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# Esterification of dextran by octenyl succinic anhydride (OSA): Physicochemical characterization and functional properties assessment

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<i>Keywords:</i> Dextran Octenyl succinic anhydride Chemical modification Emulsions Functional properties	The chemical modification of biopolymers to enhance their functional properties in the food, cosmetic, and pharmaceutical industries is an area of particular interest today. In this study, different molecular weight dextrans were chemically modified for the first time with octenyl succinic anhydride (OSA). This reaction involves an esterification process wherein the hydroxy groups of dextran are partially substituted by a carbonaceous chain, imparting hydrophobic properties to dextran molecules and, consequently, an amphiphilic nature. To assess and quantify the incorporation of OSA into the dextran structure, reaction products were analysed using NMR and FTIR. Additionally, the thermal properties, the <i>Z</i> -potential and the foaming and emulsifying capacity of both native and modified dextrans were examined. The introduction of OSA groups to dextran molecules, with degrees of substitution between 0.028 and 0.058, increased the zeta potential and the thermal stability of the polymer. Furthermore, the chemical modification of dextran backbone with this radical conferred a hydrophobic nature to the biopolymer, which enhance its foaming and emulsifying capacity. Therefore, these results demonstrate that the incorporation of hydrophobic moieties into dextran polymers improves their functional properties and broadens their potential applications in the industry.

# 1. Introduction

Dextran is a water-soluble homopolymer composed of glucose units connected predominantly by  $\alpha$ -(1  $\rightarrow$  6) glycosidic linkages, which form the main linear chain of the polymer (Robyt, Yoon, & Mukerjea, 2008). However, dextrans can also have a variable number of side branches of p-glucose units with different types of linkages, mostly  $\alpha(1 \rightarrow 4)$ ,  $\alpha(1 \rightarrow 3)$ , and less frequently  $\alpha(1 \rightarrow 2)$  (Vandamme, de Baets, & Steinbüchel, 2002). Based on their molecular weight, which can reach up to 440 MDa, dextrans can be classified into two types: those with a molecular weight higher than 40 kDa, which are called dextrans, and those which a molecular weight <40 kDa, known as oligodextrans (Díaz-Montes, 2021).

This glucose-based carbohydrate was firstly discovered as an extracellular polysaccharide or exopolysaccharide (EPS) produced by various lactic acid bacteria in the presence of sucrose in the fermentation medium. Lactic bacteria secrete enzymes into the fermentation medium, such as dextransucrase in the case of *Leuconoctoc* sp. and *Streptococcus* sp. or dextrinase in the case of *Gluconobacter* sp., which catalyse the transfer of p-glucopyranosyl residues from sucrose to dextran (Díaz-Montes, 2021). Therefore, the nature and degree of branching depend on the bacterial strain that produces the dextran (Heinze, Liebert, Heublein, & Hornig, 2006). In addition to the fermentation process, it is now known that dextran can be chemically synthesised via a cationic ring-opening polymerization (ROP) of levoglucosan (Heinze et al., 2006).

Although many researchers assert that the molecular weight and branching of dextran affect its solubility and rheological properties, there is no clear direct relationship between the structural characteristics of dextran and its functional properties (Díaz-Montes, 2021). However, as a result of the presence of at least 95 % of linear linkages, all types of dextran are considered soluble polymers, able to incorporate large amounts of water and form hydrogels. Its high solubility, low toxicity, renewability and biocompatibility, along with its capacity to act as an anticoagulant, antithrombotic, osmotic agent and lubricant, have made this polymer one of the most commonly used in the fields of medicine, pharmaceuticals, and cosmetics. (Díaz-Montes, 2021; Yu, Shen, Song, & Xie, 2018). However, the food industry is where dextran

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finds its most prominent application, as it is extensively employed in baking and confectionery for its capacity to moisturize, stabilize, and preserve food products (Díaz-Montes, 2021; Kothari, Das, Patel, & Goyal, 2015). Nevertheless, owing to its high solubility and poor hydrophobic properties, which make it a poor biomolecule for emulsifying or foaming purposes, its applications in these industries have been limited.

For this reason, in recent years there has been growing interest in the development of hydrophobically modified polysaccharides, due to their potential applications in many fields. These modified polymers present new functional properties, like self-assembly in aqueous solutions or emulsifying, surfactant and foaming properties, which make them suitable polymers for the development of therapeutic drug-delivery systems, flocculants for wastewater treatment or natural emulsifiers and surfactants for the cosmetic and food industries (Rodrigues, 2005; Wang et al., 2022). According to the available scientific literature, the most recently studied methods for the chemical modification of polysaccharides are sulfonation (Münster et al., 2020), phosphorylation (Chen, Huang, & Huang, 2021), carboxymethylation (Liu et al., 2021), esterification (Song et al., 2023) or oxidation (Dragan, Ghiorghita, Dinu, Duceac, & Coseri, 2023), among others.

One of the most frequently used methods for the improvement of the interfacial properties in hydrophilic polysaccharides is the esterification reaction carried out with the reagent octenyl succinic anhydride (OSA), which is constituted by a ring segment with a carbonaceous chain, and whose use is approved in food grade by the US Food and Drug Administration (FDA) (Zhao et al., 2022). This chemical reaction takes place in alkaline solution, where the ring fraction of OSA transforms into two negatively charged carboxylic molecules, one of them reacting with an –OH group of the substrate and the other one forming a salt when on contact with the sodium hydroxide present in the medium (Omar-Aziz et al., 2020). The incorporation of OSA groups in polymer chains leads to the formation of esters that exhibit both hydrophilic and hydrophobic characteristics, resulting in an amphiphilic nature.

Here, we hypothesise the development of OSA-modified dextrans with improved surface and functional properties, allowing for their potential application in the food, cosmetic and pharmaceutical industries. Therefore, in this research, dextrans with a variety of molecular weights (20, 70 and 150 kDa) were chemically modified using different percentages of OSA, specifically 5 and 10 % (g OSA/100 g dextran). The degree of substitution (DS), Fourier transform infrared spectroscopy (FTIR) and the zeta potential were employed to assess the modification of the polymers. Moreover, the functional properties of the OSAmodified polymers, emulsifying and foaming capacities, and the thermal properties were investigated and related with the degree of modification of dextran.

# 2. Materials and methods

#### 2.1. Materials

Dextran 20 kDa (Thermo scientific, Lot. Q26H017), dextran 70 kDa (Tokyo Chemical Industry, Lot. R3RDL-XM), dextran 150 kDa (Thermo scientific, Lot. Z11E002), cis-trans mixture of 2-octenylsuccinic anhydride (Tokyo Chemical Industry, Lot. JIEJM-HL).

## 2.2. Preparation of octenyl succinylated dextran

The modification of dextran with OSA was carried out as in the study of Song, He, Ruan, and Chen (2006), with slight variations. Briefly, dextrans of three different molecular weights were suspended in distilled water at a concentration of 30 % w/w with agitation until a transparent liquid was observed. Then, the pH of the suspension was adjusted to 8.5 with a 0.1 M NaOH solution. To start the reaction, OSA (diluted to a proportion of 1:3 with absolute ethanol) was added dropwise during an hour, and the solution was kept at pH 8.5 (PH-Burette 24 2S, Crison Instruments) for 5 h at room temperature. Then the reaction was stopped by lowering the pH to 6.5 with a 0.1 M HCl solution. In order to eliminate the salt formed during the reaction, liquid samples were dialyzed in membrane tubing with a 10 kDa pore size (SnakeSkin, ThermoFisher Scientific) in 5 L distilled water vessels for 24 h. Then, the solutions were freeze dried (Telstar Cryodos, 0.1 mbar, -70 °C for 24 h), and subsequently, washed with 2-propanol 90 % to remove the non-reacted OSA. Specifically, the solid was suspended in 40 mL of 2-propanol and centrifuged at 10,000g for 15 min (High Speed Refrigerated Centrifuge 6500, Kubota); this process was carried out 5 times. Finally, the wet solid was dried in an oven at 37 °C for 20 h (Incubat 19L, P Selecta). A proposal of the reaction can be found in Fig. 1.

To assess the different degrees of modification of dextran, three molecular weights were tested, and two different proportions of OSA/ dextran were analysed, 5 and 10 % w/w.

# 2.3. Structural characterization and determination of the degree of substitution (DS)

Nuclear Magnetic Resonance (NMR) analysis was employed to chemically characterize the modified dextran molecules. To conduct this analysis, 20 mg samples of both native and OSA-modified dextrans were dissolved in 0.75 mL of deuterium oxide (D<sub>2</sub>O) and examined at 25 °C using a Bruker AV-400 MHz NMR spectrometer (Bruker, Germany). The analysis involved a series of experiments, including 1D proton (<sup>1</sup>H), 1D carbon 13 (<sup>13</sup>C), 2D proton-proton correlation spectroscopy (COSY), 2D proton-carbon (<sup>1</sup>H—<sup>13</sup>C) heteronuclear single quantum coherence (HSQC), and 2D proton-carbon heteronuclear multiple bond correlation (HMBC) spectroscopy. Additionally, 1D <sup>1</sup>H and 1D <sup>13</sup>C experiments of OSA dissolved in deuterated chloroform we performed to characterize the structure of the reagent.

Subsequently, the degree of substitution (DS) was determined through <sup>1</sup>H NMR analysis, following the methodology outlined in the study by Whitney, Reuhs, Ovando Martinez, and Simsek (2016), with slight modifications. DS refers to the extent to which hydroxy groups are substituted by the hydrophobic OSA constituent. For the calculation of DS, Eq. (1) was applied for each <sup>1</sup>H spectrum.

$$DS = \frac{A_{0.85}}{3 \times A_{4.90}} \tag{1}$$

where  $A_{0.85}$  corresponds to the integration of the methyl protons of the OSA peak (0.85 ppm), and  $A_{4.90}$ , to the anomeric proton of the glucose unit in the dextran molecule (4.90 ppm) (Wang et al., 2019).

#### 2.4. Fourier transform infrared (FTIR) spectroscopy

The unmodified and modified dextran were analysed using a Fourier transform infrared spectroscopy (FTIR) device (670-IR, Varian, USA), which utilizes a deuterated L-alanine doped triglycine sulphate (DLaTGS) detector. Thirty-two scans were performed at a resolution of 4 cm<sup>-1</sup>, r ranging from 2500 to 600 cm<sup>-1</sup> at a speed of 5 kHz or 0.32 cm/s.

## 2.5. Thermal properties

The thermal properties of native dextran and OSA-dextran were assessed using a TGA/SDTA851 Thermogravimetric Analyzer (Mettler Toledo, USA), according to the method employed by Omar-Aziz et al., (2020). Briefly, samples were heated from 25 to 250  $^{\circ}$ C, with a heating rate of 10  $^{\circ}$ C/min and measures were carried out in a N<sub>2</sub> atmosphere.

#### 2.6. Zeta potential

The zeta potential of both modified and unmodified dextran was determined by dissolving each sample in distilled water at a concentration of 0.5 % (w/w). Using a dynamic light scattering (DLS) device



Fig. 1. Chemical modification of dextran with 2-octenyl succinic anhydride under basic conditions.

(Zetasizer Nano ZS, Malvern Instruments, UK) at a temperature of 25 °C, the zeta potential was measured using a similar approach to that outlined by Omar-Aziz et al. (2020).

#### 2.7. Emulsifying capacity and stability

#### 2.7.1. Emulsion preparation

For the preparation of emulsions, a modified version of the method described by Asgari, Labbafi, Khodaiyan, Kazemi, and Hosseini (2020) was followed. In 50 mL centrifuge tubes, 20 mL of a 0.5 % (w/w) solution of either modified or unmodified dextran was added. These solutions were mixed with an equal amount of sunflower oil, and emulsions were prepared by homogenizing each sample using a homogenizer (Silent Crusher M, Heidolph, Germany) at 12,000 rpm for 3 min.

# 2.7.2. Emulsifying capacity

Immediately after the formation of the emulsions, 10 mL of each sample was centrifuged for 10 min at 4000g using a centrifuge (High Speed Refrigerated Centrifuge 6500, Kubota, Japan). After centrifugation, the emulsifying capacity (EC) was calculated as stated in Eq. (2).

$$EC (\%) = \frac{E_v}{T_v} \times 100$$
<sup>(2)</sup>

where  $E_{\rm v}$  is the volume of the emulsion layer and  $T_{\rm v}$  is the total volume of the sample.

### 2.7.3. Emulsion stability

The storage stability of the prepared emulsions was evaluated using a Static Multiple Light Scattering (SMLS) instrument (Turbiscan Lab Expert, Formulaction, France) with an ageing station where the samples were placed at a constant temperature. The study was conducted at 30 °C over a period of ten days, during which undiluted samples were placed in test cells and subjected to backscattered light measurements at

various time intervals. The Turbiscan Stability Index (TSI) was also calculated, a critical parameter that allowed for comparison of the emulsion formulations' overall behaviour. The TSI, the sum of variations detected in samples, was determined using an equation described by Vitonyte et al. (2017).

$$TSI = \sum_{i} \frac{\sum_{i} |scan_{i} - scan_{i=1}|}{H}$$
(3)

where i is the number of scans, and H is the height of the sample vial.

#### 2.7.4. Emulsion droplet size

Emulsion droplet size assessment was done according to Ahlström et al., with a Static Laser Scattering (SLS) device (Mastersizer S, Malvern Instruments Ltd., UK) (Ahlström et al., 2022). Measurements were carried out with refractive indexes of 1.46 and 1.33 for sunflower oil and for water phase, respectively. Each emulsion was added dropwise in a small volume dispersion unit (Hydro SM, Malvern Instruments Ltd., UK) until 10–15 % obscuration was achieved, at a pump speed of 1600 rpm.

#### 2.8. Foam capacity and foam stability

For the foam capacity (FC) and foam stability (FS) tests, 0.5 % (w/w) of each modified and unmodified dextran type was suspended in distilled water until transparent samples were obtained. Foam was produced by using a homogenizer (Silent Crusher M, Heidolph, Germany) in a 20 mL volume sample, at 12,000 rpm for 3 min (Kruchinin et al., 2021). Subsequently, FC and FS were calculated as stated in Eqs. (3) and (4), respectively (Zhao et al., 2022). FS measurements were made at times zero and 30 min.

FC (%) = 
$$\frac{V_{0-V}}{V} \times 100$$
 (4)

$$FS(\%) = \frac{V_t - V}{V} \times 100$$
(5)

where  $V_0$  is the foam volume immediately after preparation, V is the volume of the initial dispersion and  $V_t$  is the foam volume after 30 min.

# 2.9. Statistical analysis

A one-way ANOVA test was performed to determine if there are significant differences through the different values obtained in the study (p < 0.05). For that, the software Statgraphics Centurion XVI, v16.1.03 was used.

# 3. Results and discussion

# 3.1. NMR analyses and degree of substitution (DS)

A detailed structural characterization of OSA-modified dextrans was obtained from the 1D and 2D spectra. New peaks were observed in both <sup>1</sup>H and <sup>13</sup>C spectra of OSA-modified dextran, along with new cross peaks in 2D spectra.

In the <sup>1</sup>H spectra of OSA-modified dextrans (Supplementary material), distinct peaks emerged at 0.85 ppm, 1.1–1.3 ppm and 1.8–3.0 ppm, attributed to the presence of OSA groups within the dextran molecules. In addition, it can be observed that for all molecular weight dextrans (20, 70 and 150 kDa), these peaks are higher when the reaction is performed with a 10 % of OSA, indicating that more OSA substituents have been incorporated. The presence of peaks at 1.85 and 2.0 ppm, corresponding to cis- and trans-OSA groups in the dextran molecule, respectively, indicates that the reactivity of the 2-octenylsuccinic anhydride is not strongly influenced by the stereochemistry of the alkene. Carbon and proton spectra show that the trans-isomer is more populated in the reagent and that the signals of both isomers are still present in the product (Fig. 2). The complexity of the spectra make it impossible to determine whether the stereochemistry of the double bond influenced the product mixture. Regarding the regioselectivity of the reaction, the esterification of dextran molecules at the hydroxy groups deshields their corresponding proton signals by about 1 ppm from their original position. In this case, it is not possible to observe these signals precisely because they appear in the same regions as the anomeric proton and the solvent peaks. When performing a presaturated proton spectrum, these

two signals can be observed, indicating that the esterification reaction takes place mainly on O-2 and O-3 of dextran. Other than stating that O-4 is disfavoured, we cannot determine the regioselectivity for O-2 versus O-3, because due to overlaps, it is not possible to quantify whether one signal is larger than the other.

Finally, we should note that OSA is racemic because C-2 is a stereocentre. Therefore, there could be stereoselectivity in the esterification reactions and also the products will contain an additional stereocentre that will cause the dextran signals to appear at different positions in the spectra of the two diastereomeric products of each regioisomer. The complexity of the spectra precluded us gathering any evidence about this question. As far as we are aware, there has been no discussion of this for any of the previous reactions of OSA with carbohydrates.

The relationship between the peak at 0.85 ppm (methyl groups of OSA group) and the peak at 4.90 ppm (anomeric proton of the glucose monomer) corresponds to the DS values of the modified dextrans, which refers to the number of OH groups of the glucose unit that have been substituted. As can be seen in Table 1, DS values fluctuate between 0.028 and 0.058 for the three types of dextran tested (20, 70 and 150 kDa) and the different OSA concentrations used (5 % and 10 % w/w) in the modification process.

It can be observed that the increase in the OSA concentration resulted in a higher DS across the different molecular weight dextran types tested, which is in line with previous studies (Cheng, Ai, & Ghosh, 2021; Omar-Aziz et al., 2020). This phenomenon can be attributed to the greater abundance of OSA molecules available for esterification reactions with the dextran hydroxy groups. In addition, DS results

#### Table 1

DS values for different molecular weight dextran and reaction with 5 and 10 % (w/w) OSA.

	DS			
	20 kDa	70 kDa	150 kDa	
OSA 5 % (w/w) OSA 10 % (w/w)	$\begin{array}{c} 0.032 \pm 0.007^a \\ 0.043 \pm 0.005^b \end{array}$	$\begin{array}{c} 0.030 \pm 0.004^a \\ 0.058 \pm 0.007^c \end{array}$	$\begin{array}{c} 0.028 \pm 0.002^{a} \\ 0.053 \pm 0.005^{c} \end{array}$	

Different superscript letters indicate significant differences (P < 0.05).



Fig. 2. Structural analysis of OSA-modified dextran, native dextran and OSA reagent, through 1D <sup>1</sup>H (A) and <sup>13</sup>C (B) NMR spectra. Proton signals are depicted in blue and carbon signals in red, each letter indicate a different carbon or proton signal in spectra.

obtained from the reactions with 5 % OSA (w/w) are very similar, which indicates that dextran molecular weight did not exert a significant effect on the chemical modification process. In contrast, a significant difference in the degree of esterification was observed among the 10 % OSAmodified dextrans. Specifically, the 20 kDa type exhibited a lower DS value compared to the 70 and 150 kDa types. This could be attributed to the fact that lower molecular weight dextran molecules have less branching points than higher ones, this branching can lead to more intermolecular interaction between dextran molecules and more steric hindrances decreasing the reaction of dextran with OSA (Zeini, Glover, Knudsen, & Nyström, 2021). These values are higher than the ones obtained by other authors who modified starch or cellulose with OSA. For instance, Zhang, Ran, Jiang, and Dou (2021) carried out an esterification reaction of sorghum starch with 5 % OSA (w/w) and obtained a DS of 0.011. In the same line, Lim, et al. studied the effect of different pre-treatments prior to the modification of potato starch with OSA, and the DS of the untreated sample was 0.006 (Lim, Zulkurnain, Yussof, & Utra, 2023). This can be explained by the native granular structure of starch that is partially crystalline leading to a lower number of hydroxy groups that are available to be substituted (Klaochanpong, Punchaarnon, Uttapap, Puttanlek, & Rungsardthong, 2017). In the case of soluble and less compact carbohydrate molecules, such as pullulan (Zhao et al., 2020) and maltodextrin, the DS values are similar to the ones obtained in the current study (Bai & Shi, 2011).

Moreover, in the <sup>13</sup>C NMR spectrum of OSA-modified dextrans, 5 new peaks related to OSA methylene groups were observed between 20 and 35 ppm: 21.78 ppm, 28.25 ppm, 30.60 ppm, 31.74 ppm, 35.06 ppm. Additionally, the 2D essays also confirmed the presence of OSA groups in the dextrans molecule. The COSY spectrum allowed the assignment of the OSA protons, dextran unexchangeable and exchangeable protons. Meanwhile, the HSQC and HMBC spectra enabled the determination of the chemical shifts of both the OSA chain and the dextran molecule. All spectra were recorded for native and OSA-modified dextrans and can be found in the Supplementary material.

#### 3.2. FTIR spectra

Modified and native dextran samples were analysed by FTIR technique to confirm the introduction of OSA within the molecule and to detect the interactions between the OSA molecules and dextran functional groups. As can be observed in Fig. 3, all dextran samples, OSA-modified and native, have similar FTIR spectra. The presence of peaks at 764 cm<sup>-1</sup> and 995 cm<sup>-1</sup> is indicative of  $\alpha(1 \rightarrow 4)$  and  $\alpha(1 \rightarrow 6)$  linkages, respectively, in both native and OSA esterified dextrans. This suggests that the molecular backbone remained unchanged after the reaction (Omar-Aziz et al., 2020). However, two spectral differences can be appreciated, specifically the appearance of two new absorption bands at 1720 and 1560 cm<sup>-1</sup>, whose presence is due to the asymmetric



stretching vibration of an ester carbonyl group (C=O) and a carboxylate group (RCOO<sup>-</sup>), respectively, from the octenyl-succinyl radical, which confirms the esterification of dextran with OSA in the modified samples (Xu et al., 2023). Moreover, based on the DS values obtained in Section 3.1, the intensity of these bands increases as the OSA concentration rises, consistent with the results obtained in other studies (Quintero-Castaño et al., 2020). Furthermore, the absence of unreacted OSA can be confirmed by the absence of peaks within the range of 1850 to 1750 cm<sup>-1</sup>, which indicates that the OSA-dextran samples were washed successfully (Shah, Vishwasrao, Singhal, & Ananthanarayan, 2016).

# 3.3. Thermal stability and thermal properties

The thermal analysis of both native and OSA-modified dextran was performed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The thermogravimetric (TG) and derivate thermogravimetric (DTG) curves of the native dextrans and the OSAmodified dextrans are represented in Fig. 4. It can be observed that both modified and non-modified dextrans had two stages of weight loss which vary a little depending on the presence of OSA groups in the dextran molecule and on the molecular weight of the polymer. In all cases, the first stage, caused by the loss of free water, ranged approximately from 50 to 150 °C; and the second stage ranged approximately from 250 to 350 °C. This second stage, caused by the pyrolysis of glucose, led to the highest mass loss in the samples. This loss was faster in native dextrans than in the OSA-modified ones, possibly due to the incorporation of OSA groups in dextran molecules making them more stable. In addition, there can be observed a small increase in the temperature of degradation of the modified polymers in comparison to the native ones. These improvements in thermal stability reveal that the introduction of OSA groups in dextran reduces the mobility of chains, leading to an increase in the degradation temperatures (Djori & Moulai-Mostefa, 2022). Understanding the precise positioning of these OSA substituents in the dextran molecule we could indeed provide valuable insights into the factors contributing to the observed greater thermal stability of the polymer. While we cannot determine if the reaction is regioselective, we can only predict, that regarding theory an esterification in carbon 3 will produce a modified dextran polymer with improved thermal properties and stability by fostering a more stable molecular structure and minimizing interference with crucial functional groups (Hiemenz & Lodge, 2007).

Additionally, the DSC analysis was performed to determine thermal parameters such as the transition temperatures (Table 2). The introduction of OSA groups in the dextran molecules produced a decrease in the transition temperature of the polymer, which increased slightly when the DS values rose. These changes may be due to the presence of hydrophobic alkenyl groups in the polymer network, which produce electrostatic repulsion forces in the matrix and weaken the hydrogen bond interactions between dextran chains (Michel & Ferrier, 2020). Similar results were observed by Chen, Chen, et al. (2021) and Wang et al. (2023) when modifying corn, potato and pea starch with OSA. Regarding the melting enthalpy, the opposite behaviour was observed, as the enthalpy increased in the OSA-modified samples, which may be due to physicochemical changes in the modified dextran molecules resulting in changes in the heat capacity of the polymer due to rearrangements and crystallisation of the structure (Schick, Wurm, & Mohamed, 2001). Additionally, the introduction of OSA groups endowed the dextran molecules with thermoplastic properties, as can be appreciated with the glass transition observed in the modified polymers between 200 and 240  $^\circ$ C. This glass transition temperature is the temperature region where there is observed a change from the rigid, glassy solid to a softer, more flexible and rubbery solid (Pacáková & Virt, 2005). It can be observed (Table 2) that native dextrans do not show any glass transition region but with increasing OSA DS values, a decrease in the transition temperatures was observed, which means that polymer chains start to move at lower temperatures. Similar behaviour was



Fig. 4. DTG (A, C, E) and TG (B, D, F) curves of native and OSA-modified dextrans. (A, B) 20 kDa dextran. (C, D) 70 kDa dextran. (E, F) 150 kDa dextran.

observed by Djori and Moulai-Mostefa (2022) when modifying waxy maize starch with OSA. They found that the introduction of OSA groups in the polymer structure decreased the glass temperature from 285 °C to 114.82 °C.

### 3.4. Zeta potential

The zeta potential of a molecule denotes the electric potential that is generated at a solid-liquid interface in response to the relative motion between the solid particles and the surrounding medium. This parameter allows the determination of the surface charge of particles and, therefore, their stability (Cacua et al., 2019). The zeta potentials of non-

modified and OSA-modified dextrans of different molecular weights are presented in Fig. 5. It can be observed that all samples, including native and chemically modified dextrans, exhibit a negative zeta potential. A higher negative charge contributes to a more stable suspension and colloidal system. Native starches have low zeta potential absolute values (-10-0 mV), being more negative when low molecular weight dextran was analysed. This phenomenon may be due to the fact that longer molecular weight dextrans, when dispersed in water, assume a more compact molecular configuration, causing the charged groups to remain inside the three-dimensional structure and decreasing the zeta potential of particles (Tirtaatmadja, Dunstan, & Boger, 2001).

Results indicate a tendency towards an increase in the negative zeta

#### Table 2

Thermal properties of native and OSA-modified dextrans.

Sample	DS	Melting temperature (°C)	Melting enthalpy (J/ g)	Glass transition range (°C)
Dex20	-	80.21	175.47	_
OSA5-	0.032 $\pm$	57.70	334.17	200.31-212.52
Dex20	0.007			
OSA10-	0.043 $\pm$	61.98	229.20	198.77-212.20
Dex20	0.005			
Dex70	_	102.10	118.07	-
OSA5-	$0.030~\pm$	60.11	379.92	213.61-226.14
Dex70	0.004			
OSA10-	0.058 $\pm$	62.14	341.73	202.66-223.73
Dex70	0.007			
Dex150	-	82.22	151.16	-
OSA5-	0.028 $\pm$	57.20	322.86	210.68-227.68
Dex150	0.002			
OSA10-	0.053 $\pm$	67.29	246.52	205.32-227.75
Dex150	0.005			



Fig. 5. Zeta potential of non-modified and OSA-modified dextrans of different molecular weights (20, 70 and 150 kDa).

potential of OSA-dextrans with respect to the native dextrans, as the carboxylic groups of OSA (-COO<sup>-</sup>) confer a negative charge to the polymer (Mu et al., 2022). Dextrans with higher DS values, and therefore, a greater number of OSA groups within their structure, exhibit higher absolute zeta potentials, a phenomenon that was more noticeable when high molecular weight dextran was used. This finding aligns with the results obtained by Zheng et al. (2022) when they modified high amylose corn starch with different percentages of OSA (3, 6, 9 and 12%). Minor variations within the same treatments are attributed to random OSA substitutions in the molecules, leading to a heterogeneous distribution of OSA groups between the inside and the surface of the structure (Fuentes, Choi, Wahlgren, & Nilsson, 2023).

It is important to point out that none of the Zeta potentials found have a greater negative value than -25 mV, indicating that the particles will not be stable under electrostatic interactions, for which values closer to  $\pm 30$  mV are required (Cacua et al., 2019).

#### 3.5. Functional properties: emulsifying and foaming capacity

### 3.5.1. Emulsifying capacity and stability

The presence of OSA groups in dextran molecules imparts both hydrophilic and lipophilic properties to them, enabling them to absorb in the interface between water and oil, thus acting as emulsion stabilizers (Li et al., 2023; Zhan, Li, Shi, Wu, & Li, 2019). The emulsifying capacity was assessed just after the preparation of the emulsions, and results are shown in Fig. 6A. The emulsifying capacity exhibits a range of values between 44 % and 70 %, with a notable increase with the higher OSA percentage. The observed disparity in the enhancement of emulsifying capacity in response to OSA concentration is particularly noteworthy in the case of the 20 kDa dextran sample, as compared to the other two variants, where the former demonstrates a relatively modest increase in contrast to the latter two. This behaviour coincides consistently with the degree of substitution in the different samples, with considerable higher values observed in the 70 kDa and 150 kDa samples subjected to a 10 % OSA concentration (Zhao et al., 2020).

Regarding the microstructural assessment of the emulsions, the initial droplet size distribution of emulsions stabilized with both native and OSA-modified dextran samples are illustrated in Fig. 6B. As can be observed, emulsions prepared with native dextrans possessed a unimodal droplet size distribution, composed in its majority of large droplets  $(\sim 300-350 \ \mu\text{m})$ ; on the other hand, emulsions prepared with 5 % or 10 % OSA-modified dextrans were composed of smaller droplets (~50-70  $\mu$ m). It is noteworthy that the emulsions prepared with the native dextran samples experienced a phase separation a few minutes after preparation, evidencing their poor emulsifying capacity. Similar findings were reported by Yu et al. (2019), Zhang, Yang, Zheng, Yuan, and Mao (2021) and Zheng et al. (2022) when modifying taro, potato, corn and high amylose corn starch with various concentrations of OSA. In addition to droplet size, it was evident that lower molecular weight dextrans exhibited a poorer emulsifying capacity compared to their higher molecular weight counterparts. This outcome may be attributed to the fact that higher molecular weight molecules possess a larger capacity for packing at the water/oil interface. Consequently, they can form a thinner interfacial layer to stabilize the system, as previously reported (Xu et al., 2020). Notably, emulsions prepared with OSAmodified dextrans displayed a wide droplet size distribution.

In addition to the droplet size distribution, the Turbiscan Stability Index (TSI) is an important parameter for evaluating the stability of emulsion systems. TSI is inversely proportional to emulsion stability; as TSI increases, the instability of the emulsion system also increases. Fig. 7A represents the global TSI of emulsions prepared with OSAmodified dextrans. It can be observed that as the OSA percentage, and therefore, the DS values increases, the TSI values are lower, indicating a more stable emulsion (Zheng et al., 2022). These results may be due to the presence of OSA groups in dextran molecules, which increases their affinity for the oil phase, facilitating their location at the water/oil interface and hence avoiding coalescence of the droplets (Fonseca-Florido et al., 2018).

The TSI value increases for all emulsions over time, especially during the first day of storage, reaching constant values after 7 days of storage (Zhan et al., 2019). As a general trend, emulsions prepared with dextran molecules modified with 5 % OSA had larger TSI values, indicating greater instability. This is especially noticeable in the cases where lower molecular weight dextrans were used (20 and 70 kDa), while in the case of dextran with a molecular weight of 150 kDa, the TSI values achieved after 10 days of storage were similar to those obtained when 10 % OSA dextrans were used (Fig. 7B).

The overall TSI values obtained are due to the different types of destabilization phenomena. Some are due to large drop size, which leads to the migration of droplets, with lower density than the continuous phase, to the sample surface according to Stoke's law and others are due to the equilibrium movement of dextran molecules between the oil/water interface and the continuous medium. This continuous molecular movement is expected to be more important when small molecules, corresponding to dextran with low molecular weight, are used. Other destabilization phenomena related to coalescence and/or Oswald ripening can arise, due to the uncovered interfaces created. The coalescence or Oswald ripening phenomena can cause free oil to appear on the surface.

Analysing samples after 10 days of storage, it was observed that emulsions prepared with low molecular weight dextran and 5 % OSA modification were the only ones that presented free oil at the surface,



Fig. 6. Emulsifying capacity (A) and droplet size distribution of emulsions stabilized with native and OSA-modified dextrans (B).



Fig. 7. Global TSI values over 10 days of storage of emulsions stabilized with different modified dextrans (A). Graphical representation of the different layers (clarification, emulsion and free oil) presented on the samples prepared after 10 days of storage (B).

corresponding to those with high TSI values. In the case of the use of dextran with a high molecular weight (150 kDa), no free oil was detected but it could be observed that the thickness of the emulsion layer increased when dextran with 10 % OSA was used instead of 5 % OSA dextran. This indicates once again that emulsion capacity increases with a larger degree of OSA modification and with larger molecular weight dextran molecules.

#### 3.5.2. Foaming capacity and stability

Foam is a colloidal system characterized by the dispersion of gas bubbles within a continuous liquid phase. Surfactants play an important role in enhancing the foaming capacity and stability of such systems due to their amphiphilic nature, which enables them to adsorb at the airwater interface, forming a thin layer that helps to stabilize the foam (Omar-Aziz et al., 2020). The foaming properties of native and OSAmodified dextrans are shown in Fig. 8. As can be appreciated, native dextrans, being hydrophilic molecules, did not have foaming properties and therefore, they could not act as surfactants. Nevertheless, the introduction of hydrophobic groups, such as OSA groups, into their structure conferred upon them a significant foaming capacity. Moreover, there exists a direct correlation between the DS of samples and their foaming capacity, as an increase in the number of OSA groups attached to the dextran molecules led to an increase in the foaming capacity. This observation is likely attributable to the heightened hydrophobic nature of the molecules. Similar findings were reported by Gahruie, Eskandari, Khalesi, Van der Meeren, and Hosseini (2020), who observed that the addition of OSA-modified basil seed gum increased the foaming capacity of egg albumin from 41.67 % to 59.09 %. In a similar study, Omar-Aziz et al. (2020) found that the modification of pullulan with OSA resulted in these originally hydrophilic polysaccharides exhibiting a foaming capacity of 60.37 % and 124 % of foaming, while the unmodified sample had no foam capacity.

Regarding foam stability, the same behaviour was observed; foam was more stable with increasing percentage of OSA and rising molecular weight of dextrans. Foam stability refers to the capacity of foam to maintain its structure and characteristics, which include foam volume, liquid content in the system and the size of bubbles and these are strongly influenced by the viscosity of the liquid phase. The presence of OSA and higher dextran molecules increased the viscosity of the system, reducing the coalescence of bubbles and increasing foam stability (Gahruie et al., 2020).

# 4. Conclusion

The chemical modification of different molecular weight dextrans with OSA enabled the synthesis of a novel biopolymer with both hydrophobic and hydrophilic properties. This hydrophobic modification had a notable impact on the structural and thermal properties of the dextrans. Although the reaction affected the three samples of different molecular weight equally, a significant difference was observed when the concentration of OSA was at its higher value, with higher degrees of substitution being reached. FTIR and NMR analyses confirmed the successful incorporation of OSA groups into the dextran molecule, resulting in an increase in the zeta potential of the particles and enhancing their thermal stability. Furthermore, the introduction of the octenyl-succinyl radical into the dextran molecular backbone endowed these molecules with emulsifying and foaming properties, providing additional evidence of the structural modification and improved surface properties of the dextrans, and their new hydrophobic character. Additionally, it was observed that OSA-dextran exhibited superior foaming capacity and stability as the molecular weight of the modified samples increased, with the 150 kDa samples displaying the best performance. It can be concluded that the introduction of hydrophobic groups into a hydrophilic molecule like dextran enhances its functional and surface properties, thereby expanding its potential applications in the food, cosmetic and pharmaceutical industries.



Fig. 8. Foaming capacity (A) and foam stability (B) of native and OSA-modified dextrans.

# CRediT authorship contribution statement

Florencia Ridella: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. María Carpintero: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. Ismael Marcet: Writing – review & editing, Visualization, Methodology, Conceptualization. María Matos: Writing – review & editing, Methodology. Gemma Gutiérrez: Writing – review & editing, Methodology. Manuel Rendueles: Supervision, Resources, Funding acquisition. Mario Díaz: Supervision, Resources, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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