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Maltodextrin molecular weight distribution influence on the glass transition temperature and viscosity in aqueous solutions

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Abstract

The intrinsic functional properties (viscosity and glass transition temperature) of three corn maltodextrins (and their mixtures) in various amount of water are predicted from the molecular weight distribution. The concentration dependence of the viscosity at constant temperature is predicted over a broad range of concentration using a combination of the Mark–Houwink–Sakurada (with a rather low exponent (0.337) compared to other carbohydrates) and Spurlin–Martin–Tennent's exponential models. The construction of a viscosity–concentration master-curve is successfully attempted when the shift factor is the viscosity average molecular weight. The glass transition temperature for dry maltodextrin samples is predicted in the light of previous investigations performed on the series of maltose oligomers. A new effective average molecular weight, characteristic of the glass temperature, is introduced and determined by the plasticizer/plasticized ratio. Couchman's model is well adapted to starch water systems and is proven here to be also appropriate for maltodextrin water mixtures where the heat capacity increment depends on the number average molecular weight.

Keywords: T_G; Viscosity; Size exclusion chromatography; Effective average molecular weight; Viscosimetric average molecular weight

1. Introduction

Glass transition (T_G) and viscosity (η) are the two key physico-chemical parameters characterising biopolymer behaviour in various food (Heyraud & Rinaudo, 1991; Roos & Karel, 1991a), flavour and pharmaceutical applications (Striegel, Plattner, & Willett, 1998). Their treatment in the same article is justified by the fact that both these parameters refer to the same phenomenon, e.g. the influence of water (in small amounts or large amounts, respectively). Among the food biopolymers of interest for spray-drying, spray-coating and extruded encapsulation, maltodextrins are especially useful due to their aqueous solubility, low viscosity and high T_G after drying (Kenyon, 1995). Maltodextrins are obtained by acid and/or enzymatic hydrolysis of starch, but to a lower extent than that required to produce starch syrups. Among the wide choice of commercially available maltodextrins, choosing the appropriate one for these applications is a matter of compromise between its properties in solution (before the process) and its properties at the glassy state (after the process) (Marchal, Beftink, & Tramper, 1999). Maltodextrins are usually supplied with the dextrose equivalent value (DE) as the only information from which all properties seem to be empirically guessed (see Dokic, Jakovlejevic, & Dokic-Baucal, 1998, for an example). This measure is realised under well-defined conditions and is a rough estimation of the similarity of the compound of interest to glucose and is directly linked to the number average molecular weight. The DE of maltodextrins has, however, been shown to be inadequate to predict product performances in various applications (Chronakis, 1998). Recently, it has been clearly shown that the molecular weight distribution is, as could be expected, a much more accurate tool to predict maltodextrin fundamental properties but it has only been applied to particular, specific issues so far (Striegel et al., 1998; Wang & Wang, 2000; White, Hudson, & Adamson, 2003). The present work is an attempt to relate T_G and η to the relevant

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molecular weight distribution parameters in a more general way. The WLF (Williams–Landel–Ferry) equation provides a relationship between properties at a given temperature related to those at T_G, and has successfully described highly concentrated starch hydrolysates (60–85% w/w) for temperatures ranging from 20 to 80 °C (D'Haene & Van Liederkerke, 1996). Therefore, with that approach, the viscosity can be predicted at any temperature and concentration in the range considered, from a single point measurement. The only information required by this technique is to know the mass fraction of components having a degree of polymerisation (DP) lower than 10 to estimate the T_G.

Besides, to determine the influence of sample molecular weight on T_G, valuable theories have already been developed on the mixture of either two different molecular species (Gordon, Rouse, Gibbs, & Risen, 1977), or dry biopolymers with dry oligosaccharides (Orford, Parker, & Ring, 1990; Orford, Parker, Ring, & Smith, 1989; Roos & Karel, 1991a,b) or biopolymers and a solvent (see Couchman (1978), for a review). The extension of these theories to polydisperse material but also including solvent (water) influence will be realised in the present work in order to describe better corn-maltodextrins. The use of one starch source is mainly caused by the experimentally required approximation of considering only the most abundant α-(1,4)-bonds, therefore, neglecting the branched, α-(1–6)-bonds originating from amylopectin (Clarke, 2002). Amylopectin to amylose ratio is known to vary with starch origin (Koch & Röper, 1991; Zobel, 1988), rendering, therefore, our approach valid only inside one plant species (e.g. amylopectin to amylose ratio). However, we demonstrate in the present work that this assumption is not a limiting factor, and thus that our approach is also valid between maltodextrins of different origins.

After the presentation of materials and methods, results are presented and discussed in the light of existing theories. Furthermore, an empirical model is presented to highlight a new average molecular weight definition, characteristic of the glass transition temperature, determined from the whole molecular weight distribution measured.

2. Materials and methods

2.1. Maltodextrin samples and DE determination

Maltodextrins of different hydrolysis degrees (Glucidex 2DE, 10DE and 19DE) were supplied by Roquette Frères (62-Lestrem, France). These were obtained by undisclosed degradation of native cornstarch. The extent of starch degradation in a maltodextrin is indicated by the Dextrose Equivalency parameter (DE) that evaluates the content of reducing-end groups. This has been measured using the Lane and Eynon standard technique (ISO 5377-1981 (F)) (Lane & Eynon, 1923) and is summarised in Table 1 for the three maltodextrin samples investigated in this study. The DE measured is in relatively good agreement with supplier's specification. Mixtures of maltodextrins of different DE have been prepared, as described in Table 2. Results on an amorphous potato starch obtained by extrusion with water (Benczédi, Tomka, & Escher, 1998) are also reported.

Table 1
Measured DE for the three different grads of maltodextrins

Maltodextrin generic name	DE measured
2 DE (corn)	2.50 ± 1.0
10 DE (corn)	12.70 ± 0.2
19 DE (corn)	17.60 ± 0.1

2.2. Sample homogeneisation

Low water content samples were prepared in a high-speed mixer (Schweizer, Lausanne, Switzerland). The maltodextrin powder was therein mixed with various amounts of water (from 0 to 10% w/w). The mixer ensures a homogeneous distribution of the water in the sample.

High water content samples were prepared by mixing at room temperature appropriated weights of maltodextrin powder and water followed by heating to 90 °C under strong stirring conditions until clear and non-turbid solutions are obtained.

2.3. Karl Fischer estimation of water content

The water content was determined by stoichiometric titration according to the Karl Fischer technique and ranges from 5.3 to 13.85% w/w. The water content was measured before and after determination of the glass transition temperatures. The loss of water during the thermal treatment was constant ($r^2 = 0.96$) for all samples and equal to 1.89% w/w over the narrow range of concentrations considered.

2.4. Size-exclusion chromatography

System. Molecular weight distributions were determined by size-exclusion chromatography of a 1 g/l solution of the different maltodextrin samples dissolved overnight at room temperature until a transparent and homogeneous solution is obtained. The chromatographic system consisted of 3 Shodex 8 mm × 300 mm OH-Pak columns (SB-802.5, SB-803, SB-804) put in series after a SB-G 6 mm × 50 mm

Table 2
Mass composition of the samples containing mixtures of maltodextrins (% w/w)

Name	2 DE	10 DE	19 DE
2-19a	25%	–	75%
2-19	50%	–	50%
2-19b	75%	–	25%
2-10	50%	50%	–

guard column, with claimed exclusion limits for pullulans of 10^4, 10^5, and 10^6 Da, respectively. The eluent was a 0.05 M solution of sodium triazide (NaN_3, 99.99%, Aldrich, Steinheim, Germany), at a flow rate of 0.5 ml/min. The instrument was an Agilent 1100 tower, made of a G-1311A quaternary pump, a G-1313A auto-sampler, and equipped with a G-1322A vacuum degasser (Agilent, Waldbronn, Germany). The injected volume was 100 µl. All measurements were made at room temperature. Detection was made with a Merck RI-71 differential refractometer ($K_{RI}=0.5468$) (Merck, Germany).

Calibration. The calibration was performed with pullulan and malto-oligomer standards of molecular weights ranging from 342 to 788,000 Da fit with a classical third order polynomial ($R^2=0.9997$). Maltose (5911.1000, Merck, Darmstadt, Germany), Maltotriose (>95%, M-8378, Sigma, St Louis, USA), Maltotetraose (98%, 35102, Acros Organics, Geel, Belgium), Maltopentaose (98.5%, 23.324.44, Acros Organics, Geel, Belgium), Maltohexaose (>90%, 63416, Fluka, Buchs, Switzerland), Maltoheptaose (>90%, 28401-7, Aldrich, Milwaukee, USA) and P-82 Shodex Pullulan standards (10401, Showa Denko, Düsseldorf, Germany) of 5900, 11,800, 22,800, 47,300, 112,000, 212,000, 404,000, 788,000 g mol^{-1}, were used for completing the calibration. Reproducibility of the method appeared to be acceptable (standard deviation on retention time at peak apex was 0.04%, on total chromatogram area <3%).

Discretisation. The discretisation of the chromatogram (concentration as a function of molecular mass) was done by a deconvolution of the chromatogram into a sum of gaussian peaks centred on each DP. The molecular weight (M_i) corresponding to a given degree of polymerisation for maltodextrin is obtained using $M_i=162DP_i+18$.

2.5. Rheometry

Viscosity measurements were carried out on freshly prepared solutions, and deionised water, at constant temperature (20 °C) on a Physica MCR300 rheometer (PAAR Physica, Stuttgart, Germany), equipped with cone and plate geometry (radius = 2.5 cm; angle = 2°; gap = 50 µm). A shear rate gradient from 10 to 1000 s^{-1} was exerted quickly after the sample was introduced between the cone and plate. Samples range from 1 to 50% w/w maltodextrin concentration and considering the duration of the experiment (10 min in total), water loss during the measurement was considered negligible. Stability of high water content solutions over time (retrogradation) was measured using identical geometry as for viscosity measurements. The shear and loss modulus were determined every 12 min for 48 hours at 1 Hz and constant 1% amplitude strain.

2.6. Phase transition analyser (PTA)

A mass of exactly 1.25 g of powder was introduced into the Phase Transition Analyser compression chamber (PTA 240, Wenger, Sabetha, KS, USA) for determination of the powder's glass transition temperature. The PTA consists of a sealed chamber that is subjected to both a constant pressure and a linear increase in temperature. The piston displacement measures the compaction of the powder. Initial conditions were as follows: the pressure was preset to 160 bar for 5 s at 10 °C and then reduced to 150 bar for the time of the experiment. The temperature range was 10–140 °C and temperature heating-rate was 5 °C/min. The glass transition temperature was then determined as the temperature at which the first derivative of the piston displacement leaves the region of linearity.

3. Results and discussion

3.1. Molecular weight distribution

Maltodextrins contain small oligosaccharides along with polysaccharides of larger molecular weight. Starch molecules exist in two forms, either linear amylose chains or branched amylopectin chains. However, no standard is available for amylopectin, and since SEC-RI cannot differentiate amylose from amylopectin, the entire distribution is approximated as being composed of amylose chains only. This approximation limits the comparison to products having similar amylose/amylopectin ratios, assuming a constant bias in the mass estimation of high molecular weight compounds. In Fig. 1a, four chromatograms from three maltodextrins and one starch are presented.

The starch shown in this study (Benczédi, Tomka, & Escher, 1998) has a distribution of large molecular weights from which small molecules are absent. Upon hydrolysis, the large molecules disappear and very small ones appear, as shown by the series of chromatograms from 2DE to 19DE.

Mixtures of maltodextrins in different ratios have been characterised using the same techniques. Their chromatograms were reconstructed from the summing up of the original chromatograms affected by their relative mass ratio. The results in Fig. 1b show that the detection is independent of chain length, as the difference between the measured and reconstructed chromatograms is not statistically significant.

The classical results (number average molecular weight (M_n) and weight average molecular weight (M_w)) calculated from the chromatograms are reported in Table 3 for the samples studied.

The M_n and M_w molecular weights for starch are underestimated due to calibration constraints, and a value of 10^8 g mol^{-1} has been reported elsewhere (Benczédi et al., 1998).

In Fig. 2, an example of the discretisation realised on one chromatogram by DP of anhydrous glucose units, is in good agreement with the measured cumulative chromatogram.

Table 4 shows the estimation of individual molecular species molar content obtained by the discretisation of the chromatogram. It reveals a low amount of DP1 for the three

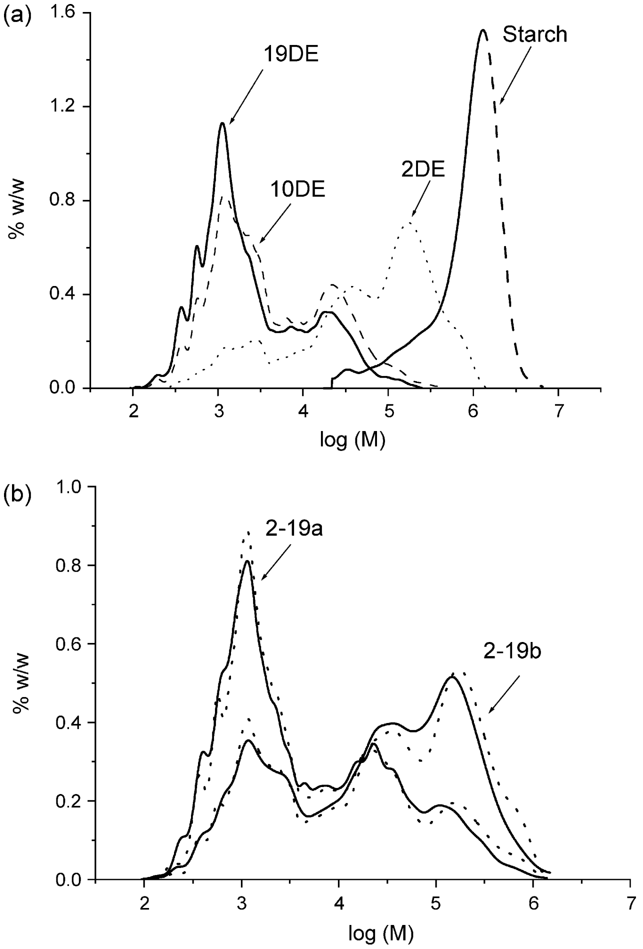

Fig. 1. (a) Chromatogram of original material used. The areas under the chromatograms are normalised. (b) Comparison of measured chromatogram with the reconstructed chromatogram. Solid lines stand for measured chromatograms (2-19a and 2-19b) and dashed lines for the reconstructed chromatograms.

maltodextrins, while DP2 and DP3 are the majority, and do increase with the hydrolysis degree. DP4 and DP5 appear reasonably constant for the three maltodextrins while fractions larger than DP6 are much more abundant in maltodextrin 2DE than 10DE and 19DE.

3.2. Behaviour at large amounts of water, viscosity

Viscosity behaviour of maltodextrins was Newtonian for all samples tested. The absence of retrogradation was ascertained for every sample studied in this work. For the sample most likely to retrograde, a 40% w/w 2DE maize maltodextrin:water solution, retrogradation appeared after around 35 h at 20 °C. A sudden change of slope in the evolution of the loss tangent at 1 Hz with time and a significant increase of the solution's turbidity are characteristic of molecular aggregation. The loss modulus increases slowly (+10% in 40 h) and continuously with time. This demonstrates that the process of aggregation is continuous and eventually leads to a physical gel structure as already known for potato maltodextrins but at much longer times than those reported for maltodextrins of potato source (SA2) (Kasapis, Morris, Norton, & Clark, 1993).

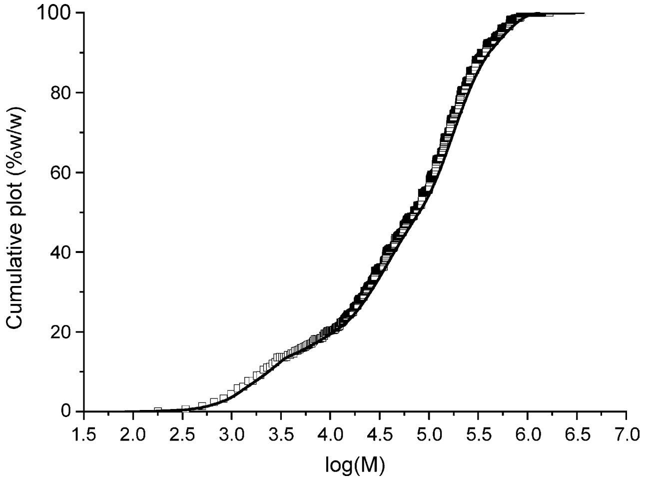

Fig. 2. Comparison between the discrete and the measured chromatogram as a cumulative plot for maltodextrin 2DE.

The viscosity of polymers is usually described using the Mark–Houwink–Sakurada empirical equation (see Eq. (1)), which is a relationship between the intrinsic viscosity and the molecular weight

$$[\eta]_0 = kM^{\alpha} \tag{1}$$

where $[\eta]_0$ is the intrinsic viscosity; M, the molecular weight of a monodispersed polymer; k and α constants are related to the degree of molecular expansion and hence depend upon the local stiffness of the polymer backbone and polymer–solvent interactions. $[\eta]_0$ can be accessed through different routes (see Eqs. (2)–(4)) and represents the volume occupied per unit mass for infinite dilution conditions

Table 3
Average molecular weights from measured maltodextrin chromatograms

Maltodextrin sample	M_n (g mol^{-1})	M_w (g mol^{-1})
2DE	7500	155,000
10DE	1700	15,000
19DE	1250	9000
2-19a	1400	34,000
2-19	1800	56,000
2-19b	3100	104,000
2-10	3200	70,000
Starch	194,000	1,100,000

Table 4
Molar fraction of individual molecular species in the maltodextrin samples calculated by chromatogram discretisation

DP	19DE	10DE	2DE
1	4.8%	5.1%	1.9%
2	18.8%	13.2%	10.0%
3	19.7%	16.1%	10.6%
4	10.3%	9.1%	10.3%
5	9.8%	8.7%	7.5%
6	12.4%	12.1%	7.6%
>6	24.2%	35.7%	52.1%

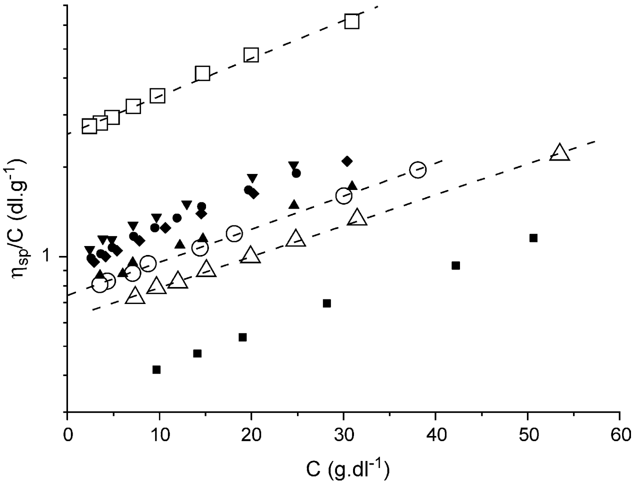

Fig. 3. Plot of Spurlin–Martin–Tennent's model for maltose (solid squares), 19DE (open triangles), 10DE (open circles), 2DE (open squares), mixtures of 2DE and 19DE (2-19a solid down-triangles, 2-19, solid diamonds, 2-19b solid up-triangles), mixture of 2DE and 10DE (2-10, solid circles).

$$\frac{\eta_{sp}}{c} = [\eta]_0 + k'[\eta]_0^2 c \tag{2}$$

$$\frac{\ln(\eta_{sp} + 1)}{c} = [\eta]_0 + k''[\eta]_0^2 c \tag{3}$$

$$\ln\left(\frac{\eta_{sp}}{c}\right) = \ln([\eta]_0) + K[\eta]_0 c \tag{4}$$

where η_{sp} is the specific viscosity; c, the concentration in g dl^{-1}; k', k'' and K are constants. Eq. (2) is Huggins equation, Eq. (3) is Kraemer's equation and Eq. (4) is known as the empirical Spurlin, Martin, and Tennent's (1946) equation and used preferentially for long chain synthetic polymers and natural carbohydrates (Phillies, 1995). Fig. 3 shows that this last model is clearly applicable to 19DE maltodextrin up to a maltodextrin concentration of 53.5 g dl^{-1}.

The intrinsic viscosity for eight samples of various molecular weight distributions has been obtained from a least square regression and an extrapolation to zero concentration for Eqs. (2)–(4) with concentrations ranging from 2.3 to 47% w/w of dry maltodextrins (taking into account the water content measured using the Karl Fischer technique). Results are presented in Table 5.

In the case of polydisperse polymeric material, the intrinsic viscosity can be represented as a function of the average molecular weight M_w as commonly proposed for gaussian distribution of high molecular weight coil-like polysaccharides (i.e. guar galactomannans (Beer, Wood, & Weisz, 1999), xanthan gum (Sato, Norisuye, & Fujita, 1984)). However, the results presented for xanthan gum degradation using enzymatic and ultrasonic treatments show that for identical values of M_w, different intrinsic viscosities are measured (Milas, Rinaudo, & Tinland, 1986). This indicates that the molecular weight distribution is incorrectly characterised by the M_w parameter for viscosity prediction. In some cases the viscosimetric average molecular weight ($\bar{M}_v$) must be used, especially when α in Eq. (1) is significantly lower than unity. $\bar{M}_v$ is determined using Eq. (5) considering the molar weight distribution

$$\bar{M}_v = \left(\frac{\sum_i x_i M_i^{\alpha+1}}{\sum_i x_i M_i} \right)^{1/\alpha} \tag{5}$$

where x_i is the molar fraction of the mass M_i and α is the same as in Eq. (1).

3.2.1. $[\eta]_0$ calculation

Literature is scarce on broad molecular weight distribution polysaccharides such as maltodextrins. In Fig. 4, α has been determined empirically from the slope of log($[\eta]_0$) as a function of log($\bar{M}_v$) (Eq. (1)). Glucose and maltose values have not been taken into account for this determination but have been added afterwards on the graph since the present study deals with polydisperse material. The optimal value found for α was 0.337 (see Fig. 4).

The value found for k, from Eq. (1), is 2.43×10^{-3} and is in line with the values found in the literature for other biopolymers (Doublier & Cuvelier, 1996). Mark–Houwink–Sakurada model can predict $[\eta]_0$ accurately, but another

Table 5
Intrinsic viscosity of measured samples

	Huggins (Eq. (2))		Kraemer (Eq. (3))		Spurlin–Martin–Tennent (Eq. (4))		Average values	
	$10^2[\eta]_0$ (dl g^{-1})	k' (–)	$10^2[\eta]_0$ (dl g^{-1})	k'' (–)	$10^2[\eta]_0$ (dl g^{-1})	K (–)	$10^2[\eta]_0$ (dl g^{-1})	$\pm 10^2\sigma$ (dl g^{-1})
Maltose	1.8	2.7	1.9	1.1	1.7	2.3	1.8	0.1
19DE	3.0	3.4	4.0	0.4	3.4	1.6	3.5	0.5
10DE	4.8	1.8	5.4	0.3	4.5	1.6	4.9	0.45
2DE	10.3	1.8	12.5	0.1	10.5	1.2	11	1.2
2-19b	7.7	2.6	9.9	0.2	9.0	1.1	8.8	1.1
2-19	6.6	2.2	7.4	0.4	6.7	1.4	6.9	0.4
2-19a	4.5	3.1	5.9	0.3	5.2	1.4	5.2	0.7
2-10	6.6	2.5	7.8	0.5	7.5	1.2	7.3	0.6
Glucose[a]	1.3	35.4	1.3	32.3	1.4	21.3	1.34	0.04

[a] From Kurata and Tsunashima (1981–1982).

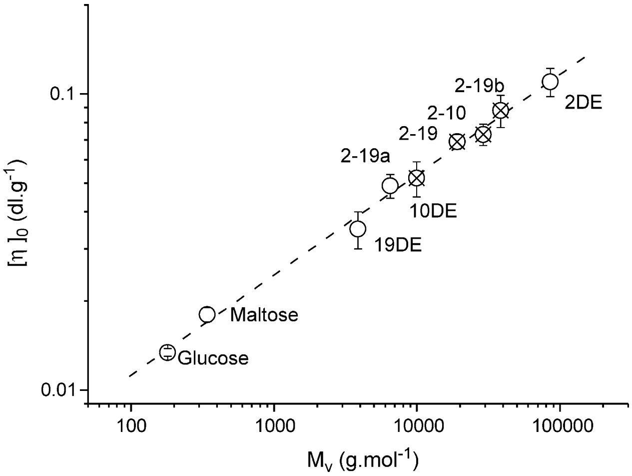

Fig. 4. Intrinsic viscosity as a function of the viscosity average molecular weight $\bar{M}_v$. Slope value of this graph and Mark–Houwink exponent for Eq. (5) is 0.337.

model must be used to predict the specific viscosity as a function of the polymer concentration.

3.2.2. Application of Spurlin–Martin–Tennent's model

Spurlin–Martin–Tennent's model was preferred for the estimation of specific viscosity as both Huggins and Kraemer models accurately fit only the low concentration region. These models result from the simplification of a more general Virial expansion to two components and Spurlin–Martin–Tennent's model has already shown accuracy up to $c[\eta]_0 = 4$ for various types of polymer (Chauveteau, 1982). This would validate Spurlin–Martin–Tennent's model up to a concentration of 36 g dl^{-1} for the most viscous maltodextrin presented here (2DE). However, to estimate the specific viscosity from Spurlin–Martin–Tennent's model, also the constant K in Eq. (4) has to be calculated. According to the values presented in Table 5, it appears that for glucose and maltose the constant K is out of the range of the experimental values observed for the different maltodextrin samples whose evolution with the chromatogram is not very clear. Therefore, we will treat K as a characteristic constant for maltodextrins having an average value of 1.34 ± 0.20.

Once K and $[\eta]_0$ are determined for a given maltodextrin molecular weight distribution, its viscosity can be estimated for a large range of concentration. Fig. 5 shows the comparison between the measurement and the calculated viscosities for three samples measured (2DE, 10DE and 19DE). The model gives fair estimations of the viscosity in the range of concentration considered. Fit is also good for the other samples (results not shown).

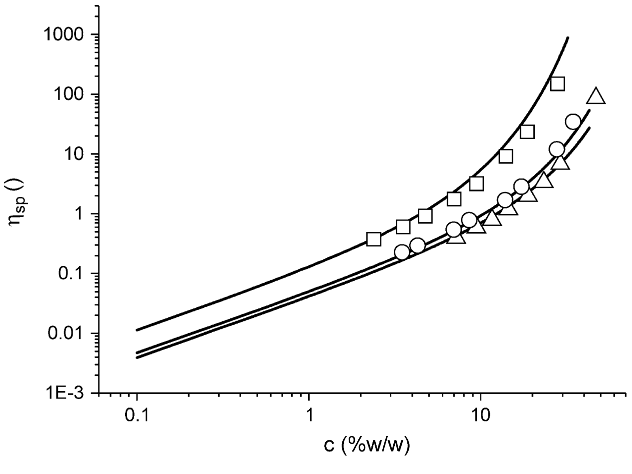

Fig. 5. Application of Spurlin–Martin–Tennent's model for specific viscosity and comparison to experimental measurements. Open squares, circles and triangles are maltodextrins 2DE, 10DE and 19DE, respectively, lines represent the calculated values.

3.2.3. Viscosity master-curve for maltodextrins

The curves from Fig. 5 have been shifted onto a viscosity–concentration master-curve where the concentration is expressed as a dimensionless reduced concentration parameter. The resulting master-curve is presented in Fig. 6.

In Fig. 6, the master-curve is drawn for the viscosity of maltodextrins with the scaling factor affecting one axis only. It has been suggested and used in the past that the weight average molecular weight M_w should scale all the data. Fig. 6 shows that a more accurate result is obtained when the scaling factor is the viscosity average molecular weight $\bar{M}_v$, affected by the Mark–Houwink–Sakurada exponent due to α being smaller than unity.

3.2.4. Structural information in solution

The Mark–Houwink–Sakurada exponent α is found to vary from 0.8 for polymer with coil-like behaviour in 'good solvent' to 0.5 in 'Θ solvent'. Values higher than unity are characteristic of rod-like polymers. However, an exponent below 0.5, as found in the present work for maltodextrins, is characteristic of branched polymers of large molecular

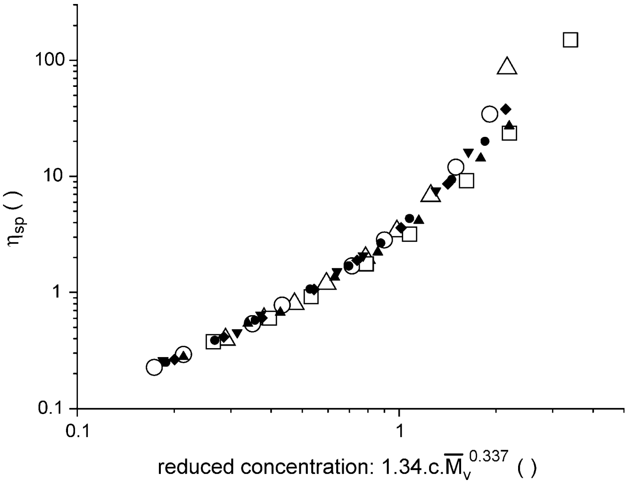

Fig. 6. Specific viscosity as a function of the reduced concentration for seven maltodextrins samples differing in their chromatograms. Open-squares: 2DE, open-circles: 10DE, open-triangle: 19DE, cross-triangles: 2-19a, open-stars: 2-19, cross-squares: 2-19b and cross-circles: 2-10.

weight. For the viscosity of sphere-like objects, Einstein equation initially developed for Brownian movements (see Eq. (6)), has shown to be appropriate (de Kruif, van Iersel, Vrij, & Russel, 1985).

$$\eta_{sp} = \tfrac{5}{2}\phi; \quad \forall M \tag{6}$$

Here, ϕ is the phase volume occupied by the spheres. In the Einstein equation, only the phase volume of the spheres in solution is relevant to estimate the specific viscosity of the ensemble. As a matter of fact, the viscosity is independent of the weight of the sphere, and so is the intrinsic viscosity. For a dispersion of spheres, α in Eq. (1) would tend to zero. Different techniques (SAXS, NMR and Ultracentrifugation) suggest that amylopectin adopts a rather flat conformation in solution: disk like shape or oblate ellipsoid with high major to minor axis ratio (Durrani, 1992). This information validates the value of α found for maltodextrins as maltodextrins structure in solution is between coil-structures in good solvent for the lowest molecular weights and ovoid-like shape rather than rod-like shape for the highest molecular weights. In fractal theories, α is assimilated to the reverse of the fractal dimension ($1/d_F$) (Nicolai, Durand, & Gimel, 1996). Ovoid like shape also correspond to a fractal dimension of 3.

Additional evidence of the structural information comes from the Huggins k' coefficient, which indicates the quality of the solvent. Usually, values ranging between 0.3 for good solvent to 1 are found experimentally. However, larger values, like those reported in Table 5 suggest a poor solvent quality, associated with a tendency to aggregation (Launay, Doublier, & Cuvelier, 1986). This again is consistent with the Mark–Houwink–Sakurada exponent, which predicts ovoid-shapes.

3.3. Behaviour at small amounts of water, glass transition temperature T_G

The T_G for different maltodextrin:water ratios was measured by PTA. A typical PTA curve is shown in Fig. 7.

At temperatures below T_G, the glassy packed powder volume decreases slowly. T_G is localised by the arrow and corresponds to the point where the slope of the piston's displacement increases significantly. This corresponds to the disappearance of interstitial space between solid particles when they become rubbery. At 120 °C, there is no more interstitial space and a plateau is observed. The sample is no more compressible. At 130 °C, the viscosity decrease forces the molten mass to leak through the O-ring seal and the piston pushes the sample out of the chamber.

The T_G for the three different maltodextrins, one starch, and two mixtures of maltodextrins is presented in Fig. 8, for different water contents, as measured by PTA.

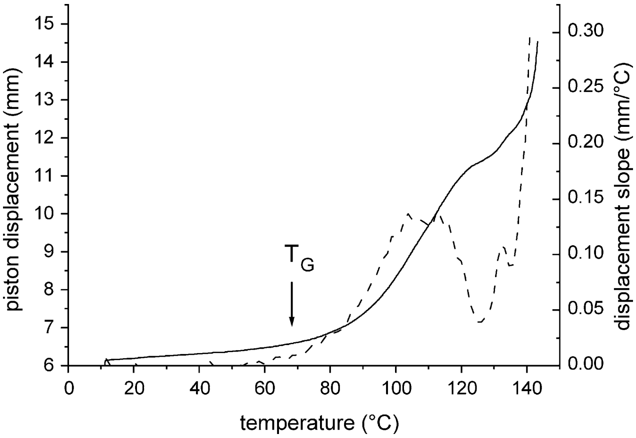

Fig. 7. Example of T_G determination from the displacement trace of the Phase Transition Analyser for maltodextrin 19DE containing 5.3% w/w of water. Solid line represents the piston displacement and dashed line represents the slope of the displacement corrected by the initial slope.

Relevant theories will be exposed hereafter in order to mathematically fit maltodextrin T_G behaviour as a function of water content. Developments already exist on mixing laws to predict the T_G of mixtures of two molecular species (Gordon et al., 1977), dry biopolymers mixed with dry oligosaccharides (Orford et al., 1990; Orford et al., 1989; Roos & Karel, 1991a–c) and (bio-) polymers mixed with a solvent (see Couchman (1978), for a review).

3.3.1. Mixture of water and single oligosaccharides

When water is added to single oligosaccharides, the entropy-based Couchman and Karasz (1978), see Eq. (7), or its empirical equivalent from Gordon and Taylor (1952) have shown good prediction of T_G within a large range of water fractions (Orford et al., 1989; Roos & Karel, 1991a,b)

$$T_{Gm} = \frac{\phi_1 \Delta C_{p1} T_{G1} + \phi_2 \Delta C_{p2} T_{G2}}{\phi_1 \Delta C_{p1} + \phi_2 \Delta C_{p2}} \tag{7}$$

Here T_{Gm} is the glass transition of the mixture, subscripts correspond to species, ϕ to weight fraction and ΔC_p is

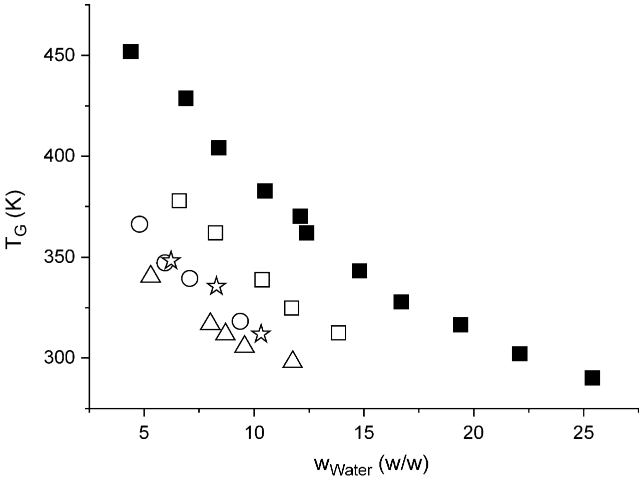

Fig. 8. T_G measured for maltodextrins open scatters (squares: 2DE; circles: 10DE; triangles: 19DE and stars: mixture of 2DE and 19DE (2-19)) and used from the literature for extruded starch (Benczédi et al., 1998) (solid squares) as a function of the water content of the sample.

the heat capacity for the individual transition. This model equation is still under discussion due to experimental difficulties to reach absolute thermodynamic values (Orford et al., 1989), but has been successfully applied to starch hydrolysates when the composition is known up to a DP of 10 (D'Haene & Van Liederkerke, 1996).

3.3.2. Binary mixtures of dry homologous oligosaccharides

It has been shown experimentally that the Couchman and Karasz model does not work in this case. Instead, a linear relationship relates the T_G of the binary mixture to the molar composition of the dry system (Orford et al., 1989)

$$T_{Gm} = \frac{x_1 T_{G1} + x_2 T_{G2}}{x_1 + x_2} \tag{8}$$

where x is the molar fraction.

This model applies to maltotriose/glucose and maltohexaose/glucose but failed with maltohexaose/galactose mixture (non-homologous sugars). Eq. (8) fits accurately experimental data whereas Eq. (7) fails possibly due to a solvent quality argument. A monomer is usually considered the best solvent for its polymer.

3.3.3. Extension to polydisperse material

Maltodextrins can be approximated as complex mixtures of homologous carbohydrate polymers, neglecting the α-(1,6)-bonds bonds randomly present (Clarke, 2002). The measured DE (see Table 1) is directly linked to the number average degree of polymerisation (DP_n*) for linear polysaccharides as it measures the reducing end groups: $DE = 100/DP_n^*$. DP_n is also determined using M_n (see Table 3). ($DP_n = (M_n - 18)/162$). A good but not perfect agreement is obtained when comparing DP_n^* and DP_n for all pure maltodextrin samples: $DP_n = 1.12\ DP_n^* + 1.4$; $R^2 = 0.9999$. This is in favour of a rather low number of branching. molecules that decreases when DE increases. To simplify, we consider maltodextrin samples as a distribution of linear polysaccharides. Therefore, extending Eq. (7) or (8) to a polydisperse mixture leads to Eqs. (9a) for non-homologous and (9b) for homologous sugars, respectively

$$T_{Gm} = \frac{\sum_i \phi_i \Delta C_{pi} T_{Gi}}{\sum_i \phi_i \Delta C_{pi}} \tag{9a}$$

$$T_{Gm} = \frac{\sum_i x_i T_{Gi}}{\sum_i x_i} \tag{9b}$$

Eq. (9b) should be applicable to dry maltodextrins T_G combined with Eq. (7) to include water influence. However, Eqs. (9a) and (9b) do not explain the plasticisation observed between populations as different as wheat starch and glucose mixtures, for instance (Ollett, Parker, & Smith, 1991).

Intuitively, the maltodextrin T_G value should be accessible, providing that the fractions of each individual polymer are known as well as (a) the molecular weight dependence of T_G and (b) the molecular weight dependence of ΔC_p. Fractions of individual polymer are indeed available by Size-Exclusion Chromatography data.

3.3.4. Molecular weight influence on T_G

The effect of molecular weight on T_G for pure synthetic polymers is well understood since Fox and Flory (1950). A linear relationship links the T_G value to the inverse of the molecular weight of a monodisperse polymer (see Eq. (10)) where a is a constant; M, the molecular weight of the polymer; and $T_{G\infty}$ is the T_G for infinite molecular weight

$$T_G = T_{G\infty} - \frac{a}{M} \tag{10}$$

This simple relationship has been widely discussed for glucose α, 1–4 oligomers of various degrees of polymerisation (Orford et al., 1989; Roos & Karel, 1991b; Slade & Levine, 1991). The optimum parameters $T_{G\infty}$ and the constant a were found to be 520 K and 53,003 K g mol^{-1} to best fit all data from the cited literature. This value of $T_{G\infty}$ largely agrees with values found for various types of starch: 500 ± 10 K (Orford et al., 1989), 516 K (Roos & Karel, 1991b) and 518 K (Benczédi et al., 1998).

3.3.5. Molecular weight influence on ΔC_p

ΔC_p values at the glass transition temperature have been reported in the literature for the same series of homologous polymers, but have not been discussed to the same extent. It has been suggested that in some cases, the product of heat capacity (ΔC_{pi}) and T_{Gi} is constant, assuming a linear relationship between the reciprocal of the heat capacity ($1/\Delta C_{pi}$) and the reciprocal of the molecular weight ($1/M$). This leads to one common rule of mixing widely used in the industry (Fox, 1956). However, ΔC_p at the glass transition can be interpreted as a degree of organisation in the glass (Gibbs & DiMarzio, 1958). Thus, the heat capacity accounts for the 'quality' of the hydrogen bonds between the molecules forming this glass. Therefore, the closer the polymer's physical state to being a crystalline, the higher the ΔC_p. This indicates that ΔC_p should decrease with increasing molecular weights, but no real rules have ever been cited and ΔC_p has only been mentioned from DP1 (glucose) to DP6 (maltohexaose) in the relevant literature, due to experimental uncertainty and also stated as constant for DP larger than 3 (D'Haene & Van Liederkerke, 1996). The formation of a glass being necessarily linked to kinetics, ΔC_p is strongly affected by the conditions leading to the glass, as shown by the large standard deviations observed (Orford et al., 1989).

According to canonical ensemble theory, the most probable configuration dominates the system thermodynamics virtually completely. Therefore, in Roos and Karel (1991b), Eq. (10) has been used to empirically

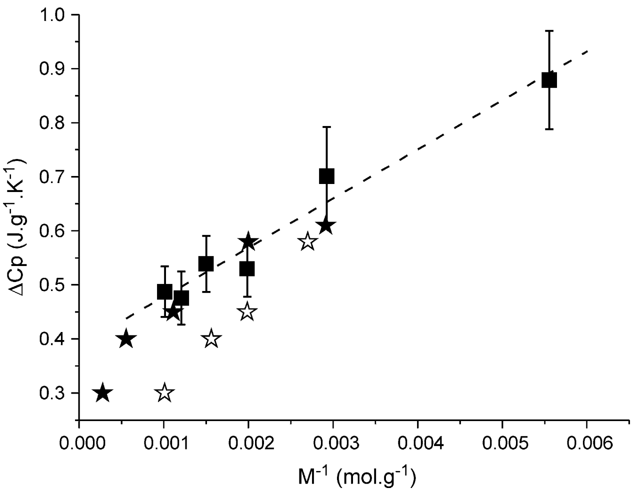

Fig. 9. Heat capacity ΔC_p at T_G as a function of molecular weight. Solid squares with linear regression are series of homologous malto-oligomers from Oxford et al. (1989); open stars are maltodextrins data from Roos and Karel (1991b) using the effective molecular weight M_E and solid stars are the same data using number average molecular weight M_n from the supplier.

determine the effective molecular weight (M_E) of a virtual monodisperse polymer whose T_G is the same as that of a given polydisperse maltodextrin. This effective molecular weight M_E is always lower than the number average molecular weight M_n given by the supplier. This indicates that the simple rule of Eq. (9b) is not suitable for broad molecular weight distributions but might be restricted to only low molecular weight mixtures (DP1 to DP10 as suggested by D'Haene and Van Liederkerke (1996)). Also, it is obvious that Eq. (8) implies that in binary mixtures, M_E equals M_n.

T_G of maltodextrins can be compared to the T_G of the series of homologous malto-oligomers. As a correlation between T_G and ΔC_p is expected (Fox, 1956), ΔC_p for maltodextrins should coincide with ΔC_p of the series of homologous malto-oligomers. Fig. 9 reports maltodextrins data from the literature (Roos & Karel, 1991b) where ΔC_p is represented as a function of both the reciprocal of the number average and effective molecular weights M^{-1}. In that figure, data for the series of homologous malto-oligomers (Orford et al., 1989) is also indicated.

The least square regression concerning the homologous series of glucose (Data from Orford et al. (1989)) corresponds to Eq. (11):

$$\Delta C_p = \Delta C_{p\infty} + \frac{b}{M} \tag{11}$$

with $\Delta C_{p\infty} = 0.387$ J g^{-1} K^{-1} and $b = 90.8$ J mol^{-1} K^{-1}.

Fig. 9 and Eq. (11) show that ΔC_p of a maltodextrin requires the use of its number average molecular weight M_n (Gibbs & DiMarzio, 1958) unlike T_G. ΔC_p was 0.400 for the 2DE, 0.44 for the 10DE, 0.466 for the 19DE and 0.438 J g^{-1} K^{-1} for samples 2–19. This in turn, denotes that during the transition from glass to rubber, the heat stored in the sample is related to the number of chains being freed rather than directly to the glass structure.

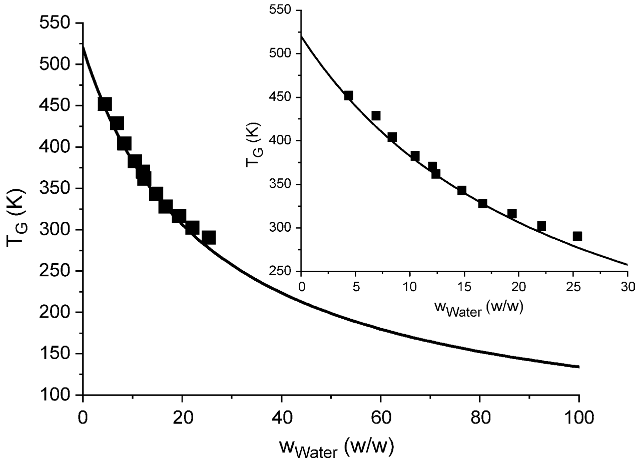

Fig. 10. T_G calculated with Eq. (7) for extruded starch as a function of water content (experimental data from Benczédi et al. (1998)).

3.4. Application

The verification of Couchman's model is straightforward for extruded starch in water, considering its extreme weight distribution (Bizot et al., 1997). According to Eqs. (10) and (11), T_G and ΔC_p for individual molecular weight, in the 10^5–10^8 g mol^{-1} range, vary between 519.5 and 520.0 K, and 0.388 and 0.387 J g^{-1} K^{-1}, respectively. The small difference between these values allows the following simplification: starch is considered here as a monodisperse carbohydrate polymer of infinite molecular weight. Therefore, Couchman's model (Orford et al., 1990; Roozen, Hemminga, & Walstra, 1991) is applicable. The glass transition temperature and heat capacity increment of water have been already largely discussed in the literature and values of 134 K and 1.92 J g^{-1} K^{-1}, respectively, were taken (Sugisaki, Suga, & Seki, 1968). Fig. 10 shows the fit of experimental data in the light of these developments.

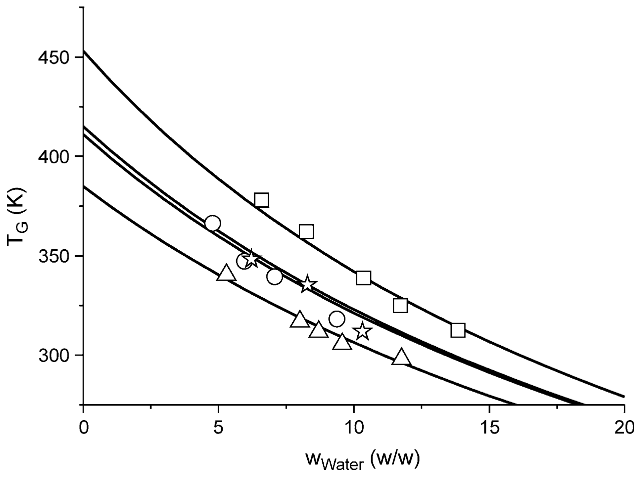

Fig. 11. Fit of experimental data for determination of dry T_G for the maltodextrins studied. Lines correspond to Eq. (7), open squares (2DE), circles (10DE), triangles (19DE) and stars (2-19) are measured values.

Table 6
Results obtained from the fit of Eq. (7) to experimental data and values of p calculated using Eq. (13)

Maltodextrin	ΔC_p (J g^{-1} K^{-1})	T_G dry (K)	M_E (g mol^{-1})	p
2DE	0.400	453	791	0.523
10DE	0.444	411	486	0.605
19DE	0.466	385	392	0.701
2-19	0.438	415	504	0.735

T_G of dry maltodextrins is determined from Eq. (7) to fit at best the experimental values with the already discussed approximation of considering maltodextrins glassy structure identical to that of a glass of malto-oligosaccharide of unique molecular weight (M_E). M_E is determined empirically from Eq. (10). The fits are shown in Fig. 11 and the results are shown in Table 6.

As suggested by Table 6, short malto-oligosaccharides affect T_G and have a plasticization role. The more these ‘small units’ are present, the greater the effect on T_G, as suggested in D’Haene and Van Liederkerke (1996). We propose to affect a weight function ($\kappa_{(M)}$) to each molecular species that is related both to its molecular weight, and the entire molecular weight distribution. Therefore, the κ function is dependent on the molecular weight distribution. Using the above considerations, we propose the following empirical relationship for κ Eq. (12)

$$\kappa_{(M)} = M^{-(p/(1-p))} \tag{12}$$

where p is a scalar and represents the molar fraction of molecules that can plasticize the long chains. This p value is calculated using Eq. (13) and is the molar fraction ranging from 0 to M_{lim}

$$p = \frac{\int_0^{M_{\text{lim}}} x \, \mathrm{d}M}{\int_0^{+\infty} x \, \mathrm{d}M} \tag{13}$$

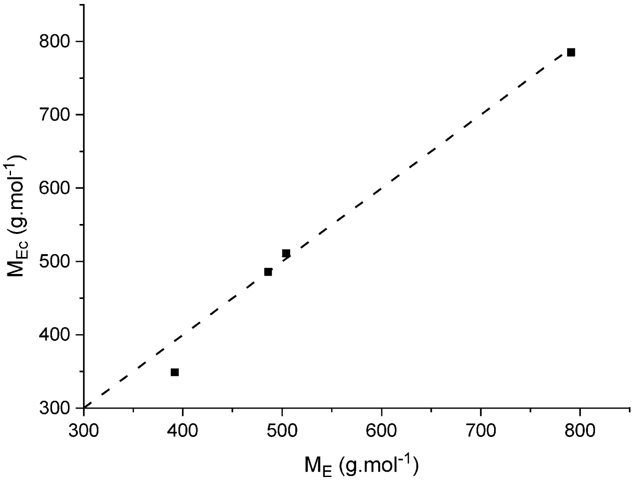

Fig. 12. Comparison between M_E (determined graphically using Eq. (6)) and M_{Ec} (determined with the chromatogram using Eq. (14)). The dashed line is the slope 1 to guide the eye.

Eq. (14) is then used to determine the effective average molecular weight directly from the chromatogram (M_{Ec})

$$M_{Ec} = \frac{\sum_i x_i \kappa_i M_i}{\sum_i x_i \kappa_i} = \frac{\sum_i x_i \kappa_i (162\text{DP}_i + 18)}{\sum_i x_i \kappa_i} \tag{14}$$

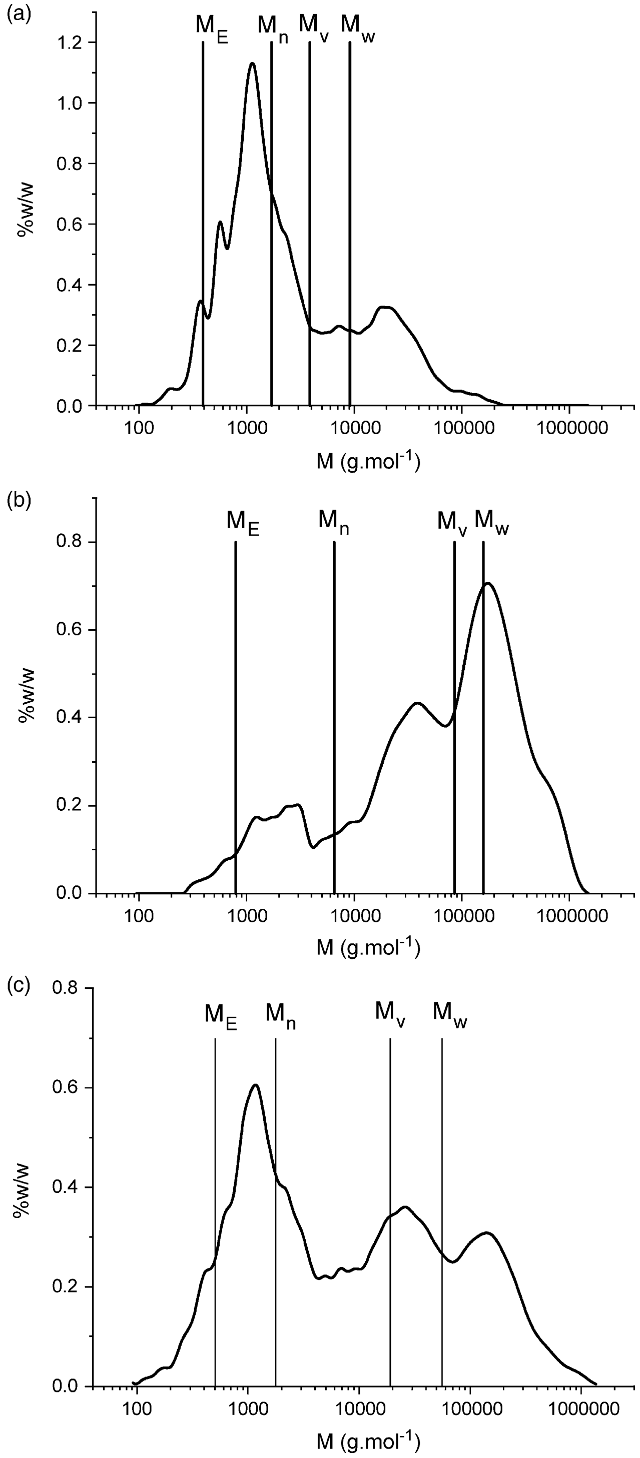

Fig. 13. Chromatograms for (a) 19DE, (b) 2DE and (c) 2-19 with localisation of the characteristic average molecular weights described in this work.

where κ is defined in Eq. (12), x is the molar fraction; M, the molecular weight; and DP is the degree of polymerisation.

M_{Ec} is identical to M_{E} only for a certain value of M_{lim} common for all the maltodextrins of this work, as shown in Fig. 12.

For corn maltodextrins studied in this work, M_{lim} is 1070 g mol^{-1}, which corresponds to a DP between 6 and 7 (maltohexaose/maltoheptaose).

The mathematical limits of the model we present need to be described. On one hand, absence of low molecular weight compounds in the chromatogram for maltodextrins ($p=0$) implies that $\kappa=1$ and that the effective mass (M_{E}) equals the number average molecular weight (M_{n}). On the other hand, the absence of *high* molecular weights ($p=1$) causes a vertical asymptote, however, in this case, the sample cannot be considered as a maltodextrin anymore.

For the maltodextrins studied here, p varies roughly between 0.5 (2DE) and 0.7 (19DE) (values reported in Table 6). Unlike Mark–Houwink–Sakurada model for the viscosity, the fact that p is a variable in our model makes the calculation of M_{E} specific to a given maltodextrin. In Fig. 13, we present the four average molecular weights characteristic for two different maltodextrins and their mixture in 50:50 ratio to stress the difference between $\bar{M}_{\mathrm{v}}$ and M_{w} on one side, and M_{E} and M_{n} on the other side.

4. Conclusion

A novel approach to predict viscosity and glass transition temperature of maltodextrins from their size-exclusion chromatograms has been presented that complements the temperature dependence of the viscosity of D'Haene and Van Liederkerke (1996). A combination of Spurlin–Martin–Tennent's and Mark–Houwink–Sakurada's models has shown to be relevant for determining the viscosity of maltodextrins in solution. The use of $\bar{M}_v$ and α appears to be a better choice than M_{w} for the modelling of viscosity versus polymer concentration relation. The low value of the α exponent (0.337) as compared to other polysaccharides and additional evidences from Huggins k' coefficient (>1) and literature (Durrani, 1992; Nicolai et al., 1996) all suggest an average ovoid-like shape of maltodextrin components in solution.

For glass transition temperature, a combination of Couchman model and a modified Orford model that includes the influence of the large polydispersity observed in maltodextrins appeared to be an essential first step in the modelling of T_{G} versus water concentration. The classical approximation of considering maltodextrins as having only α, 1–4 bonds is adequate: Fox and Flory relation between T_{G} and molecular weight and Orford data relating ΔC_p to M_{n} were combined with Roos and Karel developments. These included the approximation of considering a polydisperse sample's T_{G} as a monodisperse sample having the same T_{G} and characterised by an effective average molecular weight M_{E}. This naturally led to the simplification of also considering starch as a monodisperse species, but of infinite molecular weight. M_{E} offered a good fit when used with Fox and Flory relation to predict T_{G} as a function of water content. However, the characterisation of this transition by a single average molecular weight (M_{E}) does not reflect the length of the transition.

Interestingly enough, this M_{E} can be directly calculated from the size-exclusion chromatogram through the use of the p parameter, which expresses the ratio between plasticizer and plasticized molecules. A clear limit between these two components appeared in the chromatogram for the corn maltodextrins described in this work at $M_{\mathrm{lim}}=$ 1070 g mol^{-1}. One surprising implication of this result is that the influence of the small molecules (below M_{lim}) is therefore variable according to maltodextrin hydrolysis degree (the less hydrolysed the maltodextrin, the higher the influence of small molecules). We anticipate that this limit depends upon starch origin and post-hydrolysis purification undertaken by starch manufacturers.

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