	1589	139	121
34	1545	125	112

Paste concentration 3%, oxidation condition: gum: 5 gm/40 ml H2O, 300 watt, 0.75 gm SPB, 60°C, at different time

TABLE 6. Color strength and overall fastness properties of printed cotton using prepared oxidized gum by MW, TH and sodium alginate as a commercial one.

Thickener used	Color Strength K/S		Washing fastness		Rubbing				Perspiration							
					Dry		Wet		Acidic				Alkaline			
									Staining		Alteration		Staining		Alteration	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
Oxidized gum MW	21.71	18.5	3	3	3-4	3	3	3	3	3	3	3	3	3	3	3
Oxidized gum TH	20.20	18.34	3	3	3-4	3	3	3	3	3	3	3	3	3	3	3
Sodium alginate	19.74	17.57	3	3	3-4	3	3	3	3	3	3	3	3	3	3	3

I=freshly paste, II= stored for 3 days, MW= microwave heating, TH= traditional heating

Printing:

Printing pastes were prepared using the oxidized galactomannan fenugreek gum (o.75 PSB g/100g paste of 5% gum, pH 7, 5 min, at 60°C) by using microwave heating. For comparison other printing pastes were prepared using commercial thickener (Sodium alginate) and the other oxidized gum by using traditional heating (o.75 g/100g PSB paste of 5% gum, pH 7, 30 min, at 60°C) . Printing pastes were prepared using these thickeners along with Procion Red PX-8B.

The prepared printing pastes were employed for cotton fabric by using flat screen printing method. Storing the paste for three days prior to printing was also studied. After printing, the fabric samples were dried followed by thermos fixation at 140°C for 4 min. Table 6 shows the color strength (K/S) and overall fastness properties of printing cotton fabric. From the data listed in Table 5 it is clear that the K/S value obtained display the highest value with immediately prepared paste followed by stored paste. Similarly oxidized gum with SPB and microwave exhibit K/S valued higher than those oxidized using SPB and conventional heating as well as than commercial alginate probably due to microwave irradiation which may change the morphological structure of the gum as will be discussed later.

The overall color fastness properties for the cotton printing using oxidized fenugreek gum with SPB by using MW at 300 Watt is nearly equal to their corresponding samples printed using oxidized gum by using TH as well as commercial alginate, the values of the color fastness is ranging from good to very good.

Characterization of prepared oxidized gum:

The morphological, chemical and physical alterations of the galactomannan gum extracted from fenugreek gum were observed under different technical method with comparison between commercial and prepared oxidized gum using two different heating method (MH at power 300W, 60°C, 5 gm gum/40 ml H_2O, pH 7 for 5 min, and TH (conventional heating) at 60°C, 5 gm gum/40 ml H_2O, pH 7 for 30 min.

Scanning Electron microscope:

To get insight into the morphology of the prepared oxidized gum, scanning electron microscopy (SEM) characterization was performed to detect the difference between the prepared oxidized gum and the commercial one (Fig. 7).

Scanning electron microscopy (SEM) shows a slight difference between the heating methods concerning the shape of the particles. Conventional heating for 30 min. leads to more or less spherical aggregates, while microwave heating for 5 min at the same temperature of 60°C yields slightly elongated thread particles. This may be due to the effect of microwave irradiation. Microwave heating process could accelerate the oxidation processes resulting in lower consumption of time and energy. The microwave irradiation can easily penetrate inside the molecules and all molecules can be heated simultaneously, which lead to reducing heat transfer problems. The molecules of prepared gum will be rearranged by electromagnetic field and the molecular movement will be ordering. This accelerates reaction velocity and the mass transfer, improves partition and resulted in a decrease in the molecular size and alteration in its

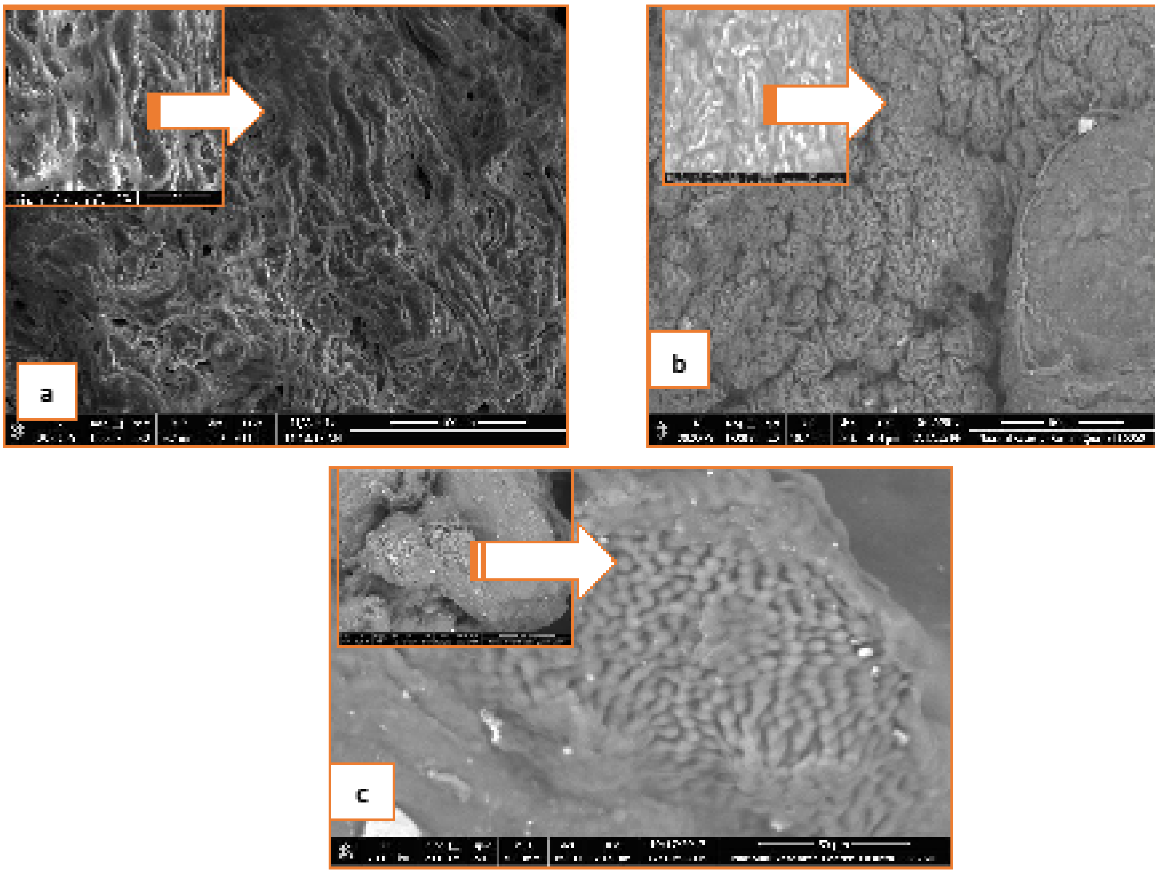


Fig. 7. Image of SEM (a) non-oxidized gum, (b) oxidized gum by using TH, (c) oxidized gum by using MH

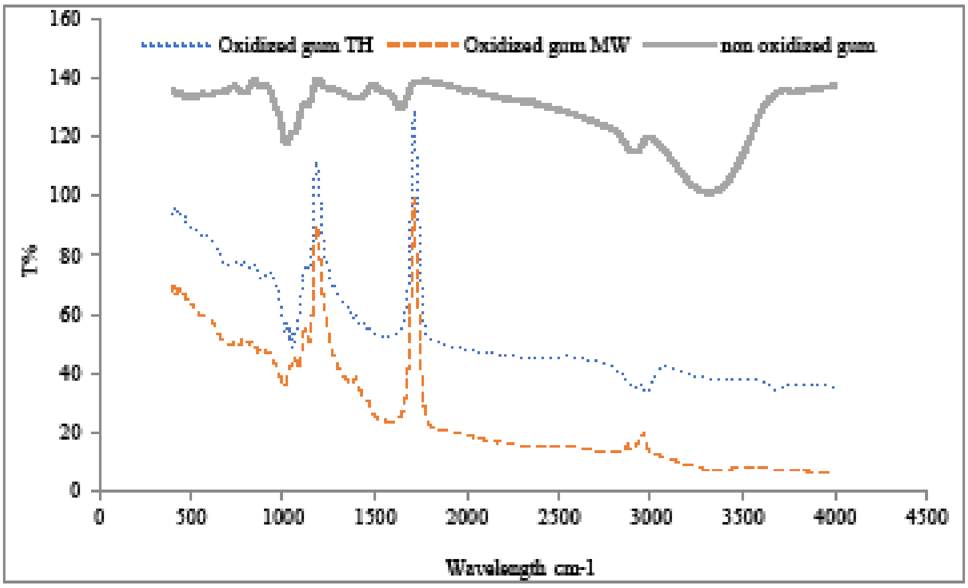


Fig. 8. FTIR of non and oxidized galactomannan gum using traditional heating as well as microwave irradiation

shape [19-24].

Fourier Transform Infrared Spectra

The chemical interaction of the non-oxidized as well as oxidized gum was examined by FTIR (Fig. 8). As shown in Fig. 7, the characteristic peak of non-oxidized galactomannan gum macromolecule appears at 3771.12 cm^{-1} with correlation intensity 94.96, 31 while in oxidized one it appears at 3831.86 cm^{-1} with correlation intensity .32.298 when using MW and at 3839.58 cm^{-1} with correlation intensity 29.48 when using TH (conventional heating), this is due to the presence of (O-H) bond. The same figure also shows a strong absorption stretching peak at 1547.69 cm^{-1} with correlation intensity 95.0061 and wagging peak at 1515.78 cm^{-1} with correlation intensity 21.4591 when using MW as well as TH, respectively, this is due to the presence of (C=O). This proves the success of the oxidation process and the formation of carboxylic acid and carboxylic group. While the absorption peak at 1547.59 cm^{-1} with correlation intensity 95.0061 indicate the presence of conjugat of bending C=O of non-oxidized gum. The peak at 1639.2 cm^{-1}, 1864.83 cm^{-1} and 1841.69 cm^{-1} with correlation intensity 89.5692, 25.4402 and 24.248 originates from the bending vibration of H-O-H in the absorbed H_2O of non-oxidized and oxidized gum by using MW and TH, respectively. The O-H stretching vibration peak absorption of OH groups which present in the glucose units are strikingly reduced; a point which means that the oxidation process occurs at OH groups existing at C2, C3, and C6 of the glucose units of the molecular chains of galactomannan gum.

Conclusion

A benign method for synthesis of oxidized galactomannan fenugreek gum extracted from fenugreek seeds was established using sodium perborate (SPB) and microwave irradiation. The oxidation was carried out under a variety of conditions encompassing SPB concentration, duration of oxidation, pH and temperature of the oxidation medium. The so obtained galactomannan fenugreek gum were submitted to quantitative determination of micro structural feature, namely, carboxyl group, carbonyl group and rheological properties in addition to application as a thickener in reactive printing. Creation of carbonyl and carboxyl groups in macromolecular structures of the gum under investigation besides the observed alterations in the rheological properties as well as the successful application in reactive printing advocate current oxidized galactomannan fenugreek gum to substitute sodium alginate which is the universally accepted thickener for printing cotton fabric with reactive dyes. Galactomannan fenugreek gum could conveniently be oxidized using 0.75 g SPB/100, 5g/40ml H2O of galactomannan gum at pH 7 and 60ºC for 5 min. The color strength values and the overall of color fastness properties for the goods printed using the prepared thickener by using microwave irradiation and the prepared one by using conventional heating is either higher or equal to the corresponding samples printed using commercial sodium alginate. The scanning electron microscopy shows a slight difference between the heating methods concerning the shape of the particles. FTIR depicts the association interaction chemistry of the produced Carboxyl and carbonyl group.

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المميزات التركيبية لصمغ الجلاكتومنان المستخلص من بذور الحلبة والمؤكسدة بواسطة بير بورات الصوديوم تحت إشعاع الميكروويف للطباعة بالصباغات النشطه

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اهتمت هذه الدراسه بأستخراج صمغ الجلاكتومنان(Galactomannan) من بذور الحلبة وذلك من خلال عدة خطوات: طحن البذور،غربلتها، ثم غسلها وتصفيتها. بعد ذلك تمت عملية ترسيب الصمغ وذلك عن طريق اضافة الكحول الإيثيلي، تلتها عملية تجفيف الراسب عند درجة حرارة الغرفة. وهكذا تم الحصول علي المنتج (الصمغ) الذي تم اخضاعة إلى عملية أكسدة مبتكرة وذلك عن طريق تعريضه لأشعة الميكروويف واجراء عملية الاكسدة بأستخدام الصوديوم بيربورايت (SPB) تحت ظروف متنوعة لتحديد انسب ظروف لأتمام عملية الاكسدة. وذلك من خلال استخدام تركيزات مختلفه من SPB، زمن الأكسدة، الأس الهيدروجيني، وكذلك درجة حرارة تفاعل الأكسدة. كما خضعت عينات الصمغ المؤكسدة التي تم الخصول عليها الي التحليل الكيميائي والميكروسكوبي للتقييم الكمي لمجموعات الكربوكسيل والكربونيل والخصائص الريولوجية لمجموعات SPB المتبقية. كما تمت دراسة التغييرات الهيكلية الحادثة في الصمغ المؤكسد بأستخدام أشعة الميكروويف ومقارنته بمثيله المؤكسد بالطريقة التقليديَّة. هذا وقد أوضحت النتائج التي تم الحصول عليها من خلال التحليل والقياسات إلى أن الأكسدة المبتكرة التي أستخدم فيها الأشعه الميكروويفه في التسخين تستهلك وقتًا وطاقة أقل إذا ما قورنت بمثيلتها المستخدم فيها الأكسدة التقليدية (باستخدام التسخين الطريقة التقليدية). كما أشارت النتائج إلى أن الأكسدة بأستخدام كلا من الأشعه الميكروويفيه أو التسخين التقليدي تضفي تركيزًا على صمغ galactomannan المؤكسدة ، والتي تحفز على تحسين ثبات الألون بشكل ممتاز عند تطبيقها كمتخنات في معجون الطباعة للصبغات النشطه. كما يمكن أستخدام الصمغ المؤكسد الذي تم الحصول عليه كبديل حقيقي لمثخن ألجينات الصوديوم والذي يتم استخدامه في الوقت الحالي لطباعة الأقمشه القطنيه بالصبغات النشطه. بالإضافة إلى ذلك، فإن صمغ galactomannan المؤكسد يعد صديقا للبيئة أثناء تحضيرة وكذلك في استخداماته.