Rheological Characterization of Combretum Glutinosum (Habeil) Gum

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Abstract: ***Rheological properties of Gum Habeil collected during three seasons had been studied. Intrinsic viscosity of aqueous solution of Gum Habeil was calculated by Fedor's equation. At a low concentration of aqueous deacetylated gum solution, the G' (viscoelastic) was appeared higher than G'' (viscosity) at frequency ranged from 1 to 10 Hz, but with increases concentration of deacetylated gum solutions G'' line was trend to appear higher than G' line at low frequency region. However, a crossover of G' and G'' lines was observed as the frequencies increased to 1.26, 3.97, and 9.99 Hz for 1.5, 3, and 5% w/w of gum solutions respectively. The concentrated crude gum dispersions 12.5 and 15% w/w were exhibited viscoelastic behavior, in contrast the 10% w/w of crud gum solution in distilled water appeared G'' higher than G' with the crosslink points at the middle of frequency range. The critical concentration C* of deacetylated gum solutions in deionized water, in sodium hydroxide alone, and in alkali with addition salt were determined to be 2.34, 2.37, and 2.41 g/dl respectively. The effect of temperature on rheological behavior was also studied.***

Keywords: Rheological; Combretum ; Gum Habeil; viscoelastic; coil overlap

1. Introduction

In west of Sudan the natural exudate of *Combretum glutinosum* Perr. ex DC. trees known as Gum Habeil, and Gum Habeil el Gebel [1,2]. The hot aqueous extraction solution of the Habeil tree leaves have been used traditionally in Sudan to treatment of several diseases such as headache, bleeding, and malaria [3], however, Habeil trees are essentially used as a wood source such as tool handles, charcoal, general carpentry [2]. C. *glutinosum,* small Savanna tree 7-10 m high sometimes with several stems. It is an indigenous tree species [4]. The author 2017 revealed that; the crude gum has irregular particle size, while the freeze dried soluble part, and freeze dried deacetylated gum has fibril form. DSC analysis indicated that the thermal transition temperature was 30.43°C. With enthalpies 0.3332 J/ g. Hydroxyl, acetyl and carbonyl were the major functional groups observed in Gum Habeil by FT-IR spectra. Gum Habeil, similar to Gum kondagogu, gum tragacanth, and gum karaya [5-7], have lower solubility, and higher viscosity, and the viscous activation energy of aqueous solution equal 19.264 kJ / mol., therefore, the viscous activation energy of the gum solution in 1M sodium chloride and 1M sodium hydroxide are 17.327 and 18.225 kJ / mol. respectively. Gum Habeil is a complex of partially acetylated polysaccharide obtained as calcium, potassium and magnesium salts [8]. The objectives of this work are to determine the dynamic rheological properties of crude, and deacetylated gum solutions, also to study the influence of alkali with and without addition salt on viscosity and degree of space occupancy, C[η], for the deacetylated gum solutions. The work also aimed to study the effect of some parameter such as temperature, concentration of solvents, on the flow properties of deacetylated gum solutions.

2. Sample Collection and Preparation

Authentic samples of Gum Habeil are collected from forest of the Blue Nile State-Sudan. The gum samples were purified from impurities, and grounded using an electrical mill. Standard methods of preparation of deacetylated gum solution was used [9, 10].

2.1Viscosity and dynamic rheology measurement

10 g /dm^3 of deacetylated gum solution was stirred overnight in several solvents, then insoluble fraction was removed by centrifugation at 500 rpm for 15min, and then the dynamic rheological and viscosity were measured at 25 ±0.1°C in AR-G550 Rheometer, which included a circulating water bath (Julabo F10, Germany) with ±0.1°C accuracy. The cone and plate geometries were used for all experiments; parallel plate geometry was used to study the flow and oscillation properties of crude gum solutions.

2.2 Intrinsic Viscosity Measurement

The viscosity measurement was carried out using Ubbelohode viscometer (75/ N 104 or 75 / N94) contained in water path (C.T-500 Series II, USA) at 25 ± 1.0°C. The gum solutions were prepared by dissolving 0.5 to 1.0 gram of deacetylated gum in 100 cm^3, 1M sodium hydroxide alone, and with 0.9M sodium chloride. The solution was then filtered through o.8 µm cellulose acetate membrane (Naglene, 25 mm). 3.0 cm^3 of the filtrate were then transferred into an viscometer and left for thirty minutes, then the flow time of gum solutions and solvents were measured. The relative viscosity was calculated by comparing the flow time of gum solution to the flow time of solvent passage through the Ubbelohde capillary tube, then the relative viscosity was converted to specific, and reduced viscosity [10]. The following Fedor's equation was used to calculate the intrinsic viscosity.

$$1 / [2\times(\sqrt{\eta_{red.}} -1)] = 1/[\eta]C - 1/ [\eta]C_{max}$$

where [η] = intrinsic viscosity, C = a gum concentration, and $\eta_{red.}$ = reduced viscosity [11- 13].

3. Results and Discussion

Fig.1 and 2 show that the viscosity of Gum Habeil solutions 1.0% w/w in sodium hydroxide was decreased steeply with increasing the concentration of sodium hydroxide at a fixed shear rate due to increases the hydrolysis of hydroxyl groups on polysaccharide backbone. Also Fig.2 shows that, the ramp up flow share rate verses viscosity exhibited that at low shear rate below 200 s^{-1} viscosity of gum solution was decreased with shear rate increase(shear-thinning), but at shear rate above 200 s^{-1} the system exhibited Newtonian behavior.

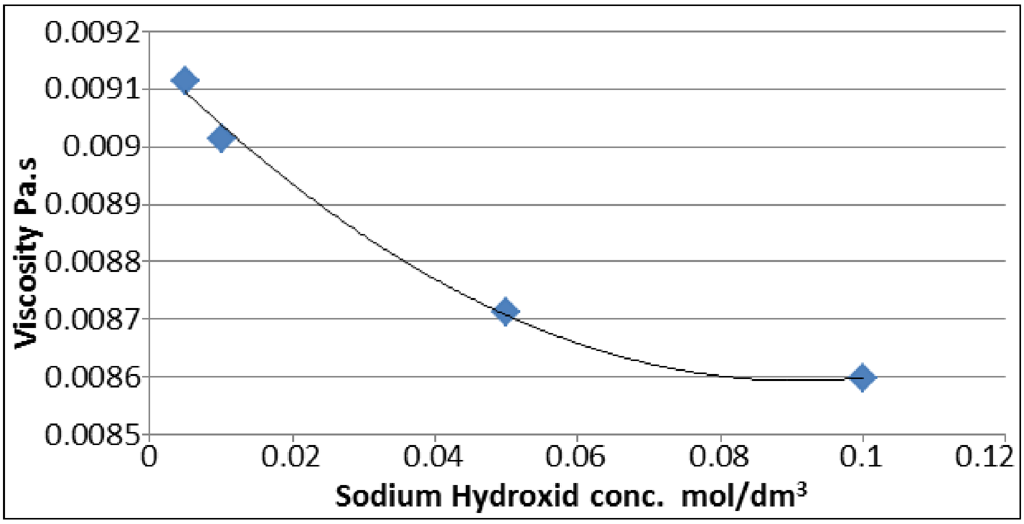

Figure 1: Viscosity of 1.0 % w/w Gum Habeil in different concentrations of sodium hydroxide at shear rate100s^{-1}(25^{o}C).

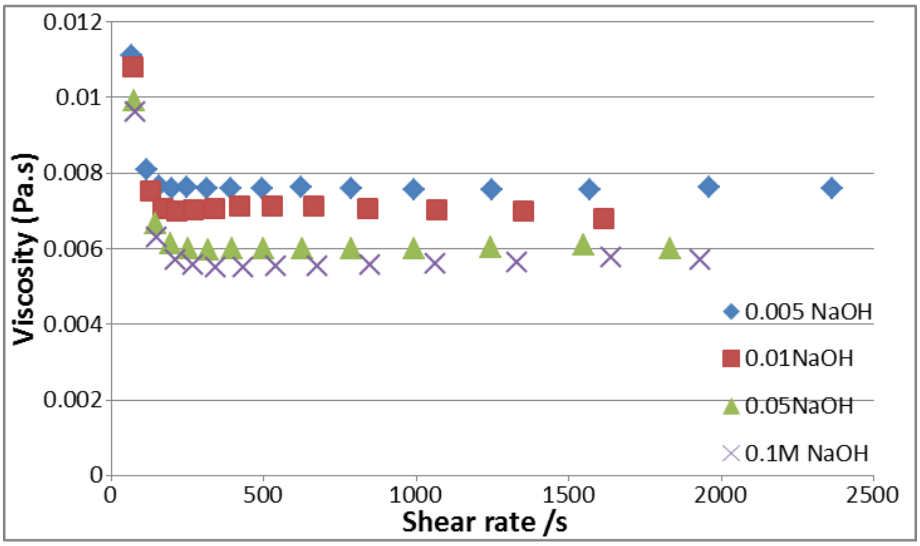

Figure 2: Flow curve ramp up for 1.0% w/w Gum Habeil in different concentrations, ♦ 0.005, ■ 0.01, ▲0.05, and × 0.1M of sodium hydroxide at (25^{o}C)

practically, solutions of 1.0% w/v Gum Habeil were prepared in 1M sodium hydroxide, 1M sodium chloride, and in distilled water. The last two solutions were prepared by stirring dry Gum Habeil (1.025 g) in 50 cm^3 2M sodium hydroxide for 5 hours and then neutralized by 1:1 v/v hydrochloric acid, and the volume of neutral was completed to100 cm^3 to prepare 1.0% w/v in 1M NaCl, then the solution was stirred overnight in roller mixer. Accurately volume (60 cm3) of salt solution was dialyzed well to remove all salt and evaporated at 50^{o}C for 4 hours and then the volume was completed to 60 cm^3 to prepare 1.0% w/v of gum solution in distilled water. Fig.3a and b show that, solution of Gum Habeil in sodium hydroxide had lower viscosity than that in distilled water under the same shear rate, and that attributed to ionization of hydroxyl groups in polysaccharide backbone (R–O-H to R –O-) and that dissociated the intermolecular association force, consequently reduction the molecular volume, and decreases the viscosity of alkali solution comparing with gum solution in distilled water, because the counter ions on sodium hydroxide attack the hydroxyl group on the polysaccharide backbone more than the charge sit on polysaccharide backbone, and this decreases the intermolecular association between polysaccharides backbone as shown in Fig.3b, while the gum solution in distilled water exhibited a higher viscosity than that in alkali and salt solvents, and this attributed to the interaction association of polysaccharides backbone [14, 15]. The study also showed that, viscosity of Gum Habeil solutions in 1M sodium hydroxide is higher than that of neutralized solution (gum solution in 1M NaCl) as would be expected from the results observed in Fig. 3a and 4, and that may be attributed to the ionic polysaccharides could display high viscosity value in water as a result of intra-chain (interaction between the opposite charge in the molecules) and inter-chains (interaction between opposite charge on two or more molecules) association and these actions may lead to increases the molecular volume, then increases the viscosity of gum solution, however, in the presence of salts, charge–charge repulsions are shielded, inter and intra molecular association are eliminated, and the salt encounter ions collapse down of the side chain on polysaccharides, and this decrease the volume of polysaccharides molecular, then decreases the viscosity of salt solution. But in case of sodium hydroxide solution the alkali encounter ions attack the hydroxyl group on the polysaccharides backbone more than the charge sit on polysaccharides backbone, this dissociated the intermolecular force without collapse down the molecular backbone [14].

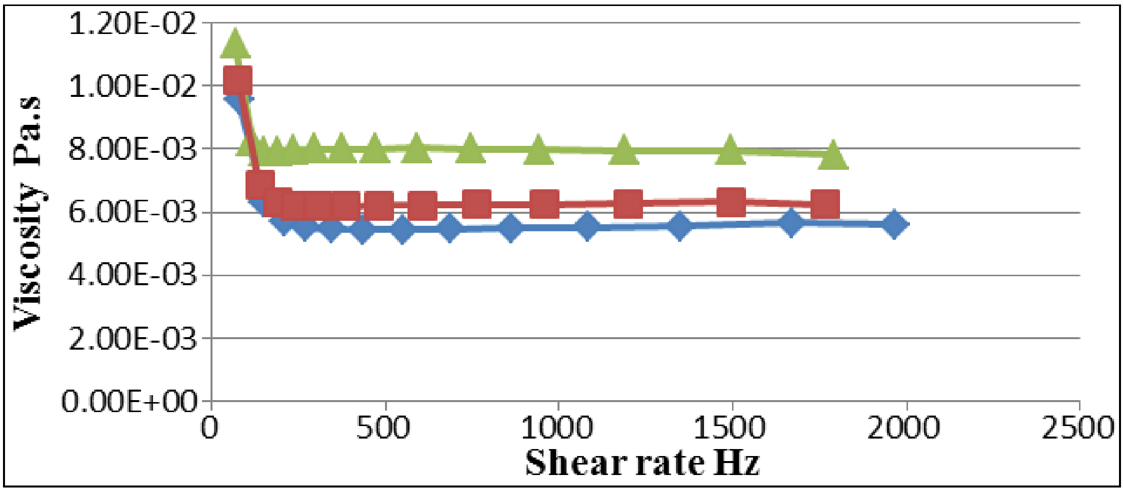

Figure 3 (a): Flow curve for 1.0% w/v Gum Habeil in 1M NaOH ▲, 1M NaCl ♦, and H2O ■ at (25°C).

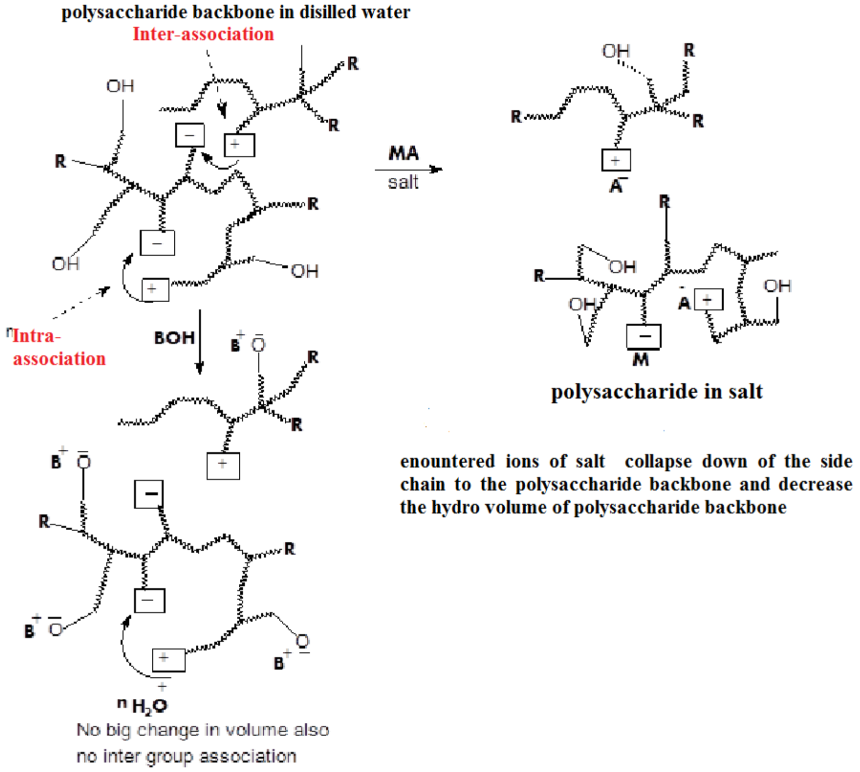

Figure 3 (b): Schematic diagram showing the hydro volume changes of polysaccharide backbone in alkaline (BOH), or in electrolyte medium (MA)

Fig.4 Shows the value of intrinsic viscosity (hydrodynamic volume) [16,17] of deacetylated gum solution prepared in 0.1M sodium hydroxide was appeared higher than that prepared in 0.1 M sodium hydroxide with added 0.9M sodium chloride. Reduction in intrinsic viscosity of deacetylated gum solution on addition of 0.9M sodium chloride may be attributed to that, the salts ions dissociated the inter and intra molecular association and this is decreased repulsion between polysaccharides backbone, causing reduction in molecular volume and hence in intrinsic viscosity of gum solution, as shown in Schematic diagram in Fig 3b.

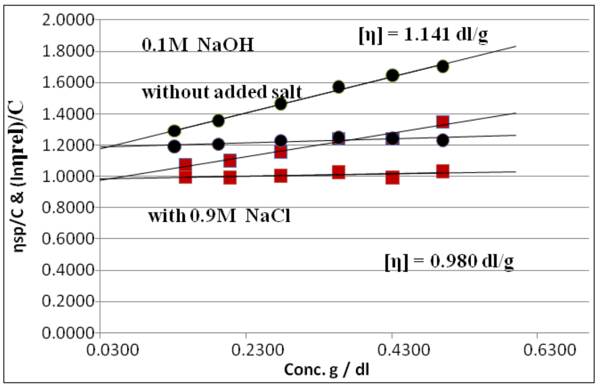

Figure 4: Reduced and inherent viscosity versus concentration of deacetylated gum solution in 0.1M NaOH with and without 0.9M NaCl at (25°C)

Fig. 5a and b show that the 'zero shear' logarithm of specific viscosity was plotted against logarithm of ,C[η]"degree of space occupancy" [18], for the deacetylated gum solutions in deionized water, and in 0.1 M sodium hydroxide alone and with addition of 0.9 M sodium chloride. The degree of space occupancy, C[η], of deacetylated gum solution in deionized water, 0.1M sodium hydroxide alone, and 0.1M sodium hydroxide with 0.9M sodium chloride equal 14.678, 2.754, and 1.659 respectively, then the critical concentration C* [19, 20] "transition from dilute to semi-dilute regime" for deacetylated gum solution in deionized water, 0.1M sodium hydroxide alone, and 0.1M sodium hydroxide with 0.9M sodium chloride equal 2.336, 2.356, and 2.409 g /dl respectively.

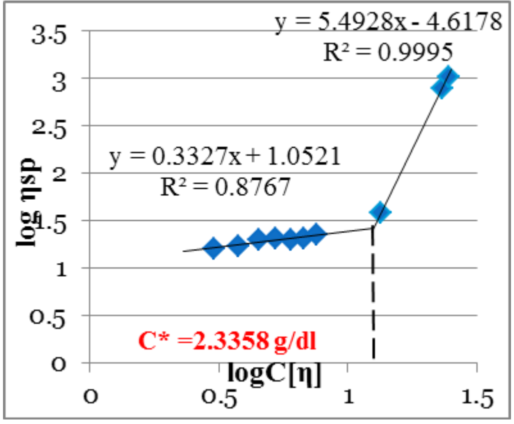

Figure 5(a): Dependence of zero-shear specific viscosity of Gum Habeil in deionized water versus degree of space occupancy at 25°C

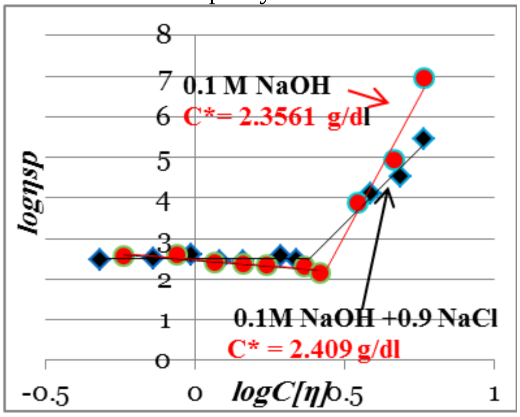

Figure 5(b): Variation of 'zero-shear' specific viscosity (25°C) with degree of space occupancy (c[η]) for gum in 0.1M NaOH (●), and 0.1 M NaOH + 0.9 NaCl (♦)

Table 1: Effect of solvents on degree of space occupancy and critical concentration (coil overlap) parameters of deacetylated gum solutions at 25°C

Gum	[η] (dl/ g)	C* a (g/dl)	C* [η]	Slope^b	
				Dilute	Entangled
H_2O	9.091	1.615	14.678	0.332	5.492
NaOH (0.1M)	1.160	2.356	2.754	.102	3.297
NaOH-(0.1M) + 0.9M NaCl	0.968	**2.409**	1.659	0.016	7.423

3.1 Effected of gum concentration on the viscosity

Fig.6 and 7 show viscosity of deacetylated gum solutions obtained for Gum Habeil at concentrations ranged from 0.5 to 4.5 w/w % in distilled water, and in 1M sodium hydroxide versus shear rate. For a dilute solution less than 2.335 % w/w in distilled water, and less than 2.039 % w/w in 1M NaOH medium, the flow curves exhibited smoothly reduction in viscosity with increases shear rate (shear-thinning) at shear rates less than 200 s^{-1}. The onset of Non-Newtonian behavior (shear-thinning) moves to progressively lower shear rate with increasing concentration of deacetylated gum solutions, while the viscosity of dilute solutions at higher shear rates will not change as the shear rate is varied (Newtonian behavior) . In shear-thinning region at low shear rates, the rate of re-entanglements between the gum polysaccharide backbone becomes higher than the rate of forced disentanglement by flow rate[21, 22].

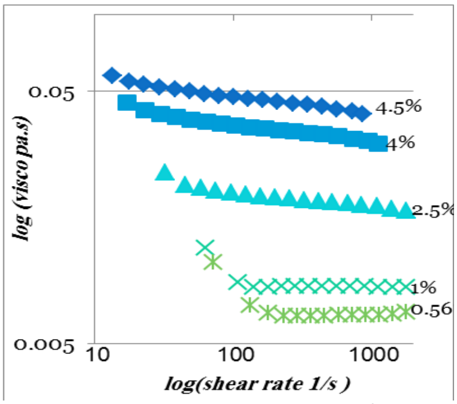

Figure 6: Flow curve (at temperature 25°C), shear rate versus viscosity of different concentrations of deacetylated gum solution in distilled water.

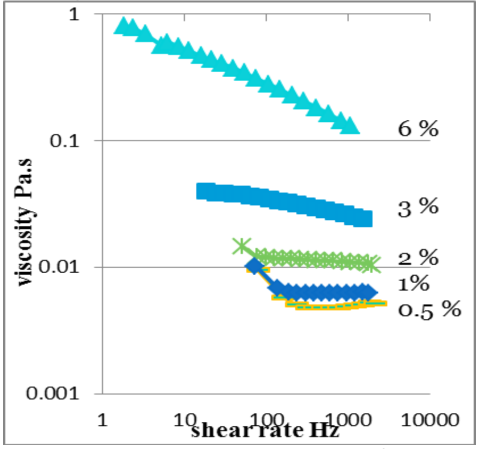

Figure 7: Flow curve (at temperature 25°C), shear rate versus viscosity of different gum concentrations in 1M NaOH.

3.2 Dynamic rheological properties

The oscillatory measurements methods were carried to study and compare the viscoelastic (G') behaviors of aqueous gum solutions, because the results are more sensitive to the chemical compositions and physical structures of polysaccharide backbone [23, 24]. Fig.8 A, B, and C Show the frequency dependence of the storage modulus (G') and loss modulus (G") at 25°C for aqueous deacetylated gum solutions as a function of concentration, at a low concentration of deacetylated gum solution in distilled water the G' (viscoelastic) was appeared higher than G" (viscosity) at low frequency region, and G" to be higher by increasing the concentration that means the system to be more viscous when the concentration was increased. However, a crossover of G' and G" lines were observed at 1.26, 3.97 and 9.99 Hz for 1.5, 3 and 5%w/v of deacetylated gum solutions respectively. Fig.8B shows that at low frequency G" larger than G', but with increases the frequency G" and G' lines intersected in the middle of frequency range due to the tendency of system to entanglement. While Fig.8C shows the crossover between G" and G' lines appeared at high frequency due to resistant the disentanglement.

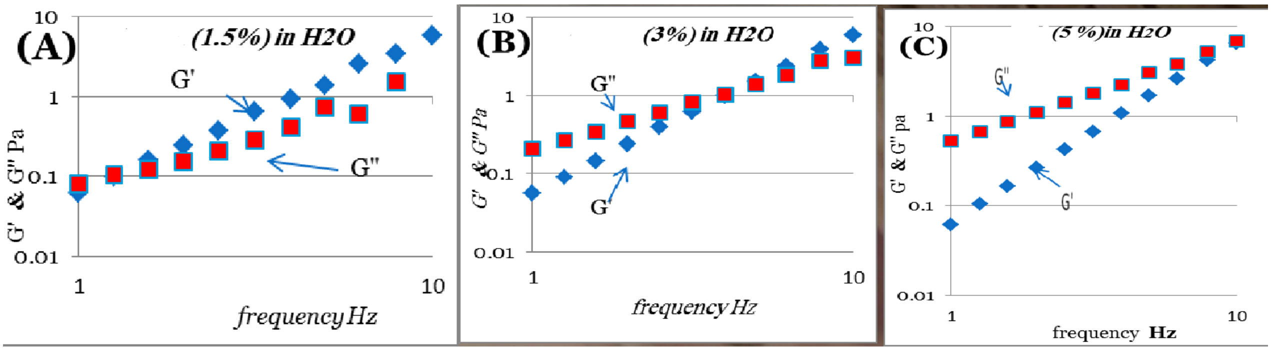

Figure 8: A, B, and C Dynamic viscoelastic parameters of deacetylated gum solutions in distilled water

The G' module dependence on frequency (f) according to the G' α fα relationship was determined from the slope of the double logarithmic plot of storage modulus (G') versus frequency [25,26]. Fig. 9 and Table 2 show that the slope values (α) of 1.5 to 5% w/v deacetylated gum solutions in distilled water increased with increasing concentration, indicating decreases the gel strength. The concentration (C) dependency of storage modulus generally obeys a power law relationship G' α C^{β} [20]. Fig.10 shows the double logarithmic plot of (G') versus concentrations (C) of aqueous solution of deacetylated gum, the storage modulus (G') was increased smoothly with increases the concentration, and the slope value (β) of deacetylated gum solutions over a concentration ranged from 1.5 to 5 % w/v equal 1.16. which is lower than the value reported for 0.2 to 2% ordered xanthan β equal 2.0, and for a polysaccharide from Sterculia striata β equal 2.8. In contrast, for concentration ranged from 0.1 to 1% w/w of Aeromonas gum solution β equal 0.41, and over a concentration ranged from 1 to 5%w/w β equal 3.97 [24].

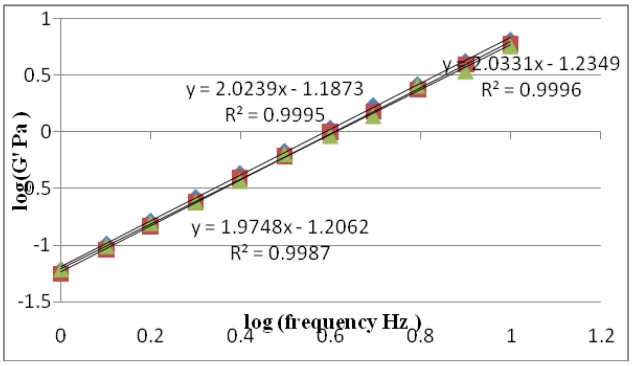

Figure 9: log (G') versus log (f) for deacetylated gum solutions in, ▲ dilute 1.5g/dl, ■ semi-dilute 3g/dl, and ♦ concentrated 5g/dl regime at 25°C

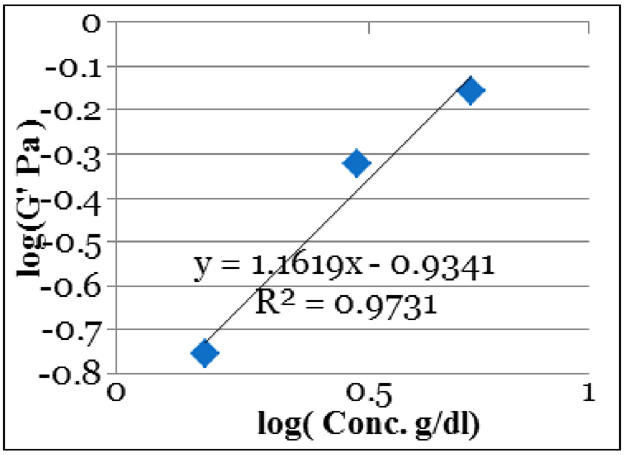

Figure 10: Double logarithmic plot of the G' module versus gum concentration in dilute, semi dilute and concentrated regime.

Table 2: The dynamic viscoelastic parameters of deacetylated gum solution in distilled water

Conc. (g /dl)	Freq. - dependent Parameter		Con. - dependent Parameter	
	α	r^2	β	r^2
0.5	1.974	0.998	1.161	0.973
5	2.023	0.999		
5	2.033	0.999		

3.3 Dynamic rheological of crude gum dispersion

The viscoelastic behavior of the crude gum dispersion was measured over the frequency ranged from 1 to 10 Hz at 25°C. Fig.11 B, and C show the frequency dependence of the dynamic viscous modulus (G") and viscoelastic modulus (G') at 25°C for 12.5 and 15% w/w of aqueous crude Gum Habeil solutions, the G' showed a weak dependence on frequency and was appeared higher than G" and this indicated the high concentrated crude gum solutions exhibited typical gel behavior. While Fig.11A shows that for

10% w/w of aqueous crude gum solution the frequency dependence of the dynamic viscous modulus (G") at low frequency was appeared higher than G', and the crosslink points between G" and G' was observed at 5.974 Hz.

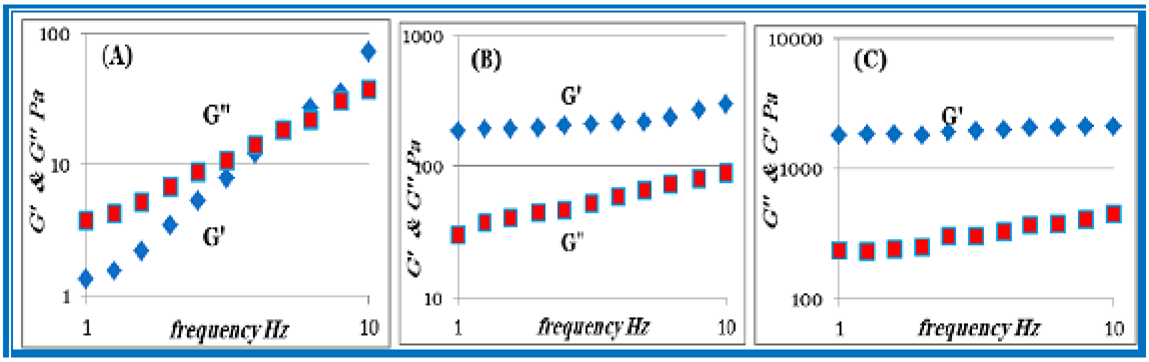

Figure 11: Effect of frequency on elastic modulus (G') and viscous modulus (G") of A 10 % w/w, B 12.5 % w/w, and C 15 % w/w aqueous dispersion of gum solutions

3.4 Temperature influences on Gum Habeil viscosity

Fig12 shows that the temperature ramp up and down – viscosity curves for the different concentrations of deacetylated gum solutions in distilled water at constant shear rate, viscosity of deacetylated gum solutions increased with increase concentration at affixed temperature and shear rate. For the dilute, semi-dilute, and concentrated solutions viscosity decreases steeply during the temperature increases, for dilute and semi-dilute solutions (1 and 2 g/dl) the viscosity measured during increasing temperature (ramp-up) from a 25 to 60°C is slightly higher than that measured during the temperature ramp-down from 60 to 25°C and this phenomenon becomes more evident in the dilute regime than in the concentrated regime. This feature can be attributed to the inertia effect, or the development of dilute–semi dilute regime and re-entanglement in concentrated-regime.

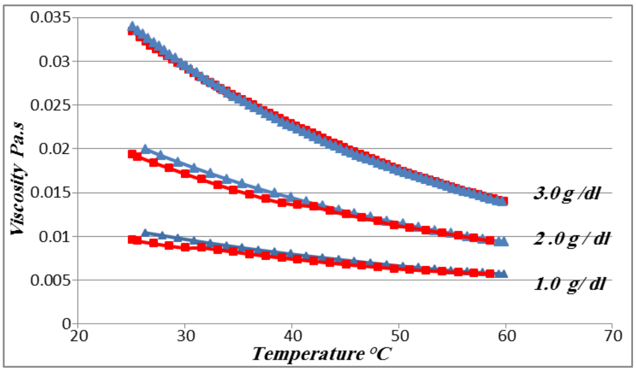

Figure 12: Ramp up (▲) and down (■) of temperature versus viscosity at constant shear rate of Dilute (1.0 g/dl), semi-dilute (2.0 g/dl), and concentrated solution (3.0g/dl) of gum dispersion

4. Conclusion

The effect of solvents (alkali alone and with salt) on the viscosity, space of occupied, and intrinsic viscosity was determined. The studies showed that 'zero-shear' log(ηsp) versus log(C[η]) for deacetylated gum solution in deionized water, 0.1M sodium hydroxide, and 0.1M sodium hydroxide with 0.9M sodium chloride is appeared in two linear regions (dilute - entangled), with slope ranged from; 0.33 to 5.49 at C[η] equal 14.678, 0.102 to 3.297 at C[η] equal 2.754, and 0.016 to 7.423 at C[η] equal 1.569 respectively. The deacetylated gum solutions was exhibited shear thinning fluids in the shear rate less than 200 s^{-1}. The dilute solution of deacetylated gum in water exhibited viscoelastic behavior, but with increases the concentration G" trend to be higher than G' due to increase the entanglements with increases the concentration. Increasing temperature from 25 to 60oC significantly decrease viscosity of Gum Habeil solution due to the increase the kinetic energy.

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