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Influence of DE-value on the physicochemical properties of maltodextrin for melt extrusion processes

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ABSTRACT

In this study, five different types of maltodextrins (DE-2, DE-6, DE-12, DE-17 and DE-19) were characterized for the physico-chemical properties. TGA, DVS and SEC analyses were carried out and additionally apparent melt-viscosity (in a micro-extruder) and the glass transition temperature (analyzed by DMA) of maltodextrin/plasticizer mixtures were also measured in order to evaluate both the effect of plasticizer nature and content and the effect of the DE-value. For this, three plasticizing agents were compared: water, D-sorbitol and glycerin. The adsorption isotherms showed that depending on the DE-value and the relative humidity they were exposed to, different behavior could be obtained. For example, for relative humidities below 60% RH maltodextrin DE-2 was the least hygroscopic. And on the contrary for relative humidities above 75% RH maltodextrin DE-2 was the most hygroscopic. The rheology measurements showed that the viscosity decreased with the increase of the DE-value and with the plasticizer content, as expected. On the contrary, no direct correlation could be established between the DE-value and the glass transition temperature. These results demonstrated that to predict maltodextrins behavior and to better adapt the process conditions, combined analyses are mandatory as the DE-value alone is not sufficient. The most compelling evidence was obtained by size exclusion chromatography, which pointed out that maltodextrins had a bimodal molecular weight distribution composed of high and low molecular weight oligo-saccharides. Indeed, maltodextrins are highly polydisperse materials (i.e. polydispersity index ranging from 5 to 12) and that should be the reason why such distinct behaviors were observed in some of the physico-chemical analyses that were performed.

1. Introduction

Maltodextrins are obtained from the acid and/or enzymatic controlled hydrolysis of starch. Maltodextrins are composed of D-glucose units connected by (1–4) glucosidic linkage to give D-glucose polymers of variable length and therefore different molecular weight. The number of the reducing sugar content is defined by the dextrose equivalent value (DE-value), which is calculated on a dry weight basis. Maltodextrins are a mixture of saccharides with a DE-value ranging from 3 to 20. Starch is associated to a DE-value of zero, and glucose to a DE-value of 100 (Dokic, Jakovljevic, & Dokic-Baucal, 1998; Levine & Slade, 1986).

Maltodextrins are one of the most common compounds used in the cosmetic, food and pharmaceutical domain. It can be employed as the main ingredient of a formulation or as an additive. Mal-

todextrins are great film forming and texturizing agents, as they can increase viscosity, retard crystallization or decrease stickiness and hygroscopicity of a mixture but also improve shelf-life stability of food matrices (Roos & Karel, 1991). Maltodextrins are popular in the food industry not only for all the previous reasons but also because they are highly soluble in water and non-sweet compared to classical sugars (Raja, Sankarikutty, Sreekumar, Jayalekshmy, & Narayanan, 1989; Schebor, Mazzobre, & Buera, 2010). Not to mention that maltodextrins are odor-, color- and tasteless so they appear as the best option to be employed as encapsulating agents either by spray-drying or twin-screw extrusion. Nowadays, maltodextrins are used as the main ingredient rather than additive for the elaboration of bio-based materials by melt extrusion (Bouquerand, Maio, Meyer, & Normand, 2008; Castro et al., 2016; Tackenberg, Marmann, Thommes, Schuchmann, & Kleinebudde, 2014).

The key for a successful encapsulation of an active compound is based on the understanding of the physicochemical properties of the wall material employed and therefore the adaptability of

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the process conditions and of the technology to be used. For maltodextrins, the main problem is the lack of experimental data concerning the physicochemical properties of these raw materials. Actually, there are more mathematical models allowing predicting the behavior of some of the physicochemical properties than studies measuring them because of the rigidity and brittleness of these carbohydrates-based materials.

Therefore in order to better understand maltodextrins, the aim of this paper was to determine in the first place the molecular characteristics (molecular weight distribution, sorption isotherm, apparent viscosity, and glass transition temperature) of five different grades of pure maltodextrins; and in a second place, to analyze the effect of the type and the amount of plasticizer on the apparent viscosity and glass transition temperature of these mixtures. Ergo, the formulations herein studied can be adapted to the principal encapsulation technologies. Thus, tuning the formulation upstream can for instance improve the flowability of the mixture inside an extruder, and control the properties of the final maltodextrin-based products.

2. Materials and methods

2.1. Raw materials

Roquettes Frères (Lestrem, France) supplied maltodextrins with different dextrose equivalent (Glucidex-2, Glucidex-6, Glucidex IT-12, Glucidex IT-19 and Glucidex 17). These maltodextrins are obtained by controlled hydrolysis of native corn-starch. The main difference between these two ranges of product is based on the powder particle size. Glucidex-IT has bigger particle size, providing a better solubilization and free-flowing properties. Two plasticizers were employed, glycerin (CAS: 56-81-5, MW = 92 g mol⁻¹) and D-sorbitol (CAS: 50-70-4, MW = 182 g mol⁻¹) both supplied by Sigma Aldrich (St Quentin Fallavier, France). Reagents used for the dextrose titration and for size exclusion chromatography were also provided by Sigma-Aldrich: Copper (II) sulphate pentahydrate (CAS: 7758-99-8, MW = 249.69 g mol⁻¹), Methylene blue (CAS: 61-73-4, MW = 319.85 g mol⁻¹), potassium sodium tartrate tetrahydrate (CAS: 6381-59-5, MW = 282.22 g mol⁻¹), sodium hydroxide (CAS: 1310-73-2, MW = 40 g mol⁻¹), Di-sodium hydrogen phosphate (CAS: 10028-24-7, MW = 177.99 g mol⁻¹), sodium phosphate (CAS: 10049-21-5, MW = 138.0 g mol⁻¹) and sodium chloride (CAS: 7647-14-5, MW = 58.44).

2.2. Determination of the dextrose equivalent value of maltodextrins

The DE-value were measured by the Hagedorn-Jensen method (Callow, 1930) in order to confirm the dextrose equivalent value established by the manufacturer. The DE-values obtained for the five different types of maltodextrins are in agreement with the DE-values indicated by the supplier (Table 1). "Theoretical" degree of polymerization and number average molecular weight were determined by the following equations (Dokic et al., 1998) and are summarized in Table 1:

$$DP_{\text{theo}} = \frac{111.11}{DE} \quad (1)$$

$$\bar{M}_{n\text{theo}} = 162DP + 18 \quad (2)$$

The molecular characteristics presented in Table 1 are used as references to compare with the experimental values obtained in this study in Section 3.1.

2.3. Size exclusion chromatography

SEC analyses were performed using a Dionex (Voisins le Bretonneux, France) size exclusion chromatography (SEC) equipped with a high-sensitivity inverse refractive index detector Prostar 350/352 from Varian Analytical Instruments (Walnut, C.A., USA).

The average molecular weights of maltodextrins were determined by gel permeation chromatography (GPC) on a PL aquagel-OH 50 columns. The column system was composed of three columns; 2 Agilent PL aquagel-OH 30 8 μm, 7.5 × 300 mm (p/n 1120-6830 Polymer Laboratories Ltd., Church Stretton, UK) and a PLgel precolumn. The column oven temperature was set at 30 °C. The eluents were 0.02 M NaCl in 0.005 M sodium phosphate buffer Sigma-Aldrich (St Quentin Fallavier, France), at pH 7 and prepared as the protocol described by Ma et al. (2012).

External calibration was made with Pullulan standards, from Polymer Laboratories (Marseille, France), with specific average molecular weights ranging from 360 and 380,000 Da, dissolved in 0.005 M sodium phosphate buffer with 0.02 M NaCl, pH 7.5.

The results were treated by Chromeleon software in order to obtain the number average (M_n), the weight average (M_w) molecular weights and the polydispersity index (Ip) of each analyzed sample. All samples were run in triplicates.

2.4. Determination of the moisture content

Moisture content of the samples was determined by gravimetric method (NF-V-ISO03-921). One gram of each sample was weighted and left to dry in an oven at 103 ± 2 °C for 24 h until there were no mass variations of the sample. Measures were run in triplicates for each sample.

2.5. Dynamic vapor sorption analyses (DVS)

Water sorption isotherms were performed on a Dynamic Vapor Sorption (DVS) Advantage System from Surface Measurement Systems (Alpertown, UK). This machine is equipped with a very accurate recording microbalance, able to measure changes in the sample mass as low as 0.1 μg. Samples were exposed to a constant temperature (25 °C) and programmed relative humidities varying from 0 to 90% divided into 15% increments (14 steps). A mixture of dry and moisture-saturated nitrogen flowing over the samples assured the changes in the relative humidity of the DVS-chamber. Ten milligrams of the sample were placed inside the chamber and before starting the data acquisition, all the samples were dried for 300 min under a stream of dry nitrogen (0% RH) at 103 °C in order to obtain the dry weight. Equilibrium was achieved, when the changes in the mass of the sample were lower than 5.10⁻³% min⁻¹.

2.6. Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed on a SETSYS-Evolution TGA-SETARAM Instrumentation KEP Technologies (Caluire et Curie, France) in order to establish the thermal stability of each compound. The temperature of analysis was set from 25 °C to 600 °C at a ramp rate of 7.5 °C/min, under inert Argon atmosphere. The samples weighted between 13 and 25 mg.

The onset temperature was mathematically determined by the intersection between the ray parallel to the plateau of the mass weight of the sample after dehydration and the ray going through the vertex of the DTG plot. The onset temperature corresponds to the start of the major sample degradation. All the graphics were plotted thanks to Origin software (OriginLab Corporation, Northampton, MA, USA).

Table 1
Measured DE-value of different types of maltodextrins (triplicates). DE-values were experimentally measured. DP_{theo} and Mn_{theo} were calculated from Eqs. (1) and (2).

Molecular characteristics	Maltodextrin DE-X				
	DE-2	DE-6	DE-12	DE-17	DE-19
DE-value	2.1 ± 0.0	6.29 ± 0.02	12.31 ± 0.02	17.7 ± 0.04	19.04 ± 0.06
DP_{theo}	52.9	17.7	9.0	6.3	5.8
Mn_{theo} (g mol ⁻¹)	8589	2880	1480	1035	963

2.7. Rheology: apparent viscosity

The apparent viscosity measurements of different maltodextrin/plasticizer mixtures, at constant temperature (80 °C), were performed on a Haake MiniLab Micro Rheology Compounder (Thermo Fisher Scientific, USA), equipped with a back flow channel, designed as a slit capillary, with two pressure transducers; one in the entrance and another one at the exit of the capillary zone. The apparent viscosity is deduced from the capillary geometry and the calculated apparent shear rate $\dot{\gamma}$, which in turn was determined from the volume flow \dot{V} and the pressure drop. Around 7 and 10 g of the maltodextrin/plasticizer mixture was introduced manually and measurements were made from 219 to 821 s⁻¹ shear rate gradient (corresponding to a screw speed varying from 50 to 250 rpm).

Viscosity measurements were obtained for the following compositions, maltodextrin/water 88/12% (w/w) and maltodextrin/plasticizer 80/20% (w/w). However viscosity measurements for the formulations containing 10% (w/w) of plasticizer were impossible because the torque alarm of the apparatus was triggered.

2.8. Dynamic Mechanical Analysis

Glass transition temperature (T_g) of maltodextrin/plasticizer films (film preparation is described below) were measured on a Triton Technology Dynamic Mechanical Analysis apparatus (Triton Technology, UK), by thermal scans in the simple geometry of the single cantilever-bending mode. The amplitude (25 μm) and the multi-frequency (1 and 10 Hz) modes were kept constant during the analysis. Samples were placed in an aluminum pocket and the temperature range of analysis was set from -100 °C to 200 °C at a scanning rate of 2 °C/min. Therefore the mechanical properties of the samples cannot be considered but all thermal relaxations in the temperature range studied, are related to the sample inside the pocket.

Maltodextrins films were prepared by casting method. They were prepared by dissolving 20 g of maltodextrin/plasticizer mixture 90/10 and 80/20 (% (w/w)) in 100 mL of tap water at room temperature and stirred with a magnetic stirrer at 1200 rpm for 10 min. Films were stabilized in a controlled humidity chamber set up at 60% of relative humidity and 25 °C for two weeks before analysis. Experiments were run in duplicates.

3. Results and discussion

3.1. Molecular characterization of pure maltodextrins

3.1.1. DE-value assessment and molecular weight distribution

The average number molecular weight and degree of polymerization of the different types of maltodextrins used in this study were calculated thanks to the measured DE-value and were compared to the results obtained by size exclusion chromatography (Table 2).

The molecular weight distribution of maltodextrins is crucial because it allows to get a better understanding of their behavior in terms of structural and functional properties (Avaltroni, Bouquerand, & Normand, 2004). For that reason, the determination of the molecular weight distribution of the four types of mal-

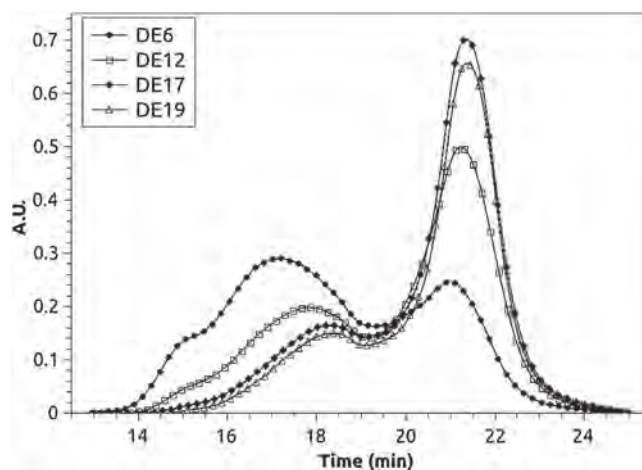


Fig. 1. SEC chromatogram of different grads of maltodextrins.

todextrins is at the bottom of this study. The molecular weight distribution of the analyzed maltodextrin became narrower as the DE-value increased, since the polymer chains were shorter.

It can be noticed, in Fig. 1, that all maltodextrins had a bimodal molecular weight distribution; they were composed of high and low molecular weight oligo-saccharides. The first peak corresponded to the higher molecular weight polysaccharides. For maltodextrins with high DE-value, the retention time was more or less the same. However, maltodextrin DE-12 presented a larger population of high molecular weight polysaccharides than DE-17 and DE-19 maltodextrins. On the contrary, the peak of maltodextrin DE-6 presented an interesting shape.

In fact, the first peak presented the shortest retention time and a shoulder peak can be appreciated at 14.5 min. This shoulder peak indicates the presence of even higher molecular weight polysaccharides. Thus maltodextrin DE-6 had the most important and largest population of high molecular weight polysaccharides.

On the opposite, for the second peak, representing low molecular weight oligo-saccharides, the order was almost inverted. Maltodextrin DE-6 presented a small population of low molecular weight polysaccharides. Whereas, maltodextrins DE-17 and 19 were composed of a considerable population of low molecular weight oligo-saccharides. However, maltodextrin DE-12 was the one having the lowest molecular weight oligo-saccharides, even though this population was restricted. Therefore maltodextrin DE-6 and DE-12 were the ones having the largest molecular weight distribution among all the others, confirmed by the high values of the polydispersity index (respectively 12 and 10) and degree of polymerization (respectively 17.7 and 9.0).

The results obtained in our study are in agreement with the literature. These commercial maltodextrins found in the market have a broad molecular weight distribution as demonstrated in the study of Dokic et al. (1998). And acid hydrolysis is known to give mixture of saccharides with a wide molecular weight range varying sometimes from monomer to polymers of the same size than starch (Wang & Wang, 2000).

Table 2

Molecular characteristics of different grades of maltodextrins (triplicates). $M_{n,theo}$ = theoretical average molecular weight determined by Eq. (2) and DP_{theo} = theoretical degree of polymerization determined by Eq. (1). M_n corresponds to the number average molecular weight and M_w corresponds to the weight average molecular weight; both were experimentally measured by SEC ($n=3$).

Maltodextrin DE-X	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	lp	$M_{n,theo}$ (g mol ⁻¹)	DP_{theo}
DE-2	–	–	–	8589	52.9
DE-6	2225 ± 57	25847 ± 583	12 ± 1	2879	17.7
DE-12	1507 ± 24	15400 ± 265	10 ± 1	1479	9.0
DE-17	983 ± 31	5672 ± 431	6 ± 1	1035	6.3
DE-19	937 ± 59	4978 ± 785	5 ± 1	962	5.8

The molecular weight distributions of maltodextrins DE-6, 12 and 19 are in agreement with the values found in the literature (Avaltroni et al., 2004; Bouquerand et al., 2008; Chronakis, 1998; Descamps, Palzer, Roos, & Fitzpatrick, 2013; Dokic et al., 1998; Normand, Alvatroni, & Bouquerand, 2006; Roos and Karel, 1991; van Sleuwen, Zhang, Normand, & Rutger, 2012; Wang & Wang, 2000).

3.1.2. Hygroscopicity

In the literature some theories concerning the DE-value and the hygroscopic character of maltodextrins are exposed. In general, maltodextrins are considered to be polysaccharides with a low hygroscopic character (Pouplin, Redl, & Gontard, 1999). Looking more closely at the DE-value of maltodextrins, it is expected that, when the DE-value increases, the hygroscopic character of maltodextrin is also increased, since the surface of contact is increased. This characteristic was confirmed by Wang and Wang (2000), where high molecular weight maltodextrins presented low moisture content and conversely low molecular weight maltodextrins had high moisture content. However, our results seemed to indicate two different behaviors depending on the relative humidity on which maltodextrins were exposed to and the transition zone where the behavior change occurred is comprised between 60 and 75% RH (Fig. 2). Indeed in this region it appeared that the adsorption behavior of all maltodextrins changed. Indeed, it is in this area that any maltodextrins changed behavior. On the one hand maltodextrin 6 remains the most hygroscopic followed maltodextrin 19. On the other hand, at 68% RH, interestingly, the three other maltodextrins intersected themselves.

In general the sorption–desorption isotherms of all maltodextrins presented a sigmoidal shape and showed a pronounced hysteresis (in this paper only sorption is represented). They were all associated to a type II sorption isotherm except for maltodextrin DE-2 that was more like a type III sorption isotherm and presented a very unique hygroscopic behavior, and will be discussed later on this paper. The transition zone ($60 \leq \%RH \leq 75$) marked a clear difference between the “bonded-water” bound onto the surface of the sample and the free-water (i.e. microcapillary water). Type II isotherms correspond to the general isotherm found in all food products. Meaning that for maltodextrins having a type II isotherm, water is first bond to the most polar groups onto the surface of maltodextrins, and then water is adsorbed on all the free hydroxyl groups corresponding to the hydration monolayer. Then, when all the polar sites are occupied, water molecules are bound to the monolayer through hydrogen bonding and/or Van der Waals interactions. This corresponds to the multilayer formation.

On the contrary, maltodextrin DE-2 seemed more like a type III isotherm, because in the curve there was no flattish part indicating the formation of the monolayer. In other words, for maltodextrin DE-2 there was an immediate formation of a multilayer system, with strong adsorption of “free water” observed at higher relative humidities. Perhaps, because maltodextrin DE-2 is longer and consequently has a high molecular weight, it is possible that the polymeric chain tends to entangle. Therefore absorption of water occurs in a “disorganized” way. The multilayer starts to form even

though there are still hydroxyl groups available on the surface but not have easy access for the water molecules. Further information will be required to prove the organization of the polymeric chain of maltodextrins DE-2 compared to high DE-value maltodextrins.

On the contrary, for the maltodextrins of high DE-value, the multilayer starts to form once all the hydroxyl groups on the surface are occupied since they are easy to access (there is no entanglement of the polymeric chains).

For all these reasons, and to sum up, two tendencies emerge from this study.

On one hand and for relative humidities below 60% RH, moisture content increases as the molecular weight of maltodextrins increases. Herein hygroscopicity increases as the DE-value decreases. Meaning that the longer the polymeric chains are, the more hydroxyl functions are available to adsorb water. Thus maltodextrin DE-6 is the most hygroscopic. The same tendency was observed for starch and hydrolysate starch products of different molecular weight studied by Shrestha and Halley (2014, chapter 5) and Slade and Levine (1993) due to the fact that the longer the polymeric chain is, the more important is the affinity for water and thus, higher is the water retention in the material. When the polymeric chains are longer, there is a high probability that chains begin to entangle with each other giving rise to a disordered system and therefore increasing the free-volume.

On the other hand, and for relative humidities above 75% RH, moisture content increases as the molecular weight of maltodextrins decreases. Therefore maltodextrin DE-19 presented the most hygroscopic character among the high DE-value maltodextrins. This is in agreement with the results obtained by (Wang and Wang, 2000) where high DE-value maltodextrins had higher moisture content than low DE-value maltodextrins. This allied what was mentioned before, that is to say that the shorter the polymer chains are, more important is the surface area of exchange.

Maltodextrins DE-2 and DE-12 have particular sorption isotherm depending on the relative humidity of the environment meaning perhaps significant changes on their macromolecular structure. Maltodextrin DE-2 behaves more as long-chain than as a small-chain polymer. In fact, its sorption isotherm is very much alike as the ones obtained for starches (Abdillahi, 2014; Godbillot, Dole, Joly, Rogé, & Mathlouthi, 2006).

The sorption isotherm permits to have a general idea of the hygroscopic character of the material and thus predict the shelf-life stability of the material under specific environmental or process conditions (Chronakis, 1998). In this case for example, maltodextrin DE-12 will be more stable than maltodextrin DE-2 when exposed to environment above 60% RH. In addition if the final application is targeting a delivery system that must be highly hygroscopic, maltodextrin DE-6 and DE-12 will be privileged over others (off course for relative humidities below 60% RH). The same remarks was pointed out in the study of Raja et al. (1989) where high molecular weight oligosaccharides lead to an increased moisture absorption. However it was reported in other study that when maltodextrins were exposed to high relative humidities (90% RH), the affinity to water for low DE-value maltodextrin increased. Maltodextrin DE-4 had a moisture content of 6% (w/w) opposed to maltodextrin DE-15

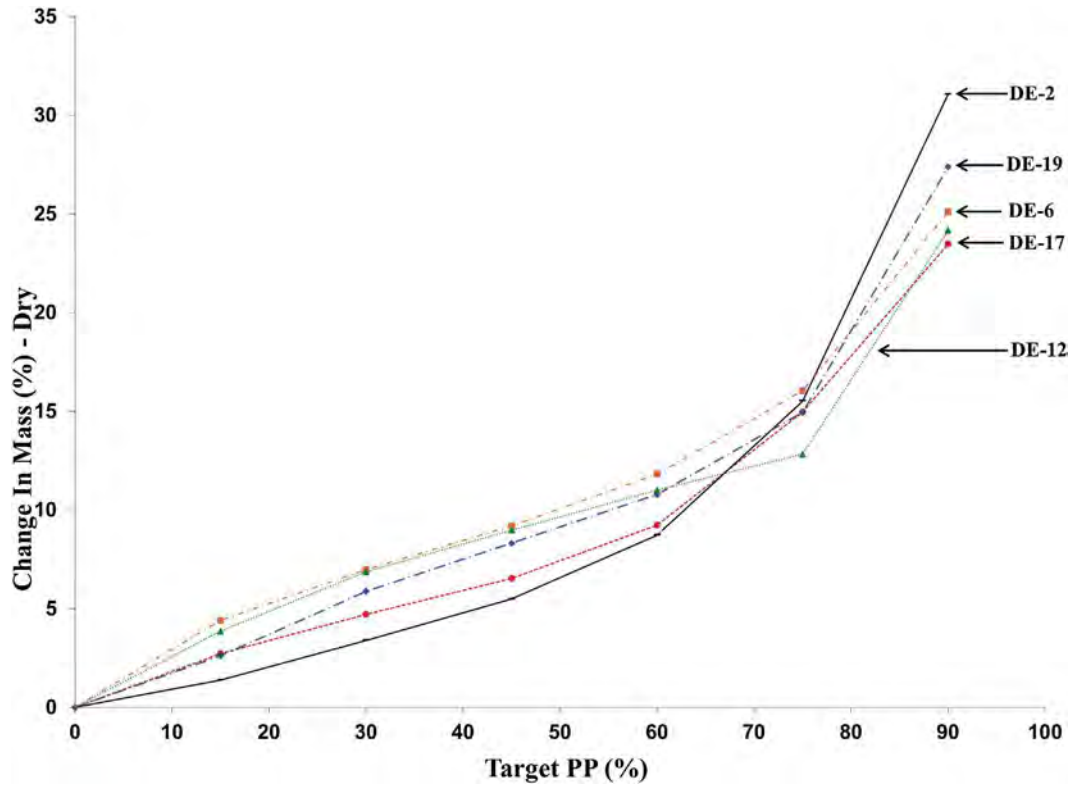


Fig. 2. Vapor sorption isotherm of the various types of maltodextrins.

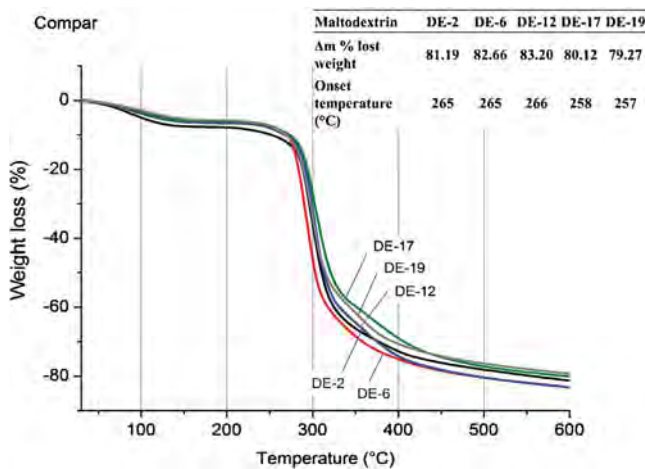


Fig. 3. TGA of different grades of maltodextrins.

which had a moisture content of 3% (w/w) (Wang and Wang, 2000). Special attention must be given when comparing all these different studies because the botanical origin of maltodextrin and the type of hydrolysis are crucial parameters affecting the final physico-chemical properties of maltodextrins. This can be one of the reasons explaining such differences disclosed in the literature.

3.1.3. TGA

Thermogravimetric analysis allows determining the thermal stability of each maltodextrin. In general, all the maltodextrins presented the same dehydration and decomposition phases corresponding to the classical thermogravimetric profile of carbohydrates (Anastasakis, Ross, & Jones, 2011; Dennis et al., 2006). As it is represented in Fig. 3, the first stage (temperature range from 25°C to 150°C) is associated to the dehydration of maltodextrins,

which is a small weight loss. For the five analyzed maltodextrins the weight loss fitted perfectly to the moisture content measured in the sorption isotherms (Fig. 2). The second stage corresponds to the region where decomposition reactions take place and where the major weight loss of the samples occurred. Since the analyses were run on an inert atmosphere, the total degradation of maltodextrins to the ash content was not completed (this part being related to the third stage, the completely degradation of the sample).

Maltodextrin DE-6 showed a more slightly rapid decomposition than the other types of maltodextrins, meaning that in this particular case the lower the DE-value is, the more rapid the decomposition will be. At the end of the pyrolysis reactions maltodextrin DE-19 had lost 79.27% of the initial weight and maltodextrin DE-6 and DE-12 have lost around 80 to 83% of their initial weight respectively.

As stated in the thermogram above, the five maltodextrins could withstand temperatures up to 250°C without fearing their degradation. This implies that temperature can be one of the process parameter, in twin-screw extrusion for example, to be modified in order to regulate the viscosity or the glass transition temperature of the system. Of course, special attention must be given when extrapolating the temperature conditions to extrusion because this thermal analysis was made at inert atmosphere.

3.2. Rheology and DMA analysis of maltodextrin/plasticizer mixtures

3.2.1. Rheology: apparent viscosity measurements

Maltodextrins are highly soluble in water and thus measurement of their viscosity is classically performed in solution but the characterization of their apparent melt viscosity was quite a challenge. Small amounts of water and plasticizer (not exceeding more than 20% (w/w)) were employed. After several trials, the chosen process temperature was 80°C to keep it as low as possible for future encapsulation of thermolabile active compounds. Also

Table 3

Flow consistency and power-law indexes of the maltodextrins mixtures with 12% (w/w) of water and 20% (w/w) of plasticizer.

Formulation	K (Pa s)	m	R^2
Maltodextrine DE-2 + water 12% (w/w)	39875	0.06	0.99
Maltodextrine DE-6 + water 12% (w/w)	22636	0.07	0.94
Maltodextrine DE-12 + water 12% (w/w)	33838	0.09	0.99
Maltodextrine DE-17 + water 12% (w/w)	334	0.64	0.98
Maltodextrine DE-19 + water 12% (w/w)	942	0.53	0.95
Maltodextrine DE-2 + glycerol 20% (w/w)	24300	0.13	0.99
Maltodextrine DE-6 + glycerol 20% (w/w)	23950	0.13	0.98
Maltodextrine DE-12 + glycerol 20% (w/w)	132	0.76	0.92
Maltodextrine DE-17 + glycerol 20% (w/w)	61	0.85	0.79
Maltodextrine DE-12 + D-sorbitol 20% (w/w)	18059	0.15	0.96
Maltodextrine DE-17 + D-sorbitol 20% (w/w)	20649	0.11	0.96
Maltodextrine DE-19 + D-sorbitol 20% (w/w)	270	0.43	0.84

to allow measurements of the viscosity of high molecular weight maltodextrins, because for temperatures below 80 °C their viscosity was too high. Indeed, for high molecular weight maltodextrins 80 °C was the perfect temperature to have a non-Newtonian fluid behavior, whereas at higher temperature there was no viscosity at all (for the same amount of plasticizer). For these reasons the temperature 80 °C was found to be ideal because allowing viscosity measurements for this wide range of maltodextrins. These results accentuated the fact that maltodextrins can be extruded at low temperature. D-Sorbitol and glycerol were used at two different ratios 10 and 20% (w/w). And water constituted the third plasticizer added at a ratio of 12% (w/w). It was not possible to test D-sorbitol, glycerol, and water at the same ratios because the viscosity behavior for each plasticizer was not the same. For example, viscosity measurements were not possible for mixtures of maltodextrins containing 10% (w/w) of water only. Besides, in the case of water at 20% (w/w) the mixtures behaved as a Newtonian fluid thus no viscosity was able to be measure.

The apparent viscosity (η) of the different maltodextrin/plasticizer mixtures was determined by the Power-law or Ostwald-de Waele equation:

$$\eta = K \cdot \dot{\gamma}^{m-1} \quad (3)$$

The apparent viscosity η (Pa s), K is the flow consistency index (Pa s ^{m}), $\dot{\gamma}$ shear rate (s⁻¹) and m is the power-law index. The flow consistency index (K) corresponds to the value of the viscosity for a 1 s⁻¹ shear rate equals. And the power-law index, m , indicates the type of fluid based on their flow behavior with respect to a Newtonian fluid. Therefore, for m values below 1, samples are considered as pseudoplastic or shear thinning fluids. According to this, all the maltodextrins/plasticizer formulations tested behaved as shear thinning fluids. In general, the results showed that the pseudoplastic index varied conversely to the flow consistency index Table 3. Moreover, the values of the apparent viscosity of all formulations were more or less in the same order of magnitude (Fig. 4).

When exposed to the same moisture content 12% (w/w) and at the same temperature 80 °C maltodextrin DE-2 had the highest viscosity among the other maltodextrins (Fig. 4). The flow consistency index of maltodextrin DE-6 was 22636 Pa s and was 33838 Pa s for maltodextrin DE-12, which indicates that viscosity of maltodextrin DE-6 was lower than the viscosity of maltodextrin DE-12. Though, maltodextrin DE-12 was supposed to have a lower viscosity since its average molecular weight is smaller than the average molecular weight of maltodextrin DE-6 (respectively 15400 g mol⁻¹ and 25847 g mol⁻¹). Maltodextrins with low DE-value are expected to have a higher viscosity (Avaltroni et al., 2004). For instance, Dokic et al. (1998) also found unexpected behavior related to the viscosity of concentrated maltodextrin solutions. In fact, maltodextrin DE-25 had a viscosity higher than maltodextrin DE-15. This discrepancy is explained due to the higher percentage of longer linear

chains and broader molecular mass distribution of maltodextrin DE-25 compared to maltodextrin DE-15. In our case, even though maltodextrin DE-6 had a more important part of high molecular weight polysaccharides than maltodextrin DE-12, the polydispersity indexes of both were about of the same range (respectively 12 and 10). Meaning that both maltodextrins had broader molecular mass distributions. Based on the power law index, maltodextrin DE-2, DE-6 and DE-12 had similar values (Table 3) very closed to 0, revealing an important entanglement of the polymeric chains due to high molecular weight oligomers.

Related to maltodextrin DE-17 and DE19, the power-law index indicates that they were the ones presenting a more plastic character among the other three maltodextrins and very low entanglement of the polymeric chains. Additionally, interesting results were obtained for maltodextrin DE-19 at 20% (w/w) of glycerol. In fact glycerol is such a good plasticizer that for maltodextrin DE-19 the mixture behaved as a Newtonian fluid (viscosity did not decrease when increasing shear rate).

Glycerol appeared to be a better plasticizer than D-sorbitol since it decreased considerably the viscosity for the same type of maltodextrin. For example, considering the same amount of plasticizer, the values of the flow consistency and the power-law indexes for maltodextrin DE-12 were much lower for glycerol ($K = 132$ Pa s, $m = 0.76$) than for D-sorbitol ($K = 18059$ Pa s, $m = 0.15$). Another argument demonstrating that glycerol was a better plasticizer than D-sorbitol is the fact that for high molecular weight maltodextrins (e.g. maltodextrin DE-2 and DE-6) viscosity measurements were possible only for mixtures containing 20 (% w/w) of glycerol.

With regard to the DE-value and viscosity (no matter how it is measured) there is a linear dependency (Avaltroni et al., 2004; Dokic et al., 1998; Levine & Slade, 1986). The viscosity of the mixture decreases as the DE-value increases. Based in our results, this linear dependency between DE-value and viscosity is respected for the mixtures containing 20% (w/w) of plasticizer. However in the case of water at 12% (w/w) this linearity is not respected. Indeed maltodextrin DE-19 presented a higher viscosity than maltodextrin DE-17 maybe because it has a more important population of high molecular weight polysaccharides than maltodextrin DE-17.

3.2.2. DMA

Glass transition temperature (T_g) has been longtime used as an accurate indicator for food matrices stability (Liu, Bhandari, & Zhou, 2006). Indeed, T_g behavior influences the properties of food materials like texture, taste and off course shelf-life stability during the stocking conditions and, last but not least, it served as an indicator to determine the melt extrusion process parameters (Sablani, Kasapis, & Rahman, 2007). Molecular weight of the material, water content and process temperature are the main parameters affecting the T_g . For those reasons, for the last 80 years, the T_g of mono- and oligosaccharides have been exhaustively studied since they are the main ingredient of food products (Angell, 1996; Orford, Parker, & Ring, 1990; Orford, Parker, Ring, & Smith, 1989; Slade & Levine, 1995; Zeleznak & Hosney, 1987).

Maltodextrins are very rigid and brittle materials and therefore their characterization and workability have been a challenge. Even though several thermodynamic models have been developed (Couchman & Karasz, 1978; Gordon & Taylor, 1952; Orford et al., 1989; van Sleuwen et al., 2012) in order to determine by extrapolation the glass transition temperature of pure and dry maltodextrins, there's still a gap between the experimental values found and those determined by the existing mathematical models (Angell, 1996; Descamps et al., 2013; Levine and Slade, 1986; Liu et al., 2006; Orford et al., 1990; Roos & Karel, 1991). After all, the determination of the glass transition temperature has always been a challenge in material science, specially the glass transition tem-

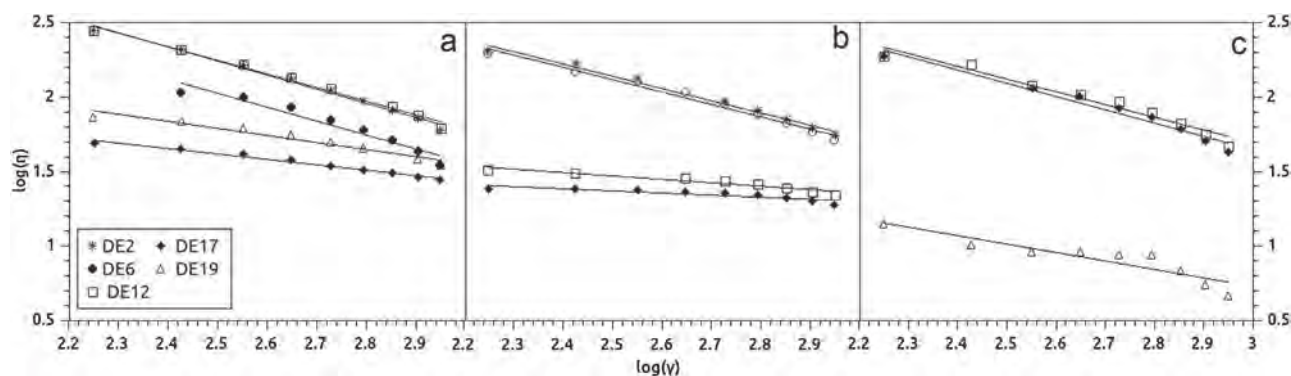


Fig. 4. Apparent viscosity of the different mixtures of maltodextrin/plasticizer tested at 80 °C: (a) maltodextrins + water 12% (w/w), (b) maltodextrins + glycerin 20% (w/w), (c) maltodextrin + D-sorbitol 20% (w/w).

perature of carbohydrates. Recent studies have pointed out the importance of the mass transfer involving the polymer and its plasticizer, and the impact of the transient moisture content of the broadening of the measured glass transition (van Sleuwen et al., 2012). Based on the literature, the glass transition temperature of maltodextrins decreases when the DE-value increases, since the length of the polymer chain is lower (DP is lower). In this part, special attention is given to the glass transition temperature of the maltodextrin/plasticizer mixture to investigate the influence of the DE-value and of the plasticizer nature.

Fig. 5 represents the thermogram obtained by DMA. In this chart, each plot is associated respectively to a mixture of a specific maltodextrin/plasticizer, in this case D-sorbitol at 10% (w/w).

The thermograms of all the maltodextrin/plasticizer films presented the same shape; especially two relaxations, α and β were observed (Fig. 5). In this paper only the thermogram for maltodextrin/D-sorbitol 10% (w/w) is illustrated. The first relaxation, noted α , is associated to polymer rich region and corresponds to the relaxation on the right of the thermogram. And the second relaxation, β , is associated to plasticizer rich phase and is the one found on the left side of the thermogram (Avaltroni et al., 2004; Gaudin, Lourdin, Ilari, & Colonna, 1999).

In our case, the classical model of Couchman-Karaz (Couchman & Karasz, 1978) used for the determination of the glass transition temperature of an homogeneous blend constituted of two components, does not fit our experimental results. The values of the β relaxation temperature measured were in agreement with the thermic relaxation associated to pure sorbitol -3 °C, pure glycerin -52 °C and pure water -137 °C (Gaudin et al., 1999). The relaxation on the right corresponded to a relaxation proper to the polymer and known to be representative of the glass transition temperature. Herein, noted as relaxation α (Fig. 5). In this study particular attention is given to the α relaxation because it controls the product final properties.

The role of plasticizers is to increase the mobility of the polymeric chains by introducing themselves between the polymeric chain, and creating H-bond interactions plasticizer/polymer (Vieira, Silva, Santos, & Beppu, 2011). This allows opening the polymeric chains and increasing the mobility and thus the free volume of the polymer. When the free volume of the polymer is increased, the viscosity of the polymer is then reduced and hence the glass transition temperature is also decreased. So, a plasticizer is classified as an excellent plasticizer when the free volume of the polymer is increased and thus the viscosity and the glass transition temperature are reduced.

For all the compositions containing 10 or 20% (w/w) of plasticizer, it is clear that there was a trend depending on the DE-value. Maltodextrin DE-12 could be considered as the hinge element of

the two tendencies observed. For low DE-value, glycerin appeared to be a better plasticizer than D-sorbitol since both of the relaxation temperatures were decreased (Tables 4 and 5). However, for high DE-value maltodextrins, D-sorbitol was a better plasticizer than glycerin since the α relaxation is slightly lower than for those with glycerin. This trend can clearly be observed thanks to Fig. 6, representing only the glass transition temperatures of the systems containing 10% (w/w) of plasticizer.

In the presence of glycerin at 10% (w/w) the α relaxation decreased when the DE-value increased except for DE-12. The same tendency was observed for D-sorbitol, the α relaxation decreased when the DE-value increased except for maltodextrin DE-6. For both plasticizers, the measured values for the β relaxation temperature were more or less of the same range and did not change much when the DE-value or the amount of plasticizer was increased.

However, for maltodextrins films with 20% (w/w) of glycerin, results were unexpected, since the glass transition temperature increased with the DE-value. Indeed, the α relaxation increased and the β relaxation decreased as the DE-value increased. This behavior was associated to a segregation phenomenon. The blend was more like a heterogeneous mixture and thus glycerin acted as antiplasticizer agent. This plasticizer/antiplasticizer behavior has already been noticed for D-sorbitol used in starch-based films. For example, at low sorbitol content (below 27% (w/w)) sorbitol acts as an antiplasticizer by increasing the glass transition temperatures of the films (Gaudin et al., 1999). For example, in the case of maltodextrin DE-17, the α relaxation increased when the amount of glycerin increased demonstrating that segregation occurs and thus the antiplasticizing effect of glycerin.

Moisture content of films containing 10% (w/w) of plasticizer (Table 4) and films containing 20% (w/w) of plasticizer (Table 5) were about the same range (from 8.6 to 12.9% (w/w)). Glycerin films presented higher moisture content than sorbitol films. Clearly because glycerin is more hygroscopic than sorbitol and as a consequence it has a higher capacity to adsorb water than sorbitol films (Shaw, Monahan, O'Riordan, & O'Sullivan, 2002). This was in agreement with other studies, where glycerin plasticized films of starch, gluten and whey protein presented higher moisture content than sorbitol films (Chaudhary, Adhikari, & Kasapis, 2011; Lourdin, Colonna, & Ring, 2003; Pouplin et al., 1999; Shaw et al., 2002). Two tendencies were observed; for low DE-value maltodextrins in the case of glycerin the moisture content decreased as the DE-value increased. On the contrary for sorbitol, the moisture content increases as the DE-value increases. As for the high DE-value maltodextrin there was no relevant behavior to stress out since the moisture content remained constant as the DE-value increased.

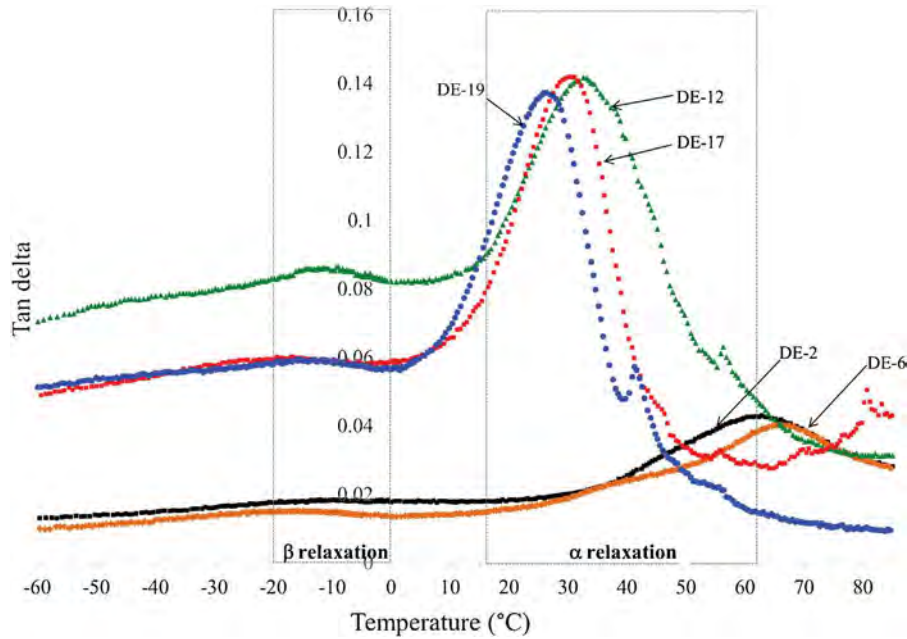


Fig. 5. Thermogram obtained by Dynamic Mechanical Analysis for different grades of maltodextrins with 10% (w/w) of D-sorbitol.

Table 4

Relaxation temperatures and moisture content of the mixtures maltodextrin/plasticizer at 10% (w/w).

Maltodextrin DE-value	Plasticizer (10%, w/w)	T α (1 Hz) °C	T β (1 Hz) °C	Moisture content % (w/w)
Maltodextrin DE-2	Glycerin	51	-59	10.6 ± 0.2
	Sorbitol	62	-10	10.0 ± 0.2
Maltodextrin DE-6	Glycerin	49	-58	9.4 ± 0.5
	Sorbitol	68	-17	10.0 ± 0.2
Maltodextrin DE-12	Glycerin	55	-55	8.7 ± 0.4
	Sorbitol	33	-12	8.7 ± 0.2
Maltodextrin DE-17	Glycerin	35	-55	8.6 ± 0.7
	Sorbitol	30	-15	12.3 ± 0.5
Maltodextrin DE-19	Glycerin	30	-55	9.3 ± 0.3
	Sorbitol	26	-15	9.8 ± 1.4

Table 5

Relaxation temperatures and moisture content of the mixtures maltodextrin/plasticizer at 20% (w/w).

Maltodextrin DE-value	Plasticizer 20% (w/w)	T α (1 Hz) °C	T β (1 Hz) °C	Moisture content % (w/w)
Maltodextrin DE-2	Glycerin	15	-51	12.9 ± 0.1
	Sorbitol	39	-12	9.8 ± 0.2
Maltodextrin DE-6	Glycerin	10	-52	10.3 ± 0.1
	Sorbitol	41	-12	10.3 ± 0.1
Maltodextrin DE-12	Glycerin	13	-30	10.6 ± 0.0
	Sorbitol	33	-12	8.9 ± 0.2
Maltodextrin DE-17	Glycerin	38	-40	10.8 ± 0.3
	Sorbitol	30	-15	8.8 ± 0.3
Maltodextrin DE-19	Glycerin	26	-45	10.5 ± 0.1
	Sorbitol	26	-15	9.0 ± 0.0

3.3. Global outline of maltodextrins behavior

The first important thing to remember of this study, before going further on the discussion, is that the use of the DE-value as a predicting tool for description of the physicochemical properties of maltodextrins is not completely the most appropriate. The degree of dextrose is a necessary parameter but not sufficient to predict the physicochemical properties of maltodextrins, given that it does not take into account the bimodal molecular distribution of these materials and their polydispersity (Fig. 1)

There were clearly two different behaviors observed depending on the DE-value. The gap seems to be marked by maltodextrin DE-12, in the case of hygroscopicity, glass transition temperature

and viscosity. Maltodextrin DE-6 and DE-12 had similar viscosities behaviors that could be explained by their very dispersive molecular weight profile, both had the highest dispersive index and degree of polymerization. Conversely, the similarities of the molecular weight profile of maltodextrin DE-17 and DE-19 were the basis of unexpected glass transition and viscosity behaviors.

Maltodextrin DE-2 was taken apart from the other four maltodextrins since it presented a completely different behavior relating to hygroscopicity and degradation. Its behavior recalled the behavior of long chain polysaccharides more like amylose or amylopectin.

Rheological and DMA results have demonstrated that glycerin is a better plasticizer than D-sorbitol for all types of maltodextrins.

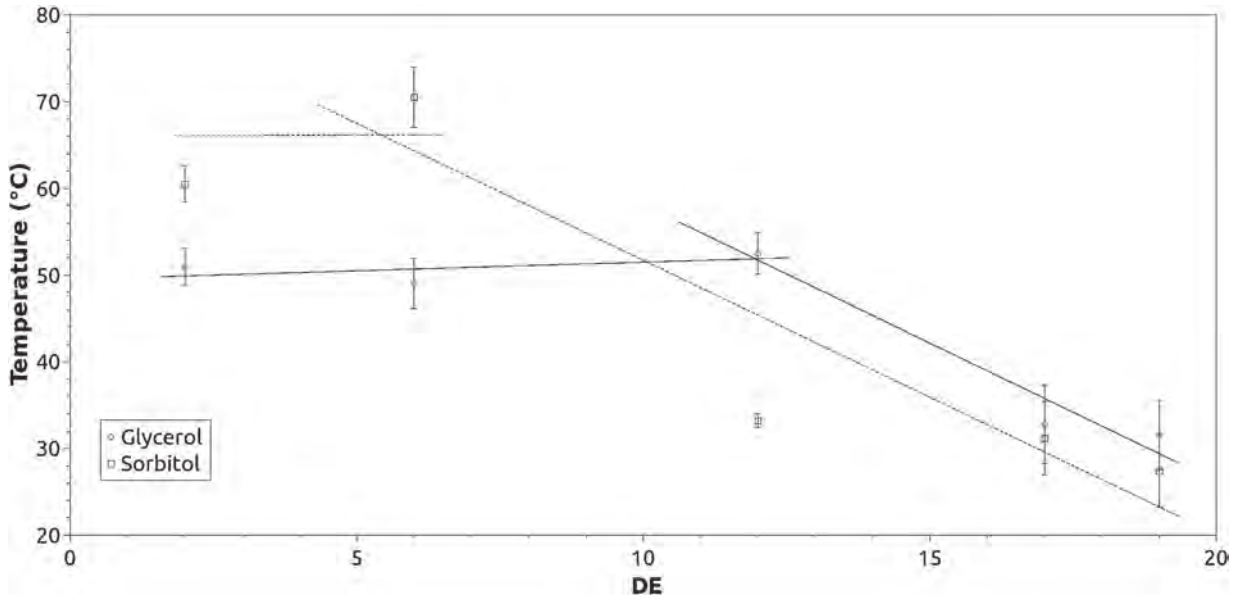


Fig. 6. Linear dependencies T_g -DE-value; T_g measured for maltodextrins/plasticizer mixtures 10% (w/w) of plasticizer ($n=2$).

For DMA tests, both the α and β relaxations presented lower values for films containing glycerin than for those containing D-sorbitol. Besides, the formulations containing glycerin presented the lowest viscosity value compared to the formulations made with D-sorbitol. Indeed, D-sorbitol has a more significant steric hindrance than glycerin, thus it is more difficult to fit within the polymer chains. Besides, for the same mass of plasticizer weighted, as D-sorbitol has a higher molecular weight than glycerin, less molecules of D-sorbitol were present in the mixture and so its plasticizer effect was lower. Our findings confirm previous results where glycerin was also found as a better plasticizer than D-sorbitol for starch-based materials (Pouplin et al., 1999).

It is hard to establish a direct correlation between the DE-value and the glass transition temperature even though, for some studies, there is a linear correlation (Avaltroni et al., 2004; Levine & Slade, 1986; Roos & Karel, 1991). The difficulty to establish this correlation is based in on the fact that the DE-value does not take into account that maltodextrins are composed of a bimodal molecular weight distribution. Expressed differently, maltodextrins are composed of a mixture of different DP-fractions and the DE-value omits this fact. Also, the DE-value neglects the molecular structure of maltodextrins, and it has been demonstrated that linear chains give rise to a higher glass transition temperature than branched chains of the same weight average molecular weight (Levine & Slade, 1986). Not to mention, that related to viscosity, linear chains have a lower viscosity than branched chains. In line with what was just mentioned, maltodextrin DE-12 had a significant proportion of high molecular weight polysaccharides that could be branched and therefore be responsible of the important viscosity. Or, in terms of molecular weight distribution maltodextrin DE-19 had a more important population of high molecular weight polysaccharides and therefore its viscosity was more important than maltodextrin DE-17's viscosity at 12% (w/w) of moisture content (Fig. 4). For this reason, it is more rigorous to correlate the whole molecular weight distribution of maltodextrins to the viscosity and the glass transition temperature.

For example, the glass transition temperature of maltodextrin DE-12 (55 °C) was higher than the glass transition temperature of maltodextrin DE-17 (35 °C) at the same amount of glycerin at 10% (w/w) (Table 4). However increasing the plasticizer amount of 20% (w/w) completely changed the trend, glass transition temperature

of maltodextrin DE-12 (13 °C) was lower than glass transition temperature of maltodextrin DE-17 (38 °C) (Table 5). Taking a deeper look inside the others maltodextrins, it is imperative to remark that there was an optimal plasticizer content for each maltodextrin. For example in the case of glycerin; for maltodextrin DE-2, increasing the plasticizer content allowed to decrease the α relaxation temperature, acting as a plasticizing agent. However for maltodextrin DE-17, increasing the glycerin content induced an increase of the α relaxation temperature acting as antiplasticizing agent (Fig. 6). For D-sorbitol, increasing the amount of plasticizer did not influence the α relaxation, for high DE-value maltodextrins. This seems to imply, that for each DE-value maltodextrins there was an optimal amount of plasticizer.

For the sorption isotherm maltodextrins DE-12 and DE-6 were the most hygroscopic among the other maltodextrins for relative humidities below 60% RH because they were the ones having a more important population of high molecular weight polysaccharides. This was expected as the higher the degree of polymerization is, the higher the amount of bounded water is. In addition, maltodextrin DE-19 was more hygroscopic than maltodextrin DE-17 because it had a more important population of high molecular weight polysaccharides. It seems that for relative humidities below 60% RH, high molecular weight polysaccharides are responsible for the water adsorption. In contrast, for relative humidities above 60% RH low molecular weight polysaccharides are responsible of water adsorption, revealing a structural change in the macroscopic organization when the threshold humidity is past. Additional experiments, as X-ray diffraction, will be interesting to verify the organization of such carbohydrates according to their molecular weight and moisture content.

4. Conclusion

To better understand the behavior of maltodextrins and hence adapt the extrusion process conditions, the DE-value is not the only parameter to take into account because in some particular cases it does not predict the behavior of T_g or the viscosity in specific environments. It is better to trust the molecular weight distribution or the sorption isotherm in order to get a better understanding.

It is very important not underestimate the botanical origin of starch, as well as the amylose/amylopectin ratio since both parameters directly affect the molecular weight distribution of

maltodextrins, and thus their physicochemical properties. Special attention needs also to be given to the type of hydrolysis since it will determine the molecular weight distribution of maltodextrins. An acid hydrolysis will give a broader molecular weight distribution conversely to the enzymatic hydrolysis. Nowadays enzymatic cocktails (amylase and pullulanase enzymes) combine with acid hydrolysis are employed in order to obtain maltodextrins with a more accurate molecular weight profile.

The role of a plasticizer in general is to improve the processability of a mixture, in both ways by allowing setting up softer processing conditions (in terms of temperatures or mechanical strength by decreasing the viscosity) and also by enhancing the incorporation and dispersion of active agents. As a consequence, the flowability of the mixture being extruded is increased.

The most important thing worth noting in this study, based on the rheological measurements, moisture content and off course, the DMA relaxations temperatures, is that glycerin is a better plasticizer than D-sorbitol. This is because glycerin is a very low molecular weight molecule and highly hygroscopic therefore, it binds easily to water and to the polymeric chains by H-bond interactions. As a consequence, glycerin allows a better disentanglement of the polymeric chains, enhancing water adsorption.

However maltodextrins are very complex materials and their window of processability is very narrow. If the plasticizer content is to be below 10% (w/w) maltodextrins are brittle and unstable. And if the plasticizer content is above 20% (w/w) maltodextrins are too ductile to be handle. We want to bring the attention to the fact that maltodextrins can be extruded at low temperature, which changes operating conditions that are commonly used. This brings a large range of applications without fearing degradation of thermolabile active compounds and reducing Maillard's reaction from taking place in carbohydrates-based materials. And last but not the least, extrusion of maltodextrins at low temperature is an appealing economical argument. Under these circumstances, maltodextrin DE-12 for example, seems to be an efficient raw material for melt extrusion applications. While maltodextrin DE-19 is more appropriate to be used for spray drying due to its lower viscosity and its hydrophilic character at high relative humidities (Reineccius, 2004; Risch, 1995, chapter 1).

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