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Influence of dextran, pullulan and gum arabic on the physical properties of frozen sucrose solutions

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Abstract

The objective of this work was to understand the mechanisms and the factors controlling the stability of frozen products through the study of the influence of polysaccharides on the physical properties of frozen sucrose solutions (to 57.5 and 67.5% w/w). The polysaccharides studied were dextran at different molecular weights (from 10^4 to 2×10^6 g/mol), pullulan (both considered like linear polysaccharide) and gum arabic (considered like branched polysaccharide).

With 1% of polysaccharide, neither the structure nor the molecular weight of polysaccharide had an influence on the viscosity. However, with 10% of polysaccharide, pullulan was the only polysaccharide that increased the viscosity of the sucrose solution. Viscoelastic behavior (characterized by storage moduli G', loss moduli G'' and loss angle δ) of sucrose solutions was not modified by the presence of dextran, gum arabic or pullulan. These results were confirmed by differential scanning calorimetry (DSC).

Keywords: Dextran; Pullulan; Gum arabic; Sucrose

1. Introduction

Polysaccharides are widely used in food products, sometimes for technological reasons such as process aids to stabilize emulsions, giving the physical structure required for packing or distribution. They are also used to enhance (or standardize) the 'eating quality' of the product (Morris, 1989).

In frozen foods, it has shown that polysaccharides increase the shelf-life of ice cream, improve organoleptic properties, decrease the ice and lactose crystal growth and increase the resistance to melting (Carrington, Goff, & Stanley, 1996; Goff, 1995; Goff & Sahagian, 1996).

The mechanism of action of polysaccharides in enhancing frozen stability is related to the control of the amorphous matrix surrounding the ice crystals (Levine & Slade, 1988). In the viscoelastic liquid surrounding the ice crystal, the polysaccharides concentration can be relatively high, exceeding its critical concentration. Consequently, polysaccharides chains can become entangled.

Recently, Goff, Caldwell, Stanley, and Maurice (1993) and Sahagian and Goff (1995) proposed a mechanism related to the action of polysaccharides in the cryo-concentrated phase. Thus, polysaccharides induce a modification in the diffusion properties of both water and solute molecules in the unfrozen phase. This effect could be explained by the properties of polysaccharides to form an aqueous gel that limits the diffusion of water and solute molecules (Goff and Sahagian, 1996; Morris, 1989). It has been demonstrated by Goff et al. (1993), that the addition of polysaccharides (like locust bean gum, carrageenan) to ice cream results in a smaller size of the ice crystals immediately after freezing.

From the study made by Simatos, Blond, and Martin (1995), polysaccharides could restrict molecular mobility by elevating $T_g{}'$ (glass transition temperature of the maximal cryoconcentration phase), and thus slow down the ice crystal growth.

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Glossary

T_g	glass transition temperature
$T_g{}'$	glass transition temperature of the maximal cryo-concentrated phase
T_{g_o}	onset point of the glass transition temperature of a frozen product
T_{g_1}	mid-point of the first elevation of the glass transition temperature of a frozen product
T_{g_2}	end-point of the second elevation of the glass transition temperature of a frozen product
G'	storage modulus
G''	loss modulus
T_α	temperature at the maximum of G''
T_o	temperature at the beginning of the increase of δ curve

Polysaccharides limit the ice crystal growth as a consequence of the rigidity that they give to the freeze-concentrated phase at a temperature above $T_g{}'$.

Thus, different mechanisms have been elucidated. However, the role of polysaccharides in frozen products is not completely understood.

In order to obtain a better understanding of the function of polysaccharides in frozen products, the objective of this study was to determine the influence of polysaccharides, branched and linear at different concentrations and molecular masses, on the physicochemical properties of frozen sucrose solutions.

Viscoelastic properties of sucrose and sucrose + polysaccharide solutions were measured by dynamic mechanical thermal analysis (DMTA). Thermal properties were determined by the differential scanning calorimetry (DSC) technique.

2. Materials

2.1. Model system

Different sucrose (58.5 and 67.5% w/w) and sucrose (57.5% w/w) + polysaccharide (1 or 10% w/w) solutions were used as a model system. The polysaccharides studied were dextran (10^4, 4×10^4, 5×10^5 and 2×10^6 g/mol), pullulan (27×10^4 g/mol) and gum arabic (384×10^3 g/mol). Dextran and pullulan are considered as linear polysaccharides and gum arabic as branched polysaccharide. According to the state diagram proposed by Blond, Simatos, Catte, Dussap, and Gros (1997) for the sucrose, the chosen sucrose concentration (57.5%) corresponds to the cryo-concentrated phase of a freezing sucrose solution at −10 °C.

2.2. Preparation of sucrose and sucrose + polysaccharide solutions

First, the sucrose was dissolved in a portion of water by heating. Then, after cooling, water was added to compensate the amount of water that evaporated during heating. In order to avoid damage due to heat on the polymer (dextran at different molecular weights, pullulan or gum arabic), this one was dissolved in cold water. Finally, the polysaccharide solution was added to the sucrose solution and mixed using a magnetic stirrer to give total solid levels of 58.5 and 67.5%.

Sucrose solutions (58.5 and 67.5% w/w) were used as references. Under the temperatures examined in this report, the solutions do not contain ice.

3. Methods

3.1. Thermal properties

3.1.1. Determination of glass transition temperature by differential scanning calorimetry (DSC)

The glass transition temperature of the maximal cryo-concentrated phase ($T_g{}'$) of the studied solutions (sucrose and sucrose + polysaccharide) was measured by differential scanning calorimetry (DSC). The DSC used was a Perkin–Elmer DSC-7 equipped with the liquid nitrogen subambient accesory. Hermetically sealed 20 μl aluminium pans were used for all the measurements; an empty pan was used as reference. The sample weight was around 10 mg. Cooling and heating rates were 10 °C min^{-1}. In order to obtain full ice crystallization, different thermal cycles of heating and freezing were used. For the highest concentrated solutions (67.5%) a heat treatment was necessary. Thus, after the first heating, the temperature was maintained to −40 °C for 4 h.

In the thermograms, glass transition of the frozen sucrose and sucrose + polysaccharide solutions was identified by T_{g_o} (onset point), T_{g_1} (the mid-point of the first elevation) and T_{g_2} (end-point of the second elevation). This was repeated at least three times.

3.2. Rheological properties

3.2.1. Viscosity

The viscosities of the different diffusion media sucrose (58.5 and 67.5% w/w) and sucrose (57.5% w/w) + polysaccharide (1 or 10% w/w) were determined in a Rheometric Scientific viscometer (Piscataway, NJ) with a plate–plate (50 mm) geometry in a temperature range from 20 to −10 °C. This viscometer works in conjunction with RSI Orchestrator software. Stress was measured as a function of shear rate. The viscosity, for solutions that have a Newtonian behavior, was calculated from the relationship

$$\eta = \tau/\dot{\gamma}$$

where η is the viscosity (Pa s), τ is the stress (Pa), and $\dot{\gamma}$ is the shear rate (s^{-1}).

When the stress versus shear rate line is constant, the liquid is thought to be Newtonian; that is, the viscosity of the solution does not depend on the shear rate. For the sucrose + polysaccharides solutions that did not exhibit a Newtonian behavior, an apparent viscosity could be calculated from

$$\tau = K\dot{\gamma}^n$$

In the case of non-Newtonian solutions, the coefficient K was approximately equal to the viscosity.

When $n < 1$, the material is said to be pseudoplastic (it undergoes shear thinning), and the viscosity falls as shear rate is increased. When $n > 1$, the material is said to undergo dilatancy/shear thickening, and the viscosity increases as the shear rate increases.

A suitable shear rate was chosen in the range of 100–360 s^{-1} with a gap between the two plates of 1 mm for all experiments. The sample was always loaded at room temperature, and the plate was slowly lowered. The samples were then equilibrated at the required temperature for at least 5 min before the evaluation of viscosity. The measurements were repeated at least three times.

3.2.2. Viscoelastic behavior: identification of storage (G'), loss (G'') moduli and loss angle (δ)

Viscoelastic behavior of sucrose + polysaccharide solutions, as a function of temperature, was studied through a dynamic mechanical thermal analysis (DMTA). A metravib Viscoanalyser (Ecully, France) equipped with a thermo-control unit was used. Low temperatures were obtained with the injection of liquid nitrogen in the chamber. The sample solutions were held by capillarity in an annular shearing device and frozen in place. Measurements were performed upon heating at a rate of 2 °C/min. The storage G' and loss G'' moduli and the loss angle δ were measured at four frequencies (5, 10, 20 and 40 Hz). This process was repeated three times.

4. Results

4.1. Viscosity of the sucrose and sucrose + polysaccharide solutions

4.1.1. Viscosity of sucrose solutions

The validity of the Bouchard and Grandjean (1995) model was confirmed by the results of viscosity obtained for the sucrose solutions, except at low temperatures. The validity of the model is from 0 to 80 °C. Experimental values of viscosity of the sucrose solutions to 58.5 and 67.5% are not significantly different from the values predicted by the Bouchard and Grandjean model.

On the other hand, viscosity of sucrose solutions at 20 °C increases with the increase in sucrose concentration, from 0.0459 to 0.2797 Pa s for the sucrose solutions to 58.5 and 67.5% w/w, respectively.

4.1.2. Effect of polysaccharides on the viscosity of sucrose solutions

The sucrose solutions (57.5%) with 1% (or 10%) of polysaccharide added showed a Newtonian behavior at the different temperatures studied. This is illustrated in Fig. 1. Indeed, there is no significant difference between the values of the sucrose solutions (57.5%) with 1% of polysaccharide added and the reference solution at the same dry matter content (Fig. 1, line—$\alpha = 0.01$). At this concentration (58.5%), all the solutions presented a Newtonian behavior. However, in relation to the reference solution (sucrose 67.5%) the addition of 10% in polysaccharide induces an important modification in the viscosity. Results are presented in Fig. 1 and Table 1. The effect observed depends on the type of polysaccharide and on temperature. Indeed, the presence of pullulan induced the highest contribution on viscosity of the sucrose solution. In the case of the sucrose solutions with different dextrans added the viscosity increases as a function of their molecular weight. The sucrose solutions with added dextrans, at the lowest molecular weight, showed a Newtonian behavior at the different temperatures studied (Fig. 1). However, the sucrose solutions with dextrans added at the highest molecular weight (5×10^5 and 2×10^6 g/mol), showed a pseudoplastic behavior at 0 and −10 °C (Table 1).

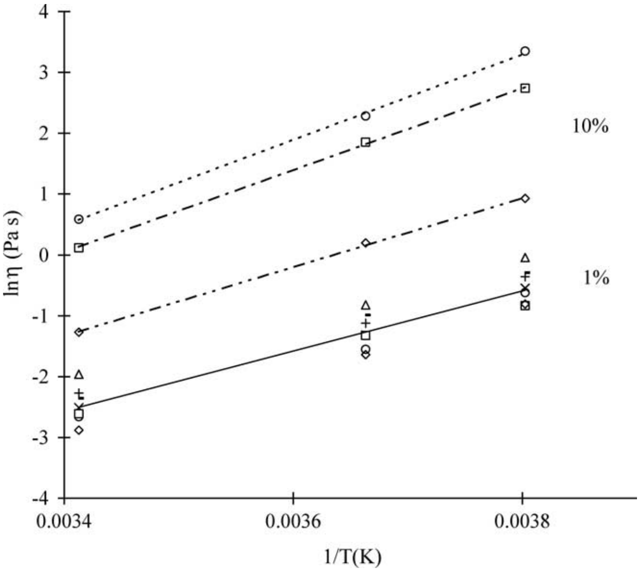

Fig. 1. Arrhenius representation of viscosity as a function of temperature for the Newtonian solutions of sucrose and sucrose (57.5%) + polysaccharide (1 or 10%). Polysaccharide: dextran (□) 10^4, (○) 4×10^4, (–) 5×10^5, (△) 2×10^6, (×) gum arabic and + pullulan. Reference solution: (◇) sucrose 58.5% (or 67.5%).

Table 1
Viscosity of the sucrose (57.5%) + polysaccharide (10%) solutions

Solutions	Temperature (°C)				
	20 (η (Pa s))[a]	0		−10	
		k	n	k	n
Sucrose (57.5%) + dextran 5×10^5 (10%)	5.31	376	0.36	432	0.54
Sucrose (57.5%) + dextran 2×10^6 (10%)	6.85	536	0.56	685	0.68
Sucrose (57.5%) + G. arabic (10%)	2.06	93.6	0.85	221	0.61
Sucrose (57.5%) + pullulan (10%)	12.23	–	–	–	–

[a] Reference: Contreras, Champion, Hervet, Blond, and Le Meste (2000).

The sucrose solutions with gum arabic and pullulan added showed a Newtonian behavior at 20 °C (Table 1). But, at the lowest temperature, these solutions showed a pseudoplastic behavior ($n < 1$). In these conditions, power law was used to calculate the consistence (K) and fluidity (n) parameters.

4.1.3. Effect of temperature and activation energy of viscosity

The Arrhenius representation of viscosity ($\ln \eta = (E_a/RT) + \text{constant}$), for the sucrose solutions with 1% polysaccharide added showed an increase in viscosity with the decrease in temperature (Fig. 1). For the solutions containing 10% dextran, gum arabic or pullulan a similar behavior was observed (Fig. 1, Table 1).

From the Arrhenius representation, the activation energy of viscosity was calculated in Fig. 1. The values of the activation energy for the solutions, with or without polysaccharide (dextrans, gum arabic or pullulan) at the same dry matter, are not significantly different. Polysaccharides structure seems not to have any effect on activation energy. Only an increase in the activation energy, from 41.7 ± 2.5 to 56.2 ± 2.8 kJ/mol, was observed with the increase in dry matter (from 58.5 to 67.5% w/w).

4.2. Viscoelastic behavior of frozen sucrose and sucrose + polysaccharides solutions

4.2.1. Evolution of G', G'' and δ for the frozen sucrose solutions

An example of the dynamic mechanical thermal analysis (DMTA) of the sucrose solution (58.5% w/w) is shown in Fig. 2. The main relaxation, associated to the glass transition, is characterized by a decrease of storage modulus (G'), a peak of loss modulus (G'') and an increase in loss angle (δ). At the glassy state, storage modulus G' presented the highest values (2×10^8 Pa). But, with the increase in temperature, G' decreases due to the decrease in viscosity and to the ice melting. With regard to the loss modulus (G''), this shows a maximum at the glass transition.

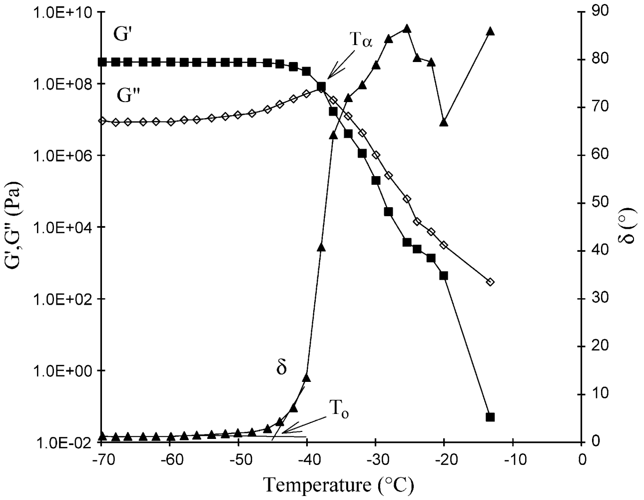

Fig. 2. Identification of G', G' and δ to 5 Hz, for a sucrose solution to 58.5%.

In the curve of δ, a different phenomena can be distinguish (Fig. 2). First, at the lowest temperature ($T < T_g$), δ presented the lowest values ($\delta < 3°$); this could indicate a good freezing of the sample. Then, after the glass transition ($T > T_g$) δ increase, the solution goes from the glassy state to the liquid state.

In the graph (Fig. 2), two temperatures were measured: T_α (at the maximum of G'') and T_o (at the beginning of the increase of δ curve).

4.2.2. Effect of the addition of polysaccharides on G', G'' and δ

For the sucrose solutions with 10% dextran, gum arabic or pullulan added, a thermal treatment at −40 °C was applied in order to reach the maximal freezing. The evolution of G', G'' and δ in the presence of the different polysaccharides is presented in Fig. 3.

4.2.3. T_α, T_o and E_a of the sucrose + polysaccharide solutions

The values of T_α (at the maximum of G''), T_o (beginning of the increase of δ) and activation energy, calculated from the Arrhenius representations (ln frequency (Hz) vs. $1/T_\alpha$ (K)) for sucrose and sucrose + polysaccharide, are presented in Tables 2 and 3. There are no significant differences between the values of T_α (or T_o) of the sucrose solutions with the addition of 1% (or 10%) dextran, gum arabic or pullulan.

The activation energy of the α relaxation was calculated with the T_α values (maximum of G'') at different frequencies. The activation energy of the sucrose solutions (57.5%) with the addition of different polysaccharides (1%) varies from 351 to 596 (kJ/mol) (Table 2). For the solutions with 10% polysaccharide added, the values of E_a are lower for the solutions containing dextran 4×10^4 and 2×10^6 g/mol than for the solution with gum arabic added as well as for the reference solution (sucrose 67.5%) (Table 3).

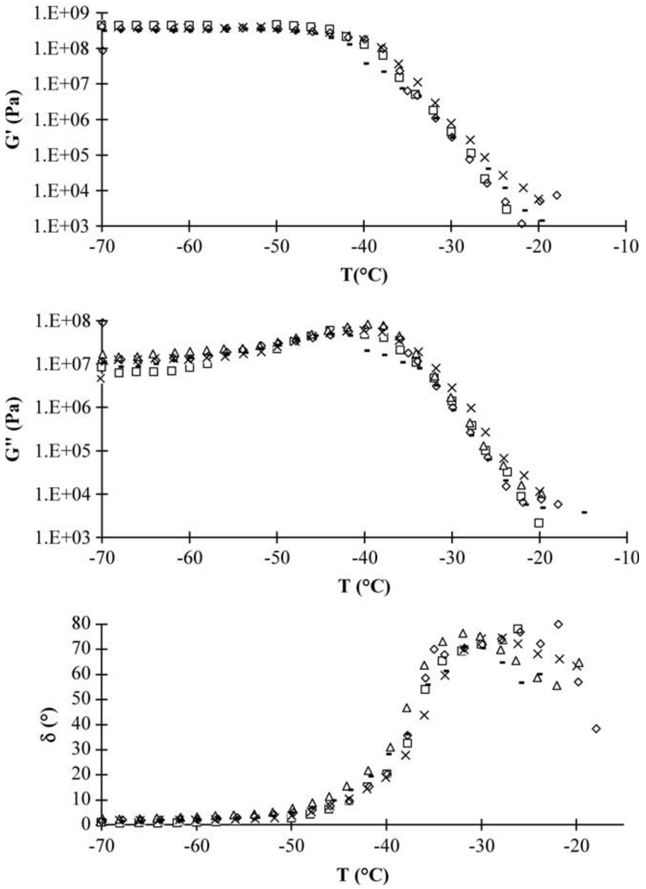

Fig. 3. Evolution of G', G'' and δ to 5 Hz as a function of temperature for the different sucrose 57.5% + polysaccharide 10% (dextran (□) 10^4, (–) 5×10^5, (△) 2×10^6, (×) gum arabic) solutions and also for the sucrose solution (◇) to 67.5%.

4.3. Thermal properties

4.3.1. Thermogram of sucrose and sucrose + polysaccharide frozen solutions determined by differential scanning calorimetry (DSC)

The thermograms determined by DSC for the sucrose and sucrose + polysaccharides solutions with 67.5% in dry matter are shown in Fig. 4. For the sucrose solution with 58.5%, the thermogram shows a double transition where T_{g_o}, T_{g_1} and T_{g_2} were identified. However, for the solutions with 67.5% (added or not of polysaccharide), only a simple transition was observed (Fig. 4). This behavior suggests that the concentrated solutions had not reach an equilibrium state (maximal ice formation). In order to reach the maximal cryo-concentrated state, a heat treatment just to $T>T_g'$ (−40 °C during 4 h) was carried out.

Table 2

T_α (maximum of G''), T_o (δ curve) measured to 5 Hz, and activation energy of the main relaxation for the sucrose (57.5%) + polysaccharide (1%) solutions

Sucrose 57.5% + polysaccharide 1%	T_α (°C) (max. G'')	T_o (°C) (δ curve)	Activation energy (kJ/mol)
Dextran 10^4	−38.6	−41.1	596
Dextran 4×10^4	−38.3	−40.4	351
Dextran 5×10^5	−38.1	−39.5	423
Dextran 2×10^6	−37.8	−39.1	480
G. Arabic	−37.6	−38.8	552
Pullulan	−37.8	−38.9	449
58.5% Sucrose	−38.3	−39.6	465

Table 3

T_α (maximum of G''), T_o (δ curve) measured to 5 Hz and activation energy of the main relaxation for sucrose (57.5%) + polysaccharide (10%) solutions

Sucrose 57.5% + polysaccharide 10%	T_α (°C) (max. G'')	T_o (°C) (δ curve)	Activation energy (kJ/mol)
Dextran 4×10^4	−36.5	−38.0	296
Dextran 2×10^6	−39.2	−41.1	272
Gum arabic	−40.0	−41.8	668
67.5% Sucrose	−38.6	−41.1	734

The thermal treatment revealed a double transition (Fig. 5). Thus, in the thermograms, T_{g_o} (onset point), T_{g_1} (mid-point of the first elevation, this is associated to the glass transition of the maximal croconcentrated phase) and T_{g_2} (end-point of the second elevation) of the sucrose solutions (added or not of polysaccharide) were identified. Ablett, Izzard, and Lillford (1992) suggested that T_{g_2} corresponds to the onset of ice melting and consequently dilution.

Concerning the definition of the glass transition temperature of the maximal cryoconcentrated phase (T_g'), different proposals have been made: T_{g_o} (Roos & Karel, 1991), T_{g_1} (Ablett et al., 1992) and T_{g_2} (Levine & Slade, 1988). For this study, we consider T_{g_1} as the value of T_g'.

The values of T_{g_o}, T_{g_1} and T_{g_2} for the sucrose and sucrose + polysaccharide solutions are presented in Table 4. There is no significant difference between the values of T_{g_o}, T_{g_1} and T_{g_2} of the sucrose solution with 58.5% (or 67.5%) and the sucrose solutions with 10% added in polysaccharide. For the solutions with dextran 10^4 g/mol added, the values of T_{g_o} and T_{g_1} are the highest. However, T_{g_2} is not significantly different from the values of the other solutions with gum arabic, pullulan or dextran (at the different molecular weight) added.

For the sucrose solution with 67.5% and for the solution sucrose solution with dextran 10^4 g/mol added, different thermal treatments were tested. However, for the sucrose solution with 67.5%, only one transition was observed.

5. Discussion

5.1. Effect of polysaccharides on the viscosity of sucrose solutions

The concentration and the kind of polysaccharide are the most important factors affecting the viscosity of sucrose

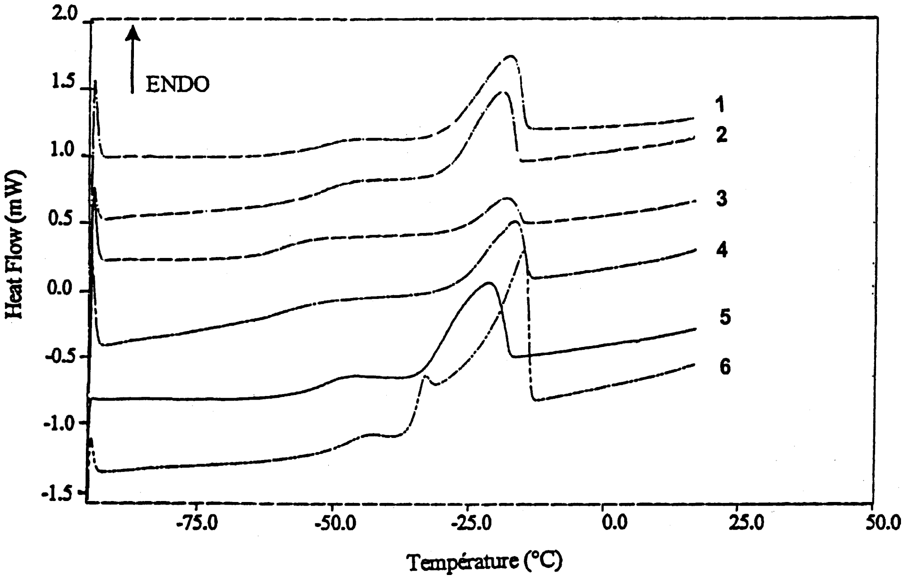

Fig. 4. Thermograms of the sucrose (58.5%) and sucrose (57.5%) + polysaccharide (10%) (1. Gum arabic, 2. Dextran (10^4 g/mol), 3. Pullulan, 4. Dextran (2×10^6 g/mol), 5. Sucrose 67.5%, 6. Sucrose 58.5%) solutions, after a thermal treatment at −30 °C during 5 min.

solutions. Indeed, with 1% w/w in polysaccharide neither the structure nor the molecular weight of polysaccharides had an effect on viscosity (Fig. 1). These results agree with the results obtained by McCurdy, Goff, Stanley, and Stone (1994). They showed that dextran at low concentrations has a low effect on the viscosity of sucrose solutions and there is a Newtonian behavior observed. A pseudoplastic behavior was observed in the solutions with 1.5% w/w added (McCurdy et al., 1994). Tsujisaka and Mitsuhashi (1993) showed that pullulan and gum arabic at low concentration (<1% w/w) have a little effect on viscosity.

With 10% w/w in polysaccharide, a particular effect of each polysaccharide was observed in the viscosity of the sucrose solutions (Fig. 1 and Table 1). Gum arabic (384×10^3 g/mol) and dextran (4×10^4 g/mol) at 20 °C presented a similar influence on the viscosity of sucrose solutions. It seems that the branched structure of gum arabic does not have any effect on the viscosity of the medium. These results confirm the ones obtained by Mitchell (1979) and Nussinovitch (1997). They showed that gum arabic, at a concentration of <10%, presents a low contribution on viscosity and on a Newtonian behavior. However, at a concentration >30%, the branched structure of gum arabic induce an important increase in viscosity (Nussinovitch, 1997).

Pullulan was the only polysaccharide that showed an important influence on the viscosity of the sucrose solutions. The effect of this polysaccharide cannot be explained by its

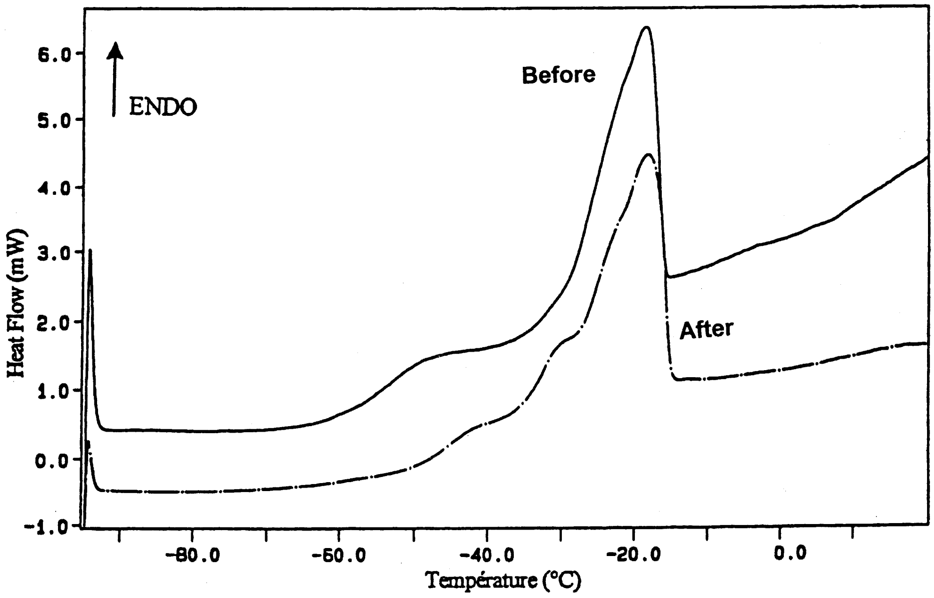

Fig. 5. Thermogram of the sucrose solution (57.5%) with 10% of dextran (5×10^5 g/mol) added, before and after a thermal treatment at −40 °C during 4 h.

Table 4
T_{g_o}, T_{g_1} and T_{g_2} for sucrose and sucrose + polysaccharide solutions

Sucrose 57.5% + polysaccharide 10%	T_{g_o} (°C)	T_{g_1} (°C)	T_{g_2} (°C)
Dextran 10^4	-44.8 ± 1.5	-40.8 ± 1.3	-31.8 ± 1.6
Dextran 4×10^4	-50.9 ± 1.6	-46.2 ± 1.9	-32.5 ± 1.1
Dextran 5×10^5	-53.4 ± 2.3	-48.0 ± 1.4	-34.2 ± 1.0
Dextran 2×10^6	-51.0 ± 2.8	-45.8 ± 2.1	-30.5 ± 0.9
Pullulan	-53.8 ± 3.8	-47.9 ± 3.0	-31.6 ± 2.8
Gum Arabic	-52.0 ± 1.9	-46.3 ± 1.6	-34.9 ± 0.7
58.5% Sucrose	-51.02 ± 2.8	-45.7 ± 2.1	-30.5 ± 0.9
67.5% Sucrose	-50.00 ± 0.1	-43.9 ± 0.2	–

molecular weight (2.7×10^5 g/mol); dextran at the highest molecular weight studied (2×10^6 g/mol) has a lower effect on viscosity than pullulan. The intrinsic viscosity of pullulan, could explain the influence of this polysaccharide on the viscosity of sucrose solution. Indeed, compared to gum arabic which shows a branched structure (25.4 ml/g to 1.2×106 g/mol) (Mitchell, 1979) and dextran (linear) (0.63 ml/g to 5×105 g/mol) (Belder, 1993), pullulan with a linear structure shows the highest intrinsic viscosity (207 ml/g to 10^6 g/mol) (Launay, Doublier, & Cuvelier, 1986).

The activation energy of the viscosity is independent of the type of polysaccharide added to the sucrose solution; this was only a function of the concentration in dry matter.

5.2. Visco-elastic behaviour of frozen sucrose + polysaccharide solutions

The results of the visco-elastic behaviour of the frozen sucrose and sucrose + polysaccharide solutions showed that T_α (maximum G'') and T_o (increase of δ) are not influenced by the presence of dextrans, gum arabic or pullulan (Tables 2 and 3). These results were confirmed by differential scanning calorimetry (DSC); T_{g_o}, T_{g_1} and T_{g_2} are not modified by the presence of the different polysaccharides. Indeed, the presence of these macromolecules does not induce any change in the two phases that control the visco-elastic properties of frozen solutions: ice crystals and cryo-concentrated phase. Blond (1994) observed a similar behavior in sucrose solution (50% w/w) with macromolecules (maltodextrines, dextran (4% w/w) or guar gum (1% w/w)). In the study presented by this authors, T_α and T_o are not modified by the presence of these polysaccharides. However, Simatos et al. (1995) observed an increase in T_α with the addition of 25% of dextran (or gelatin).

In the presence of 10% dextran, gum arabic or pullulan, G'' and G' moduli are not modified at the glassy state (Fig. 3). $T > T_g{}'$, G'' and G' moduli revealed a decrease; this behavior is due to the glass transition of the cryo-concentrated phase and to the ice melting. Blond (1994) observed an increase of G' and G'', to $T > T_g{}'$, in the presence of maltodextrin, dextran (4% w/w) or guar gum (1% w/w). Goff et al. (1995) also observed that at low concentrations (0.33–0.56% w/w) the presence of gum guar in ice creams induce an increase in the loss and storage moduli and a decrease of δ.

With regard the activation energy of glass transition, the sucrose solutions with different polysaccharides (dextran, gum arabic or pullulan) showed typical values of the main relaxation (from 200 to 400 kJ/mol) (Champion, 1998) (Table 2). The reference solutions (sucrose 67.5%) and the sucrose solutions with gum arabic (10%) showed the higher values of activation energy) (Table 3). These results could be explained by the presence of two closed phenomena: glass transition and ice melting. With the increase in temperature, the system traverses the glass transition and immediately ice melting begins. This means that the system is not balanced and the maximal formation of ice was not reached. In these conditions, the ice melting affects the measurement of activation energy of the main relaxation.

5.3. Effect of polysaccharides on glass transition

The thermograms obtained by DSC for the sucrose solutions with 67.5%, added or not with polysaccharide, after a heat treatment at −30 °C, show a change in the baseline just before the melting peak (Fig. 4). This behavior suggests an incomplete freezing of the solution. It is probable that the freezing rate is too high in relation to the ice kinetic crystallization. Thus, the water susceptible to turn into ice, does not have enough time to crystallize during the decrease in temperature. In these conditions, glass transition is observed at relatively low temperatures. Studies carried out by Ablett et al. (1992) and Blond and Simatos (1998) showed the same behavior in concentrated sucrose and dextran solutions (50% w/w). They suggest that the viscosity, due on one hand to the concentration of the solution, and on the other, to the presence of polysaccharide, does not allow reaching the maximal cryo-concentration. The high viscosity, induced by the polysaccharides chains in the concentrated phase, could explain these results.

In order to reach the maximal cryo-concentration of the solutions to 67.5%, a heat treatment was carried out at −40 °C during 4 h. After the thermal treatment, two peaks in the thermograms can be observed. These peaks describe the glass transition of the frozen solutions (Fig. 5).

The results showed that the presence of polysaccharides does not have any influence on T_{g_o}, T_{g_1} (ou $T_g{}'$) and T_{g_2}. Only, in the presence of dextran 10^4 g/mol, T_{g_o} and T_{g_1} are higher, but T_{g_2} is similar to the other solutions (Table 4). Sahagian and Goff (1995) observed a similar effect of the xanthan gum, gelatin and guar gum with 0.5% in sucrose solutions to 20%. At higher concentrations of polysaccharide, Blond and Simatos (1998) and Simatos et al. (1995) observed an effect on T_{g_2}. Indeed, the presence of dextran or gelatin (>20% w/w) in the sucrose solutions induces a significant increase of T_{g_2}, while the values of T_{g_o} and T_{g_1} are not modified.

Contrary to the behavior observed in the sucrose + polysaccharide solutions, the sucrose solutions with 67.5%

showed only one transition. Ablett et al. (1992) obtained a similar result in sucrose solutions at concentrations superior to 66%, after a heat treatment at −30 °C during 30 min. The distribution of the particle size shown in the matrix must be considered. From the free volume theory, the presence of small molecules favors the mobility of big molecules or segments of polymers. Compared to the reference solutions, the addition of polymers, creating heterogeneity in the system could favor the mobility of water molecules in the concentrated sucrose matrix and promote the glass transition of the cryo-concentrated phase. However, the quantity of polymer present in the sucrose solution is not enough to modify the temperature of the glass transition. A complementary study is necessary in order to explain the behavior of concentrated sucrose solutions.

6. Conclusions

The influence of polysaccharides on the viscosity of sucrose solutions depends on the structure and concentration of polysaccharide. Pullulan at 10% w/w had a higher influence on the viscosity of the sucrose solution.

The differential scanning calorimetry (DSC) made it possible to determine the variations in the thermal properties (glass transition temperature) of the cryo-concentrated phase of the sucrose solutions with or without polysaccharide. On the other hand, the viscoelastic properties of these solutions were determined by the dynamic-mechanical-thermal analysis (DMTA) that represents the mobility of the system at a macroscopic level.

In the two techniques utilized, DSC and DMTA, the problem of the concentrated solutions reaching a maximal cryo-concentration was observed. Indeed, in the measurements of DSC, the sucrose solutions added or not to polysaccharide, showed only one transition at low temperature. That means, the concentrated solutions do not reach the maximal cryo-concentration, probably due to the viscosity induced by the presence of polysaccharides. In the case of DMTA, at the lowest temperatures $\delta > 3$, the solutions are not completely frozen.

The results of the viscoelastic analysis of the studied solution showed that T_α and T_o are close. These temperatures are close to the values of T_{g_1} determined by DSC. This could confirm T_{g_1} as a value of $T_g{}'$. On the other hand, the variation between T_α (determined by DMTA) and T_{g_1} (determined by DSC) could be explained by the difference in the cooling and heating used in both types of measurements. In the case of the DSC method, the glass transition is a function of the kinetic variation in the temperature $\mathrm{d}T/\mathrm{d}t$. However, in the case of DMTA, the temperature of the main relaxation (maximum G'') is a function of the frequency.

Finally, the results of differential scanning calorimetry and the viscoelastic behaviour showed that the presence of polysaccharides studied (dextran, pullulan or gum arabic) have a low influence on the glass transition temperature of the maximal cryoconcentrated phase ($T_g{}'$). During the freezing, the ice formation seems to be decreased by the increase in the concentration. However, the addition of polysaccharides, particularly pullulan, could promote ice formation. In order to confirm this hypothesis, a complementary study must be carried out.

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