

SOME FUNCTIONAL PROPERTIES OF POLYSACCHARIDES FROM DIFFERENT SOURCES FOR APPLICATION IN FOOD PRODUCTS

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ABSTRACT

Functional properties of *Rhizobium* polysaccharide (RPS), xanthan, gellan, carrageenan and guar gums were measured under different conditions. Solutions of polysaccharides had a dynamic viscosity that was dependent on shear rate and gum concentration. Xanthan, RPS, and guar gum gave highly viscous solutions at 0.4% (w/w) concentration. Low levels of Ca^{++} cation were more effective gel-formers than Na^+ cation in a 0.5% carrageenan and gellan solutions, only 1/30 to 1/50 of the monovalent cation concentration was needed to form divalent cation gels with similar strength. With decreasing pH down to 3.5, gellan and carrageenan formed more strong gel with and without Na^+ and Ca^{++} cations. Addition of 0.5% (w/w) of RPS, xanthan and guar gum to the aqueous phase considerably reduced the oil weight required to form emulsion to 15.87, 20.0 and 20.0 g respectively compared to 70 g for control emulsion. Less than 0.1% of different polysaccharides was needed to improve the foam capacity and stability of stiff foam (milk protein, water and sugar).

Key Word: *Rhizobium* polysaccharide, Xanthan, Gellan gum, Carrageenan, Guar gum, Viscosity, Gel formation, Emulsion capacity, Foaming capacity and stability

INTRODUCTION

Polysaccharides are polymers composed of one type of sugar structural unit (homoglycans) or of several types of sugar unit (heteroglycans). They are obtained from a variety of sources (i.e. seaweeds; seed gums; exudates gums and microbial biosynthesis). Polysaccharides commonly referred to as "gums" are used in foods as thickeners, stabilizers; gelling

agents and in some as cases emulsifiers (Ma and Barbosa-Canovas, 1993; Sanderson, 1996 and Belitz and Grosch, 1999).

Xanthan, gellan and *Rhizobium* gums are microbial heteropolysaccharides produced by the fermentation of *Xanthomonas campestris*, *Sphingomonas elodea* and *Rhizobium meliloti* respectively (Nishinari *et al* 1996 and Tavernier *et al* 1997).

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(Received September 4, 2002)

(Accepted October 7, 2002)

Xanthan gum solution has some useful properties, stability against pH, temperature and existence of salts in the solution, and high viscosity even at low concentration. It is completely soluble in water giving novel weak gel rheology, and its solution is pseudoplastic (Roller and Dea, 1992 and Xuewu *et al* 1996).

Rhizobium polysaccharides (RPS) are commercially useful for modifying rheological properties of aqueous systems (Tavernier *et al* 1997 and Nagwa *et al* 1997).

Gellan gum gives aqueous solution with low viscosity at elevated temperature but forms gel upon cooling. Cations such as calcium, magnesium, potassium and sodium are required for gelation (Roller and Dea 1992 and Tang *et al* 1997).

Carrageenans are sulfated polymers which extract from certain red marine. Three main fractions have been identified, Iota, Kappa and Lambda and commercial carrageenans are mixtures of these three fractions. Carrageenan has been used for its gelling, thickening, stabilizing, emulsifying and suspending properties (Dziezak, 1991; Paulo *et al* 1994; Ridout *et al* 1996 and Williams and Langdon 1996).

Guar gum is obtained from the ground endosperm of the guar plant, (*Yamposis tetraganolobus*). It is non gelling, and is used chiefly as a viscosity builder, stabilizer and water binder. Since guar gum is non ionic, it is very stable from pH 4 to 10 (Dziezak, 1991 and Chinachoti, 1995).

Selection of the best polysaccharide for a given application in processed foods and a wide variety of food products depended almost exclusively on their func-

tional properties in solution. Therefore, the present investigation was carried out to study the functional properties of some polysaccharides under different conditions to provide a useful data on solution properties that may employed as guidelines in formulating food stuff containing different polysaccharides.

MATERIAL AND METHODS

Polysaccharides

Polysaccharides from different sources including xanthan, gellan, carrageenan and guar gums obtained from Sigma Chemicals Co. (st. Louis, Mo), USA are used in this study. *Rhizobium* polysaccharide (RPS) produced by fermentation of *Rhizobium meliloti* (EMCC-10011) as described by Madkour *et al* (1997) is also used.

Functional properties

Thickening

Thickening ability of different solutions of polysaccharides, due to their ability to record high values of dynamic viscosity was measured. Dynamic viscosity measurements of 0.1, 0.2, 0.3 and 0.4% (w/w), solutions of the tested polysaccharides were determined by using the Rotational Viskometer (Rheotest 2-Medingen-Germany) according to Swiderski *et al* (1993) at shear rates 3, 5.4, 9, 16.2, 27, 48.6, 243, 729 and 1312 s⁻¹ at room temperature. The dynamic viscosity was calculated as follows :-

$$\eta_{dyn} = \tau / \dot{\gamma}$$

$$\tau = z \cdot a$$

$$\eta_{dyn} : \text{Dynamic viscosity (Pa.s)}$$

- τ : Shear stress (dynes/cm²)
 z : Cylinder (constant)
: 5.81 constant of cylinder (s_1)
 α : Read out value
 γ : Shear rate (s⁻¹)

Solubility

Solubility of different polysaccharides in cold water (4° C) and hot water (90°C) was tested according to Sharma (1981).

Gel formation

The ability of different polysaccharide solutions to form gel at different concentrations was studied according to Comfort *et al* (1996). The effect of monovalent (NaCl), divalent (CaCl₂) cations at different levels, sucrose concentration and pH values on gel formation was also studied . Polysaccharide was dissolved in hot water at 90°C for 20 min to prepare a solution and then cation salt was added . The ability of different polysaccharides solutions to form gel was observed during cooling of the hot solution (Tang *et al* 1997).

Emulsion capacity

Control emulsion (without polysaccharide) was prepared using 70 g corn oil, 27 g water and 3.0g egg yolk powder as emulsifier according to Hennock *et al* (1984). Effect of kind and level (0.1, 0.2 and 0.5%) of polysaccharide on emulsion capacity (the oil weight required to form oil/water emulsion with constant aqueous phase, 30 g) was measured. Emulsion was prepared using a Waring commercial food blender and was sheared typically for 2-3 min .

Foaming capacity and stability

Stiff foam, which is used as a part of short nougat formula, was prepared by whipping of 0.3 g high quality modified milk protein, 6.4 g icing sugar and 3.8 g water for 5 min DMV-International (1997). Effect of kind and level of polysaccharide on foam capacity and stability was measured . Foam capacity (FC) was calculated according to Matringe *et al* (1999) as follows :

$$FC\% = \frac{\text{Foam volume} - \text{Initial suspension volume}}{\text{Initial suspension volume}} \times 100$$

Foam volume stability (FVS) was followed during 24 h at room temperature and was calculated according to Mahran *et al* (1994) as follows :

$$FVS\% = \frac{\text{Foam volume}}{\text{Initial volume of foam including liquid}} \times 100$$

RESULTS AND DISCUSSION

Thickening properties

The ability of thickening aqueous solutions (refers to viscosity) is one of the important application of polysaccharides in foods. Therefore, the dynamic viscosity of different aqueous solutions of polysaccharides was measured at different shear rates at 25°C and the results are illustrated in Figures (1 and 2). Increasing of shear rate from 3 to 48.6 s⁻¹ resulted in a significant decrease of dynamic viscosity for various solutions of polysaccharides . This may be accounted for changes in the structure of the solutions due to the action of considerable shearing stresses.

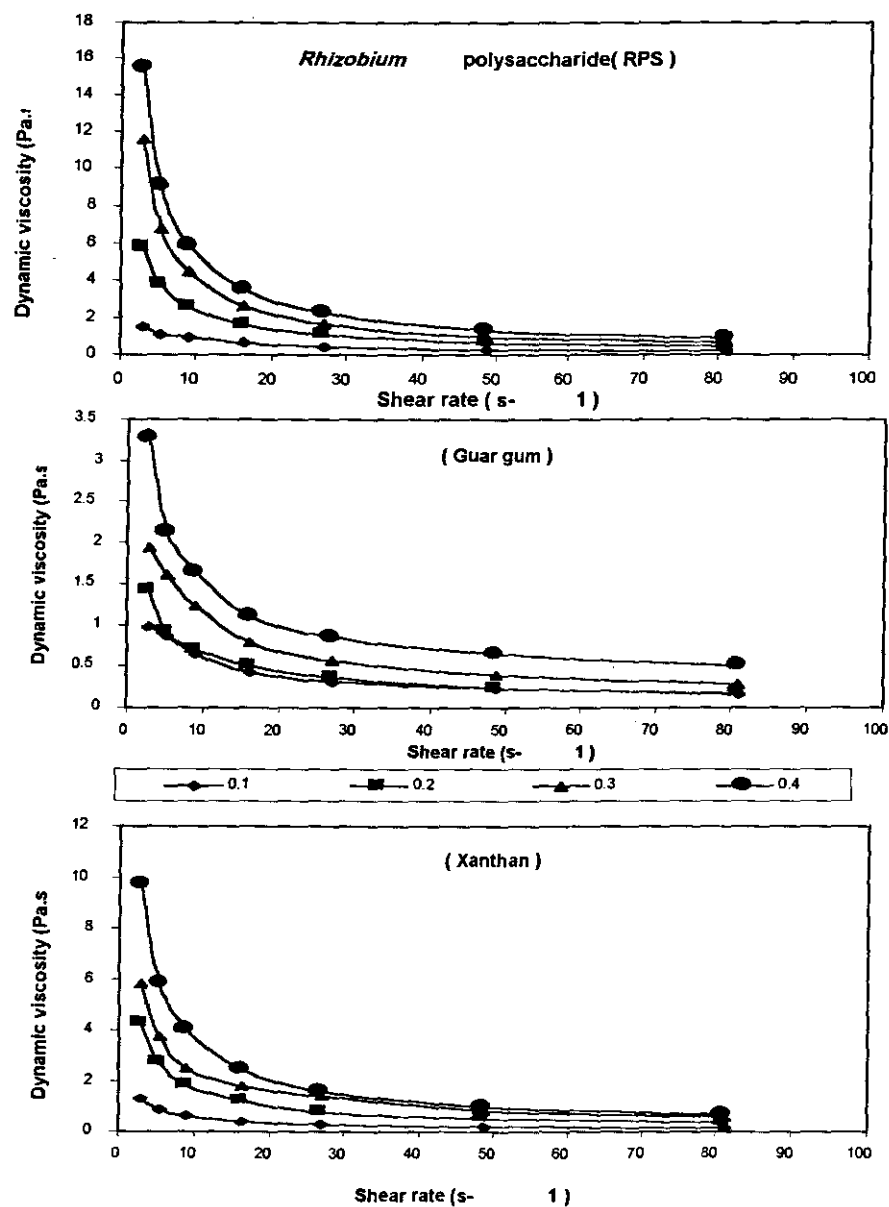


Fig. 1. The effect of shear rates on the dynamic viscosity of different concentrations of (RPS), guar gum and xanthan at 25°C.

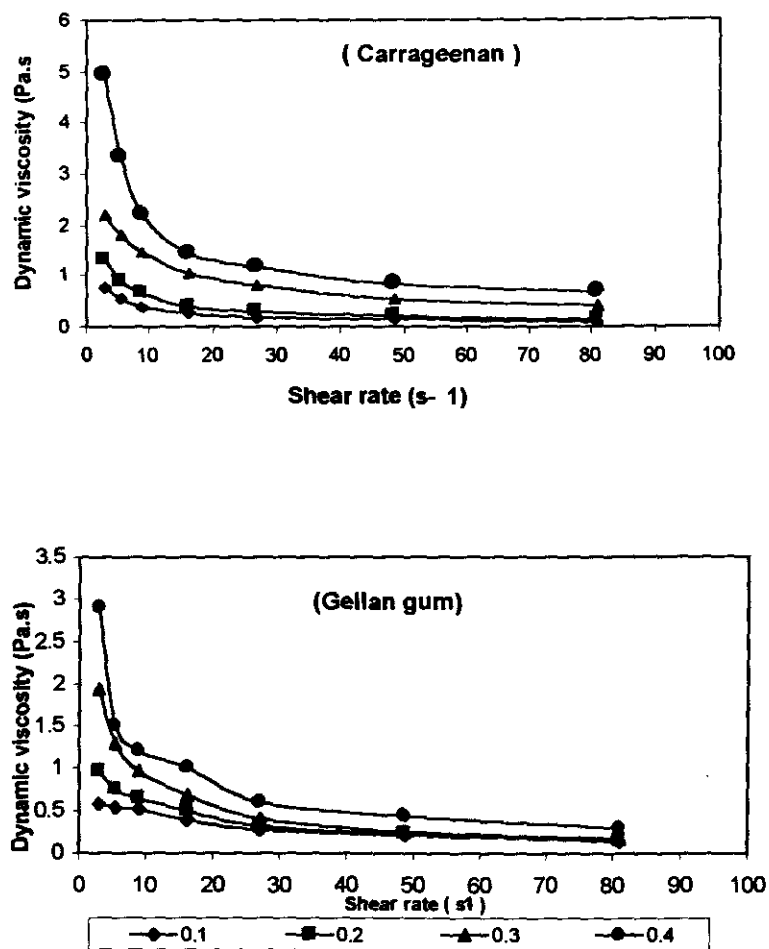


Fig. 2. The effect of shear rates on the dynamic viscosity of different concentrations of carrageenan and gellan gums at 25°C

resulting in destruction of the structures formed (Swiderski *et al* 1993). No considerable change of viscosity was observed as the shear rate was increased above 48.6 s^{-1} .

Results also showed that the viscosity increased with increasing of polysaccharide in the solution, indicating that the solutions become more pseudoplastic when rising the level of gums. At shear rate 48.6 s^{-1} the dynamic viscosity was 0.3 Pa.s for 0.1% *Rhizobium* polysaccharide (RPS) and it was increased to 1.32 Pa.s for 0.4% (RPS). The same trend was observed for the other tested polysaccharides. These results are in agreement with those obtained by Beyer and Melton, 1987; Swiderski, *et al* 1993; Pastor *et al* 1994 and Xuewu *et al* 1996.

The effect of kind and concentration of polysaccharide on dynamic viscosity of their aqueous solutions measured at constant shear rate 48.6 s^{-1} and 25°C are given in Fig (3). Results showed that dynamic viscosity is directly proportional to polysaccharides concentration. The highest viscosity was observed for 0.4% of RPS and xanthan solution. However, the lowest viscosity was obtained for 0.4% gellan solution. Similar results are obtained by Nagwa *et al* (1997).

Gel formation

The ability of different polysaccharides to soluble in hot or cold water and to form gel at different concentrations are given in Table (1).

Table 1. Gelling ability and solubility of some polysaccharides

Polysaccharides	Concentration (%)			Solubility	
	0.1	0.5	1.0	Cold water	Hot water
RPS	-	-	-	+ *	+ *
Xanthan	-	-	-	+ *	+ *
Carrageenan	+	+	+	+ *	+ *
Guar gum	-	-	-	+ *	+ *
Gellan	-	+	+	- *	+ *

RPS : *Rhizobium* polysaccharide .

(-) : cannot form gel

(+) : form gel

(- *) : cannot dissolve

(+ *) : soluble

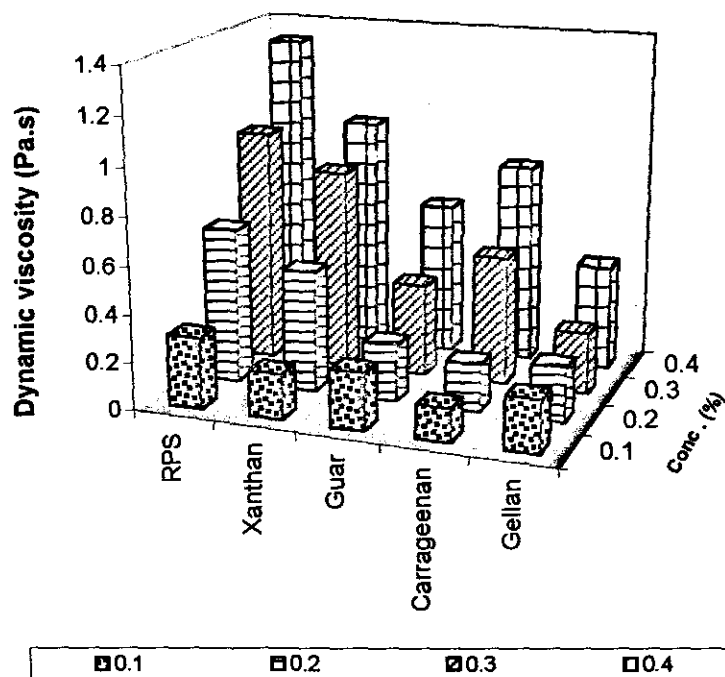


Fig. 3. The effect of kind and concentration of different polysaccharides on dynamic viscosity of their aqueous solutions at 25°C and 48.6 S-1.

Xanthan, RPS and guar gum can not form gel at different tested levels but formed only highly viscous solutions. Oppositely, carrageenan had the ability to form gel at different tested levels and it was more firm at high level. Depending upon the level of gum in solution, gellan exhibited differences in gel forming, i.e. it formed gel at high level only (0.5 and 1.0 %). Generally, carrageenan formed firm gel than gellan gum at a given concentration. Most of the tested polysaccharides completely soluble in both cold and hot water, except of gellan which can not dissolve in cold water.

Similar results are obtained by Sharma (1981).

Results in Table (2) represented the influence of different levels of monovalent Na^+ and divalent Ca^{++} cations on gel forming of 0.5% (w/w) gellan and carrageenan solutions.

Gellan solution can form gel with different strength in the presence of only high levels of Na^+ cation. With all tested levels of Na^+ cation, carrageenan formed clear gel but it was less firm than that of gellan gel specially over 0.3 M of Na^+ cation. Both of gellan and carrageenan formed gels with similar strength in the presence of low levels of Ca^{++} cation.

Table 2. Effect of different levels of monovalent and divalent cations on gel formation of 0.5 % solution of carrageenan and gellan gums.

Added cations (M)		Carrageenan	Gellan
Na ⁺	0.00	+ *	+
	0.01	+	-
	0.03	+	-
	0.05	+	-
	0.10	+	-
	0.20	+	+
	0.30	+	++
	0.40	+	+++
	0.50	++	++++
	0.60	++	++++
	0.70	++	++++
Ca ⁺⁺	0.00	+	+
	0.01	++	++
	0.03	+++	+++
	0.05	+++	+++
	0.10	+++	+++

(-) : cannot form gel

* : form gel with different strength : -

(+) : weak

(++) : medium

(++) : strong

(++++) : very strong

Also, much higher levels of Na⁺ cation are required to form gel from gellan and carrageenan solutions than Ca⁺⁺ cation, only 1/30 to 1/50 of the monovalent cation concentration was needed to form divalent cation gels with similar strength. Similar results are obtained by Moritaka *et al* 1995; Tang *et al* 1995 & 1997.

They indicated that divalent cations are more effective gel formers than monovalent cations in gellan solutions.

Effect of pH values on gel formation of 0.5% of gellan and carrageenan solutions in the presence of either 0.5 M Na⁺ or 0.03 M Ca⁺⁺ are given in Table (3).

Table 3. Effect of pH and 0.5M monovalent or 0.03M divalent cations on gel formation of 0.5% solution of carrageenan and gellan gums.

Added cation (M)	0.5% carrageenan			0.5% gellan		
	pH (values)			pH (values)		
	7.9	6.0	3.5	6.5	6.0	3.5
0	+ *	+	++	+	-	+
0.5 Na ⁺	++	+	++	++++	++++	++++
0.03 Ca ⁺⁺	+++	++	+++	+++	++	+++

(-) : cannot form gel

* : form gel with different strength :

(+) : weak

(++) : medium

(+++) : strong

(++++) : very strong

At pH 3.5, carrageenan gel (without cations) became more firm than at high pH. However, either at pH 7.9 or 3.5 carrageenan solution formed gels with similar strength in the presence of Na⁺ or Ca⁺⁺ cations. On the other hand, gellan solution (without cations) formed similar weak gels at pH 6.5 and 3.5 and failed to form gel at pH 6.0. With 0.5M Na⁺, gellan solution formed gels with similar strength at different tested pH. With 0.03M Ca⁺⁺, gellan solution formed similar firm gels at pH 6.5 and 3.5 than at pH 6.0. Similar results are obtained by Moritaka *et al* (1995). They found that hydrogen ions compensate negative charges of carboxyl groups and shield the electrostatic repulsion of gellan gum molecules. Therefore, the increase in hydrogen ions may enhance the number of junction zones in gellan gels.

Effect of sucrose level (20, 40 and 60%) and pH-values on gel formation of 0.5 % (w / w) of carrageenan and gellan

solutions are given in Table (4). At different sucrose levels, carrageenan solution formed gels with similar strength at various pH, except for sample with 60 % sucrose and pH 3.5 which formed more firm gel. Gellan solution lost its ability to form gel in the presence of different levels of sucrose except with 40% sucrose and pH 3.5 which formed strong gel than control (without sucrose). Comfort *et al* (1996) reported that depending upon the level of soluble solid in a system, gellan gum exhibits differences in gelation behavior with resulting textural changes.

Emulsion capacity

Consumption of low calorie sauce is increasing every day in comparison to traditional emulsified sauces that contain around 70% oil. In a light sauce formulation it is necessary to substitute a great part of oil, mainly with water (Ferragut *et al* 1993).

Table 4. Effect of sucrose level and pH values on gelling ability of 0.5% solution of carrageenan and gellan gums.

Sucrose Levels (%)	0.5% carrageenan			0.5% gellan		
	pH (values)			pH (values)		
	7.9	6.0	3.5	6.5	6.0	3.5
0	+	+	++	+	-	+
20	+	+	+	-	-	-
40	+	+	+	-	-	++
60	+	+	++	-	-	-

(-) : cannot form gel

* : form gel with different strength : -

(+) : weak

(++) : strong

Therefore, the influence of different levels of polysaccharides on emulsion capacity (the oil weight required to form emulsion with constant aqueous phase (30 g) are given in Fig (4).

Addition of different sources polysaccharide to the aqueous phase considerably reduced the oil weight especially at high level. Addition of 0.5% (w/w) of

xanthan, RPS and guar gum considerably reduced the oil weight to 15.87, 20.0 and 20.0 g compared to 70 g for control emulsion (without polysaccharide). This could be referred to high viscosity of the emulsion formulated with xanthan compared to the emulsions made with other polysaccharides. Similar results are obtained by Ma and Barbosa-Canovas (1995).

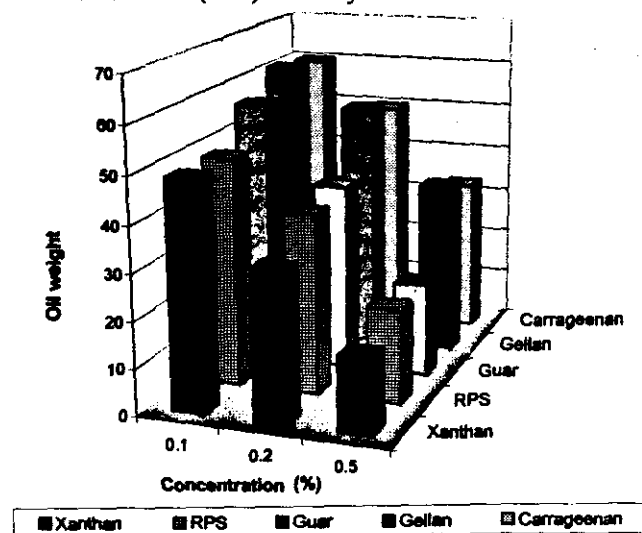


Fig. 4. Effect of kind and concentration of polysaccharide on emulsion capacity (the oil weight required to form oil / water emulsion) with constant aqueous phase (30).

Foam capacity and stability

High quality modified milk protein is an industrial whipping or aerating agent used in all recipes of some confectionery as stiff foam (high quality modified milk protein, water and sugar) such as sponges, nougat and meringues. Therefore, the influence of some polysaccharides on stiff foam capacity was measured as a function of the gum concentration and the results are given in Table (5).

Depending upon the level and the kind of polysaccharide, stiff foam exhibited differences in foam capacity. Addition of high levels of both xanthan and RPS (0.2%) and low levels of carrageenan, gellan and guar gums (0.005%) completely inhibited the foaming properties of milk protein. The air incorporation capacity of the samples decreased when the xanthan, carrageenan and guar gum level increased above 0.01%. This

result is in agreement with those previously reported for different hydrocolloids, Ghita *et al* 1992 and Camacho *et al* (1998).

Influence of kind and level of polysaccharide on stiff foam volume stability has been followed throughout 24 h at room temperature and the results are represented in Fig (5). Low stability was observed for different samples containing low levels of polysaccharides during storage, whereas for the rest of the formulations it remained more stable. The maximum foam stability (100%) occurred for samples with 0.05% and 0.1% xanthan, 0.1% RPS and 0.2% guar gum. Camacho *et al* (1998) found that changes in mechanical parameters and overrun during chilled storage of the foam, were inhibited by the gums at weight percentages higher than 0.05% and so the higher the emulsion viscosity the greater the foam structure preservation.

Table 5. Effect of kind and concentration of polysaccharides on foam capacity (%) of stiff foam.

Conc . of Polysaccharides (%)	RPS	Xanthan	Carrageenan	Guar gum	Gellan
0 (control)	350.0	350.0	350.0	350.0	350.0
0.005	437.5	437.5	-	-	-
0.01	462.5	550.0	512.5	450.0	412.5
0.05	525.0	375.0	462.5	412.5	412.5
0.1	300.0	250.0	387.5	375.0	500.0
0.2	-	-	362.5	350.0	400.0

RPS : *Rhizobium* polysaccharide

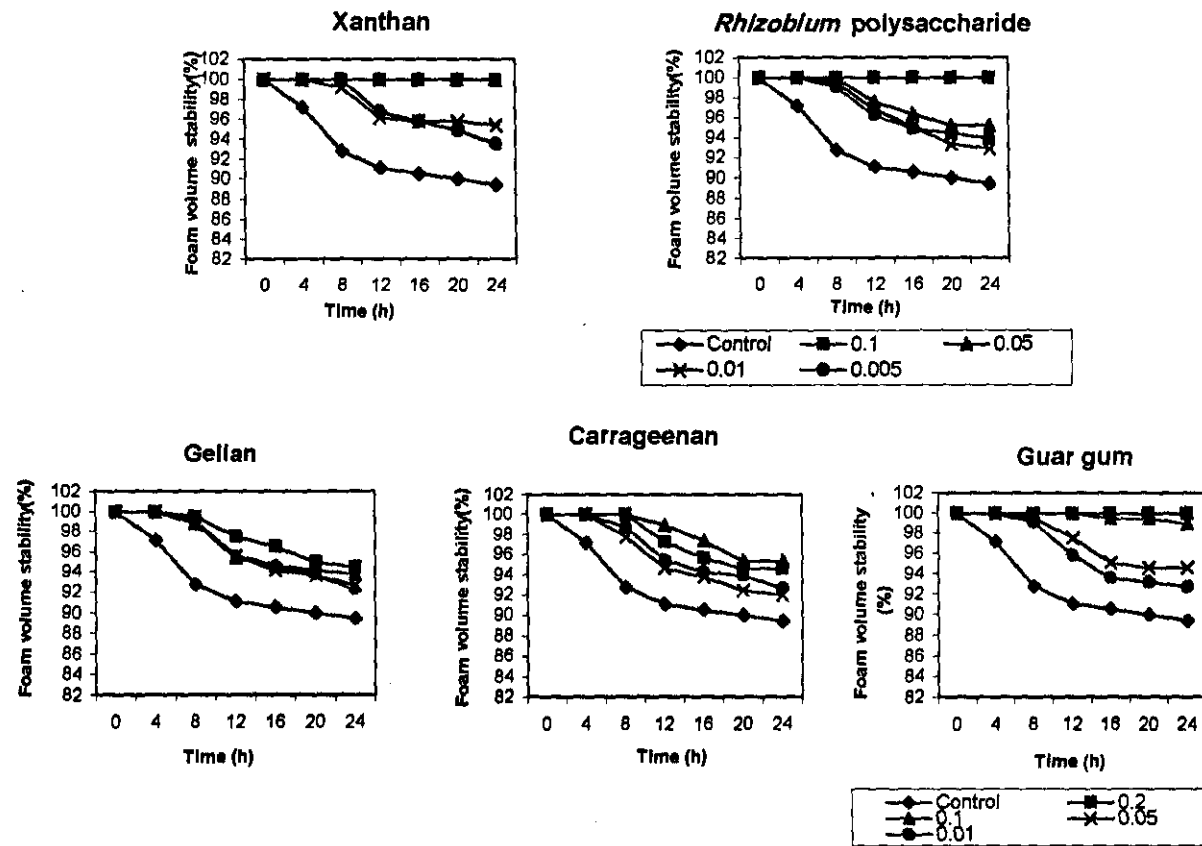


Fig (5) . Effect of kind and concentration of polysaccharides on foam volume stability(%) of stiff foam during 24 h of storage at room temperature .

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مجلة حوليات العلوم الزراعية ، كلية الزراعة ، جامعة عين شمس ، القاهرة ، م (٤٧)، ع (٢)، ٧٠٧-٧٢١، ٢٠٠٢

بعض الخصائص الوظيفية للسكريات العديدة من مصادر مختلفة لاستخدامها في المنتجات الغذائية

[٤٥]

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١- قسم علوم وتكنولوجيا الأغذية - كلية الزراعة - جامعة عين شمس - شبرا الخيمة - القاهرة - مصر

مماثل في القوة من الكاتيونات الثنائية. ويؤدي خفض رقم الحموضة إلى قيم ٣,٥ إلى تكوين جيل أكثر قوة من الجيلان والكاراجينان في وجود أو عدم وجود كاتيونات ص⁺، كا⁺⁺. كما أن إضافة ٠,٥% من كل من الزانثان ، RPS وصمغ الجوار إلى الوسط المائي أدى إلى خفض ملحوظ في وزن الزيت اللازم لتكوين المستحلب إلى ١٥,٨٧ ، ٢٠,٠ ، ٢٠,٠ جم على التوالي بالمقارنة بعينة الكنترول حيث كان وزن الزيت ٧٠,٠ جم. ووجد أن إضافة تركيز أقل من ١% من السكريات العديدة إلى stiff foam أدى إلى تحسين سعة وثبات الرغوة الناتجة.

قدّرت الخصائص الوظيفية للسكريات العديدة من الـ *Rhizo- polysaccharide bium* (RPS) ، الزانثان ، الجيلان ، الكاراجينان وصمغ الجوار وذلك تحت ظروف مختلفة. وجد أن للزوجة الديناميكية لمحاليل هذه السكريات العديدة تتوقف على معدل القص وتركيز الصمغ. وأعطى RPS والزانثان وصمغ الجوار محاليل عالية اللزوجة عند تركيز ٠,٤% (وزن / وزن). واتضح أن المستويات المنخفضة من كاتيونات كا⁺⁺ كانت أكثر كفاءة في تكوين الجيل في محاليل ٠,٥% من الكاراجينان والجيلان وذلك عن كاتيونات ص⁺ ، حيث نحتاج فقط ٣٠/١ إلى ٥٠/١ مول من تركيز الكاتيونات الأحادية لتكوين جيل

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