Rheology, dynamic light scattering and physicochemical characterization of octenyl succinic anhydride (OSA) modified starch in aqueous solution

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Abstract Physicochemical and rheological properties of hydrophobically modified starch by octenyl succinic anhydride (OSA) have been evaluated in order to investigate the effects of concentration and temperature on its aggregation phenomenon in an aqueous solution. The analysis of particle size distribution showed the existence of two modes of aggregation by intramolecular bonds, whereas beyond the critical aggregation concentration a second population appears which seems to be induced by the intermolecular interactions. From the rheological analysis of OSA starch solutions, three behaviour classes were observed. The first class presents a non-Newtonian shear-thinning behavior characterized by two Newtonian regions. The second class exhibits a gel like behavior due to the entanglement of the macromolecular chains by intermolecular bonds, where its destructuring makes it possible to find the first morphology of the aggregated macromolecules. The third class exhibits a liquid behavior in a concentrated domain due to the phase separation between the modified and unmodified parts. Otherwise, the thermo-rheological analysis demonstrated indeed the presence of a thermosensitive behavior in tangled solutions of OSA starch.

Keywords OSA starch · Aggregation · CAC · Particle size distribution · DLS · Rheology

Introduction

Over the last two decades, natural substances and in particular those obtained from polysaccharides which are abundant and inexpensive, have been intensively used in the food industry (Colinet et al. 2009; Yahoum et al. 2016; Colivet and Carvalho 2017). These products compared to synthetic ones have a major advantage by their polyfunctionality, and are often integrated for their viscosifying, texturing properties and especially surface activities (Dickinson 2009).

Among these products, the octenyl succinic anhydride starch (OSA starch) is very popular in the manufacture of vinaigrette and mayonnaise sauces (Alimi et al. 2013), as well as in the dairy industry (Gentès et al. 2016) where it is used as a texturing and emulsifying agent (Hadradev et al. 2015; Krstonosic et al. 2015) in a very wide pH range. However, when milk proteins (caseins) are used for the same functions, they coagulate at low pH; in addition their cost is increasingly high (Zwiercan et al. 1987).

OSA starch is a corn starch, modified by an esterification reaction between the hydroxyl group of starch and the octenyl succinic anhydride group (Sweedman et al. 2013). Substitution with the OSA moiety can occur at the carbons 2, 3 and 6 in the glucose molecule. The degree of substitution for food applications is between 0.01 and 0.03 (Shogren et al. 2000; Wang et al. 2013). In addition, the use of OSA starch is authorized by the food and drug administration (FDA) after studies of toxicity, genotoxicity, and carcinogenicity (JECFA 2014).

Several researchers worked on the synthesis of this macromolecule, including those who focused on optimizing the degree of substitution (Zhang et al. 2011; Bai et al. 2013) and those who evaluated the effects of various process parameters such as time, temperature, reaction pH, and

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reagent concentrations (Plate et al. 2012; Shi and He 2012). Other researchers have been interested in the physico-chemical properties of OSA starch and in particular the critical micelle concentration (CMC), which has been determined by tensiometry and viscometry (Sovilj et al. 2013). This parameter was deliberately confused by other authors, considering it as a critical aggregation concentration (CAC) quantified also by tensiometry (Krstonosic et al. 2011) and fluorimetry (Tizzotti et al. 2013).

Although there are many studies on molecular properties of OSA starch such as hydrodynamic radius, molecular weight, and conformation which have been investigated, especially by the dynamic light scattering method (Zhu et al. 2013) and by steric exclusion chromatography (Zhang et al. 2013), there are few works reported in the literature on its macromolecular organization combined with the rheological and thermo-rheological properties. So, the aim of this work was to study the intra- and intermolecular interactions which lead to the aggregation of the macromolecules of OSA starch in aqueous media. The macromolecular solutions were characterized in terms of rheology and thermo-rheology, particle size distribution and, macroscopic aspects.

Materials and methods

Materials

OSA starch was obtained from National Starch and Chemicals (Arnas, France). It is a modified starch based on waxy maize under the trade name N-Creamer®46. The chemical reagents used are of analytical grade and were purchased from Sigma-Aldrich (Schweiz, Switzerland).

Preparation of OSA starch solutions

A stock sample (15%, w/v) was prepared by dispersing the appropriate amount of biopolymer in deionized water, with mechanical stirring for 1 h. The resulting solution was centrifuged at 12,000 rpm for 30 min to optionally remove unreacted reticulate particles. Finally, 3 mM of sodium azide were added to the solution in order to preserve it against microbial contamination. Samples were obtained by dilution and filtration (0.45 µm).

Determination of the degree of substitution

The degree of substitution (DS) of OSA starch was determined according to the method described by Plate et al. (2012). The DS was then calculated using Eq. 1:

$$DS = \frac{162 \cdot 10^{-3}(A \cdot M)/W}{1 - [210 \cdot 10^{-3}(A \cdot M)/W]} \quad (1)$$

where A is the titration volume of NaOH, M is the molarity of NaOH and W is the mass of starch. Numbers 162 and 210 represent the molar mass values of the glucose unit and the OSA hydrophobic moiety, respectively.

Determination of the molecular weight

The molecular weight of OSA starch was determined using a viscometric method (Dokic et al. 2008). The first step consists in calculating (Eq. 2) the different values of the specific viscosity (η_{sp}) as a function of the passage time (t) of solutions at various OSA starch concentrations in 1 N KOH solution used as solvent at 35 °C.

$$\eta_{sp} = \frac{t - t_0}{t_0} \quad (2)$$

In this equation, t_0 represents the time of passage of the solvent into the capillary tube.

The intrinsic viscosity ($[\eta]$) is deduced from the Huggins equation (Eq. 3):

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C \quad (3)$$

where k' is the Huggins constant.

The calculation of the molecular weight from the Mark-Houwink equation requires the knowledge of the constants a and K obtained from the literature and which are adequate for the solvent used and temperature (Millard et al. 1997).

$$[\eta] = K * M^a \quad (4)$$

Dynamic light scattering (DLS)

The granulometric distribution of OSA starch in solution was analysed at ambient temperature using a laser granulometer (Horriba Nanosizer SZ100) at a diffusion angle of 90°. The macromolecules, under a Brownian motion, undergo radiation at a wavelength of 532 nm. Thus, an auto-correlation function is recorded, making it possible to evaluate the relaxation time (τ) of the colloids which is linked to the wave vector (q) and the diffusion coefficient (D) by the Fick law ($D = \frac{1}{\tau q^2}$). The hydrodynamic radius is then calculated using the Einstein-Stokes relation and, which is translated in diameter using Eq. 5.

$$R_h = \frac{K_B T}{6\pi\eta D} \quad (5)$$

where K_B is the Boltzmann constant, T is the absolute temperature, η is the dynamic viscosity, R_h is the

hydrodynamic radius and q^2 is the wave vector with a refractive index (n) of 1.333. The wave vector is given by Eq. 6:

$$q = \frac{4\pi n}{\lambda \sin\left(\frac{\theta}{2}\right)} \quad (6)$$

where λ is the wavelength of the radiation and θ is the detection angle.

The particle size distribution was determined based on the autocorrelation, employing cumulants method (Chakraborty et al. 2011) and using the SZ-100 software.

Rheological analysis

The rheological measurements at different concentrations of OSA starch were performed with an Anton Paar rheometer (Anton Paar, GmbH, Germany) using a plate-plate measuring system (diameter of 25 mm and gap of 1 mm) at 20 °C. For each concentration, the analysis was repeated three times, and the experimental results were processed by Rheoplus US200 software. The experiments were realized in oscillatory mode to describe the viscoelastic behavior of polymer solutions. For this purpose, various tests were performed in order to characterize the rheological behavior.

Flow curves were first recorded over a shear rate range varying from 0.001 to 1000 s⁻¹. Then, the viscoelastic behavior was studied by recording the variation of the elastic modulus (G') as well as the loss modulus (G''), as a function of deformation over a range of 0.01–100% at constant frequency settled at 0.1 Hz. This test makes it possible to determine the linear viscoelasticity domain, which is defined by the independence of the modules G' and G'' as a function of the deformation. Finally, the effect of temperature on the macromolecular chains of OSA starch was studied using round-trip ramps, by recording the variation of G' and viscosity as a function of temperature ranging from 20 to 80 °C (2 °C/min), which was varied using a Peltier unit and maintained at an accuracy of ± 0.01 °C. A solvent trap was used to avoid evaporation.

Statistical analysis

The effects of biopolymer concentrations on rheology and particle size distribution were statistically compared using a one-way analysis of variance (ANOVA). Additionally, differences between means were identified using Tukey's honestly significant difference test. Analysis was performed by SigmaPlot software (version 11.0) and significant differences in results were accepted when $p < 0.05$.

Results and discussion

Degree of substitution

The obtained degree of substitution (DS) was equal to 0.0288 ± 0.0008 . This value confirms the food grade of the product used. According to the US FDA regulations, the modification of starch by OSA is limited to 3% by weight of starch to obtain a DS value of about 0.02 (Plate et al. 2012; Bai et al. 2013).

Molecular weight

Using the constants of Mark-Houwink equation ($K = 0.00014$ and $a = 0.73774$), the molecular weight was about $60,376.68 \pm 866.95$ g/mol. However, Dokic et al. (2008) have found relatively low molecular weights for other commercial samples of OSA starch (Purity gum 2000 and Hi-cap 100); this difference is probably due to the nature and grade of the OSA starches used and, also to the values of K and a employed to calculate correctly the value of the molecular weight.

The Huggins constant equal to 9.6658 ± 0.36 ($k' \geq 1$) provides information on the solvent quality and aggregation tendency of the macromolecules. According to the results obtained, OSA starch has a high tendency to self-aggregation. This result confirms those obtained by Dokic et al. (2008) where they observed that the macromolecules of Hi-cap 100 were more self-associated. The same observations were noted by Krstonosic et al. (2011) where they found for two other octenyl succinate modified waxy corn starches the values of k' higher than 1, confirming the tendencies to self-aggregation of the samples used.

Particle size distribution and morphology

The evolution of the diffused intensity as a function of polymer concentration is shown in Fig. 1a for low concentrations of OSA starch ($C_{OSA} \leq 0.1\%$) and in Fig. 1b for high polymer concentrations ($0.3 \leq C_{OSA} \leq 3\%$). This is done in order to provide information on the associative behavior of the amphiphilic macromolecules in solution.

For very low concentrations, the particle size distribution is characterized by a rapid relaxation mode (Fig. 1a), which reflects the existence of a monomodal population consisting of modified polysaccharide monomers dispersed in the solution. Differences in mean diameter values are statistically significant ($p < 0.05$), while for the last two concentrations, the diameter decreases and then remains constant where there is no statistically significant difference between the measured values ($p = 0.909$).

Fig. 1 Effect of OSA starch concentration on the relaxation time as a function of frequency (**a** diluted solutions; **b** concentrated solutions)

According to the Stokes–Einstein relation, the relaxation time is proportional to the apparent hydrodynamic diameter, so the decrease in relaxation time may be attributed to the reduction in the monomer size due to the self-assembly mechanism resulting from the contraction of the biopolymer chains induced by the intramolecular hydrophobic associations to form unimolecular micelles of about 36.25 nm (Agach, 2012). To explain this phenomenon, Krstonosic et al. (2011) proposed the mechanism of micellization of the monomers by intramolecular interactions in order to minimize contact with water by reducing the hydrodynamic size of the macromolecules. While Zhu et al. (2013) justified the reduction in size, when the concentration increases, by the electrostatic repulsion interactions between OSA starch particles which are negatively charged.

In the concentrated regime, OSA starch solutions exhibited another behavior (Fig. 1b), characterized by two relaxation times where the first one is fast; it is of the same nature of that obtained for low concentrations indicating the existence of free monomers in the solution. The second relaxation time is slow (five times), so the size of the aggregated molecules is five times greater than the size of the free monomers (Esquenet et al. 2004). The association

of polymer macromolecules is dominated by intermolecular hydrophobic interactions rather than intramolecular hydrophobic ones. The unimolecular micelles will agglomerate to form superstructures of 150 nm diameter, by a multi-micellar aggregation mechanism (Zhang et al. 2016). The same phenomenon was observed by Lu et al. (2016) with cationic polyacrylamides, where they noticed the presence of a first population of 60 nm diameter which decreases to 20 nm when the concentration increases; this variation was attributed to intramolecular interactions. They also noted the presence of a second population of 300 nm. To explain its existence, they assumed that there is an aggregation between the monomers by intermolecular interactions.

Rheological and thermo-rheological properties

The rheological behavior of OSA starch solutions was observed to be largely influenced by the polymer concentration, which can be classified into three classes. Figure 2 shows the flow curves of the first class of concentrations, varying from 0.1 to 2% (w/v). For this class, the rheological behavior shows the existence of two Newtonian regions (zero shear viscosity and infinite shear viscosity), which can be adjusted by the model of Cross or that of Carreau. The curves seem to be confounded in a cloud of points, which suggests the insensitivity of the apparent viscosity to the polymer concentration in the studied range. The differences between the obtained values are statically significant ($p < 0.05$).

The characteristic parameters of the two Newtonian regions and of the shear-thinning intermediate behavior were estimated in relation to all the experimental curves, based on the two rheological models. It was noticed that the fitting results by the Cross model (Eq. 7) are better with a coefficient of determination R^2 close to 1.

Fig. 2 Flow curves of OSA starch of the first group of concentrations

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{1 + (k\dot{\gamma})^n} \quad (7)$$

where η_0 is the zero shear viscosity, η_{∞} is the infinite shear viscosity, the parameter k is characteristic of the relaxation time; its inverse represents the critical shear rate ($\dot{\gamma}_c$) from which a destructuring is observed, marking the beginning of the shear-thinning behavior. The last parameter (n) is the exponent of the Cross model which measures the Newtonian anomaly (for $n = 0$, the fluid is Newtonian). The values of the four characteristic parameters are grouped in Table 1.

These results clearly show that when the concentration ranges from 0.1 to 2% ($0.1 \leq C_{OSA} \leq 2\%$), the viscosity of OSA starch solution exhibits a non-Newtonian behavior which is certainly due to the inter-macromolecular interactions; this indicates that the critical concentration, corresponding to the diluted regime, is less than 0.1%. The viscosity of the liquid at rest is about ten units, it falls from four decades to extreme shear, which proves that it is in the semi-diluted domain because of the absence of Newtonian behavior (Arvidson et al. 2006).

The flow curves of the second class corresponding to concentrations between 1.5 and 13% ($1.5 \leq C_{OSA} \leq 13\%$) are shown in Fig. 3; the curves are divided into three regions of shear rates. In region I (from 0.001 to 0.05 s^{-1}), the viscosity significantly decreases ($p < 0.05$). This suggests the formation of a rigid network at rest, leading to the formation of a gel with a yield stress, since all the curves are confounded. The intensity of the formed gel force is insensitive to the variation of the concentration in this area (Esquenet et al. 2004). For the region II (from 0.05 to 10 s^{-1}) and after the first destructuring and breakdown of the intermolecular bonds, new structures appear; they are composed of partially separated macromolecules which resist to the shear effect by recording a quasi-Newtonian behavior that appears as a bump followed by a second destructuring. In this case, the macromolecules undergo deployment or deformation and breakage of the

Fig. 3 Flow curves of OSA starch of the second group of concentrations

intramolecular bonds in order to minimize the flow resistance (Sinquin et al. 1996), as a consequence the viscosity drops.

In region III (from 10 to 1000 s^{-1}), all the macromolecules are deployed, deformed and dispersed in solution in the direction of shear, which gives a second Newtonian zone. This zone is characterized by the sensitivity to the variation in concentration due to the increase in the number of free macromolecules in solution (Ballard et al. 1988). Jin et al. (2013) showed in their work on modified chitosan, that aggregation exists in the aqueous solution but appears only under shear, which gives shear-thickening domain translated by a bump on the flow curves. The mechanism of aggregation of macromolecules in aqueous media is due to intermolecular hydrogen bonds.

The flow curves of the third class corresponding to very high concentrations are illustrated in Fig. 4. The gel behavior disappears to the detriment of a liquid behavior with a significant slackening of the structure which causes the decrease in viscosity to very low values due to the phase separation. This phenomenon is the consequence of the formation of small aggregated domains while the entire hydrophilic chains remain in solution (separation in micro-phase). The macro-phase separation exhibited by the cloud

Table 1 Characteristic parameters of the Cross model

Concentration (% in wt)	η_0	η_{∞}	k	n	R^2
0.1	6.279 ± 0.384^b	$0.0009 \pm 4.67E-05^a$	53.601 ± 10.51^b	1.446 ± 0.00294^a	0.999
0.3	5.135 ± 0.437^b	0.001 ± 0.00^a	39.645 ± 2.087^b	1.497 ± 0.00453^a	0.992
0.5	5.317 ± 0.237^b	$0.00109 \pm 4.38E-05^a$	49.146 ± 5.924^b	1.483 ± 0.00385^a	0.995
0.7	10.053 ± 1.594^c	$0.00127 \pm 4.32E-05^b$	17.851 ± 4.021^a	1.560 ± 0.107^a	0.999
0.9	4.484 ± 0.242^b	$0.00121 \pm 4.24E-05^b$	12.195 ± 1.932^a	1.739 ± 0.236^a	0.987
1.0	2.508 ± 0.0693^a	$0.00121 \pm 4.31E-05^b$	19.213 ± 3.669^a	1.597 ± 0.233^a	0.990
2.0	4.928 ± 0.0924^b	$0.00197 \pm 1.67E-04^c$	45.067 ± 4.567^b	1.455 ± 0.132^a	0.999

Values are mean $\pm$ SD of three replications ($n = 3$). Means followed by the same letter in the column are not significantly different ($p > 0.05$)

Fig. 4 Flow curves of OSA starch of the third group of concentrations

point is followed by the appearance of two phases, one consisting of collapsed polymer chains which expelled most of the associated water and the other is water.

The thermal characteristics of OSA starch were estimated by a heating/cooling cycle at a temperature ranging from 5 to 80 °C over a series of samples at different concentrations. Figure 5 shows the variation of the elastic modulus (G') as a function of temperature. Two different behaviors were observed depending on the concentration regimes, where for the first group (ranging from 0.5 to 1%), G' is insensitive to the variation of temperature. However, for the second group whose concentration is greater than 1%, in heating ramp, G' remains also insensitive up to the gelation temperature which is equal to 80 °C. For concentrations ranging between 3 and 8%, this gelation is carried out in a brutal way, contrary to concentrations varying between 10 and 13%, where it starts at 40 °C, and increases progressively with temperature. In return ramp, G' resists to the decrease of temperature and then it falls after a partial melting since it does not find the initial value. The same phenomenon was observed on the aggregation of

Fig. 5 Variation of elasticity modulus as a function of temperature effect of polymer concentration

proteins, which depends on their concentration and duration of heating (de la Fuente et al. 2002).

Conclusion

The hydrophobic modification of starch by OSA groups gives the molecule of starch an amphiphilic nature and surface active properties. Thus, the formation of micelles is carried out by intramolecular bonds from a critical aggregation concentration in which the diameter of the macromolecules decreases to 36 nm. The micellar solution has a shear-thinning behavior with two Newtonian regions which can be fitted by the Cross model. By increasing concentration, intermolecular bonds occur and a second population appears, its diameter was found to be about 150 nm and its rheological behavior illustrates the formation of three-dimensional networks. In this case, the solution behaves like a gel until the phenomenon of phase separation occurs due to the strong aggregation between the macromolecules. The effect of temperature on the viscoelastic behavior in solutions appears from a concentration of aggregation, demonstrating the thermosensitive character of OSA starch.

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