



IR spectroscopy and chemometrics for physical property prediction of structured lipids produced by interesterification of beef tallow

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ABSTRACT

The aim of this study was the application of infrared spectroscopy and chemometrics to predict slip melting point (SMP), melting points at different melted fat percentages (MP85, MP90, MP95), and consistency of structured lipids to provide fast and reliable methods for their characterization. Tallow was chemically or enzymatically interesterified with corn, canola, or safflower oils, at different ratios. Fourier-transform mid-infrared (FT-IR) and near-infrared (FT-NIR) spectra of melted and solid samples were collected. Partial-least-square regression models constructed after different spectra pre-treatments and variable selection were satisfactory. The best models were obtained with solid sample FT-NIR spectra: in cross-validation, determination coefficients and root mean square errors were, respectively, 0.85 and 1.7 °C for SMP, 0.85 and 2.8 °C for MP90, and 0.91 and 14 MPa for consistency. Infrared spectroscopy can be considered a promising tool to determine physical properties of interesterified fats.

1. Introduction

Beef tallow is considered as a low-value fat since it is not suitable for direct human consumption due to its high melting point, wide plastic range, and low levels of polyunsaturated fatty acids (Kowalska, Żbikowska, & Kowalski, 2004). Therefore, physical properties of tallow need to be modified to enhance its value and potential uses. Modifications can be achieved by either chemical or enzymatic interesterification (Engelmann et al., 2018). Chemical interesterification provides new physical properties to the modified lipids by the random incorporation or the restructuring of acyl residues of triacylglycerols (TAG). On the contrary, enzymatic interesterification leads to the attachment of specific fatty acids to specific positions of TAG structure to produce new products (Martin, Reglero, & Señoráns, 2010). One of the goals of interesterification processes is to modify fat consistency, which is an important quality aspect, usually defined as spreadability and hardness (De Graef, Vereecken, Smith, Bhaggan, & Dewettinck, 2012).

Tallow is hard at ambient temperature, thus its use in several food products is limited. High melting and slip melting points (about 40–60 °C) are other handicaps that prevent the direct use of tallow in foods. Thus, for use in edible products, tallow should be modified to obtain fats with desirable properties (Bhattacharyya, Bhattacharyya, &

De, 2000).

Infrared (IR) spectroscopy is a promising technique for the analyses of fats and oils, with the advantages of being fast, non-destructive, and easy-to-use; moreover, minimum or no sample preparation is required before analysis. In the scientific literature, there are many examples of IR spectroscopy applications to determine fat and oil properties (Cascant et al., 2018; Gertz & Behmer, 2014; Hocevar, Soares, Oliveira, Korn, & Teixeira, 2012; Özdemir et al., 2018). For instance, in a study about the direct characterization of lard (i.e., without performing sample pretreatment steps like melting or homogenization) by means of Fourier-transform near-infrared (FT-NIR) spectroscopy, the results of the multivariate model calibration showed that the selection of the most relevant wavelengths enables the accurate prediction of iodine number and fatty acid profile (Foca et al., 2016). The suitability of IR spectroscopy in monitoring lipase-catalyzed interesterification of bulky fats was also demonstrated (Chang, Lai, Zhang, Søndergaard, & Xu, 2005). Mid-IR spectroscopy in combination with chemometric techniques such as partial least squares regression was successfully employed for the determination of the composition of waste frying oils consisting of soybean oil, palm oil, and hydrogenated vegetable fat (Hocevar et al., 2012). In another study, the possibility of monitoring hydrogenation process of soybean oil by a compact near-IR spectrometer and the

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suitable data elaboration was demonstrated (Pereira et al., 2018).

However, to the best of our knowledge, no studies regarding the prediction of physical parameters of interesterified products using IR spectroscopy have been published. The hypothesis of this research is that IR spectroscopy, coupled to chemometrics, is able to characterize physical properties of structured fats obtained by interesterification. Actually, interesterification reactions modify fat physical features by TAG rearrangement. The exchange of acyl groups among TAG leads to changes in molecular vibrations that can be detected by IR spectroscopy. The aim of this study was, therefore, to investigate the capability of FT-NIR and Fourier-transform mid-infrared (FT-IR) spectroscopy to predict some physical properties (consistency, slip melting point, and melting point) of structured lipids produced by chemical and enzymatic interesterification of tallow with different ratios of canola, corn, or safflower oils.

2. Materials and methods

2.1. Production of interesterified lipids

The tallow used for interesterification reactions was obtained from two different breeds (Montafon and Holstein) of 2-years old calves immediately after slaughter. Canola, corn, and safflower oils were obtained from local market. Calf breed and oil type were not considered as experimental variables. Sodium methoxide was provided by a local oil processing plant. Lipase solution from *Thermomyces lanuginosus* was purchased from Sigma–Aldrich (St. Louis, MO).

Sixty different structured lipids were manufactured by chemical and enzymatic interesterification following published procedures (Bryś, Wirkowska, Górska, Ostrowska-Ligęza, & Bryś, 2014; Kowalska, Zbikowska, & Kowalski, 2014). All structured lipids were prepared at three different tallow/oil blend ratios (6:4, 7:3, and 8:2 w/w). Chemically interesterified lipids were produced by adding the catalyst at different concentrations (0.75, 0.875 or 1 g/100 g). For the manufacturing of enzymatically interesterified lipids, the reaction was achieved by adding 10 g/100 g enzyme. After production, all structured fats were stored at -20°C until analyses.

2.2. Determination of slip melting and melting points

Slip melting point (SMP) of structured fats, non-interesterified blends, and tallow was determined according to AOCS method Cc 3–25 (AOCS, 1989). Samples were heated to 60°C in a thermostatic chamber for complete melting of the crystals. Capillary tubes filled with melted samples were chilled at 4°C overnight before being immersed in a beaker of distilled water at ambient temperature. The water was heated at a rate of 1.2 K/min and the temperature at which the column of fat rose in the tube was recorded as SMP. This measurement was carried out at least twice for each sample.

Melting point of structured lipids, non-interesterified blend, and tallow was measured by differential scanning calorimetry (DSC) using a Q10 calorimeter (TA Instruments, Crawley, UK). Samples (9–10 mg) were placed in hermetically sealed aluminum pans. DSC analysis was carried out from 20 to -40°C and from -40 to 80°C at a scan rate of 10 K/min compared to an empty pan (Rodríguez, Castro, Salinas, López, & Miranda, 2001). Data analysis was performed with the dedicated software IFEOSTOS which was assembled by some of the Authors for handling raw calorimetric data according to the suggestions of Barone, Del Vecchio, Fessas, Giancola, and Graziano (1993). Briefly, the output signal in mW units was divided by the product of sample mass and heating rate to be converted into apparent specific heat and it was scaled with respect to the baseline to obtain the excess (with respect to the melted state) specific heat trace, C_p^{exc} [J/(K·g)]. Thanks to this treatment, the area beneath the recorded peaks directly corresponds to the relevant transition enthalpy, $\Delta H_{\text{overall}}$. Accordingly, the degree of the overall melting process as a function of temperature, $\alpha(T)$ (ranging

from 0 to 1), was obtained by the following equation:

$$\alpha(T) = \frac{\int_{T_0}^T C_p^{\text{exc}} dT}{\Delta H_{\text{overall}}} \quad (1)$$

i.e., the ratio of the partial area at a given temperature to the overall area of the DSC peaks was used to obtain the percentage of the melted material in the sample at each temperature.

2.3. Consistency measurements

Structured lipids and tallow samples (5 g) were put into 10 mL glass beakers and heated to 60°C in a thermostatic chamber for complete melting. Then, they were conditioned for 24 h in another thermostatic chamber at 25°C . Consistency of samples was determined by penetration tests carried out using a 45° acrylic cone fitted to a TA.XT Plus texture analyzer (Stable Micro Systems, Surrey, UK). A penetration depth of 4 mm with a 20 mm/s speed was applied, and consistency was calculated as “yield value” according to the following equation (Silva et al., 2009):

$$C = \frac{KW}{p^{1.6}} \quad (2)$$

where C is the yield value (MPa), K is a constant depending on the cone angle (4700 adimensional), W is the compression force (N), and p is the penetration depth (m). Measurements were performed in triplicate.

2.4. FT-NIR spectroscopy analyses

FT-NIR spectra were acquired with a MPA spectrometer (Bruker Optics, Milan, Italy) on both melted and solid structured lipids as well as on tallow, and non-interesterified blends. After melting in a temperature-controlled chamber at 60°C for 2 h, the samples (50 mL) were transferred in a water bath at 60°C and FT-NIR spectra were acquired in transmittance mode (1 mm pathlength) by a fiber optic reflection probe (1.5 m length) inserted directly in the lipid. A spectral range of $12500\text{--}3600\text{ cm}^{-1}$ was used, with 8 cm^{-1} resolution, and 32 scans for both background and samples. For measurements on solid samples, melted lipids were poured in disposable glass vials (8 mm pathlength) and incubated overnight at 25°C in a temperature-controlled chamber. FT-NIR spectra were then collected in transmission mode by using the same analytical conditions applied for the melted samples. All spectra were acquired in duplicate and the instrument control was performed by OPUS software (v. 6.5 Bruker Optics, Ettlingen, Germany).

2.5. FT-IR spectroscopy analyses

FT-IR spectra were acquired with a Vertex 70 spectrometer (Bruker Optics, Milan, Italy) controlled by OPUS software (v. 6.5 Bruker Optics, Ettlingen, Germany) on both melted and solid structured lipids as well as on tallow, and non-interesterified blends. Spectra were collected over the range of $4000\text{--}700\text{ cm}^{-1}$, at 4 cm^{-1} resolution, by using a single reflection ZnSe ATR cell (MIRacle™, PIKE Technologies, Inc., Madison, WI) and 32 scans for both samples and background. Measurements were replicated twice on samples prepared as already reported for FT-NIR analyses. Melted samples were poured on the ATR cell by means of a pipette, while solid fats were spread on the ATR crystal by means of a spatula.

2.6. Data analysis

FT-IR and FT-NIR data are complex so, to extract useful information, multivariate analysis techniques were applied by means of The Unscrambler X software (v. 10.4.1, CAMO Process A/S, Oslo, Norway). Four data matrices with 71 samples including tallow (2), interesterified lipids (60), and non-interesterified blends (9) were constructed with FT-

NIR and FT-IR spectra of both melted and solid samples. The following wavenumber ranges were selected in order to keep the most informative and less noisy segments of the spectra:

- FT-NIR: 9002–4497 cm^{-1}
- FT-IR: 3051–2599 and 2052–597 cm^{-1} .

For all matrices, the replicated spectra were averaged prior to the application of various pre-processing techniques including smoothing (moving average, segment size: 7), standard normal variate (SNV), multiplicative scatter correction (MSC), first (d1) and second (d2) derivatives (Savitzky-Golay, 11 smoothing points). The partial least squares regression (PLS) analysis was applied to each pre-treated data matrices in order to predict the physical properties of interesterified lipids. Due to the limited number of samples, models were validated only by an internal cross-validation procedure, considering 5 randomly created cancellation groups. The best models were selected based on the following figures of merit: determination coefficient (R^2), root mean square error of calibration (RMSEC) and cross-validation (RMSECV), number of latent variables (LVs). Variable selection was carried out by the Martens uncertainty test implemented in The Unscrambler X.

A Pearson correlation matrix for SMP and melting points at the different percentages of melted fat was calculated (Statgraphics Centurion 18, Statgraphics Technologies Inc., The Plains, VA, USA).

3. Results and discussion

3.1. Physical properties of structured lipids

SMP of structured lipids ranged from 31.8 to 47.1 °C as reported in Table 1. Interesterification reactions, as expected, caused a decline in SMP of structured lipids in comparison to the tallow and the non-interesterified blends, due to the changes in TAG composition caused by the reactions (Oliveira, Rodrigues, Bezerra, & Silva, 2017).

The detailed picture of the melting behavior of structured lipids was obtained by DSC, which provides useful information about the crystal thermal stability of interesterified fats. As an example, in Fig. 1 the DSC melting profile of a chemically interesterified sample of a canola-tallow blend is shown. A complex endothermic trace can be observed, with at least three main endothermic peaks with shoulders, across a wide temperature range, corresponding to the melting of different TAG crystals. Actually, in the present work tallow was interesterified with different vegetable oils, therefore different TAGs were created in the structured lipid throughout the reaction. The overall inspection of the DSC measurements suggests that the low temperature melting peak (Peak 1) is associated with TAGs of vegetable oils, i.e. can be attributed to the presence of a high content of mono- and poly-unsaturated fatty acids. Peak 2 represents middle-melting TAG species, naturally present

Table 1

Minimum-maximum ranges of physical properties for structured lipids (60 samples) produced by chemical or enzymatic interesterification of tallow with different vegetable oils. Data for tallow (2 samples) and non-interesterified blends (9 samples) are also reported.

Response	Structured lipids (min-max value)	Tallow (min-max value)	Non-interesterified blends (min-max value)
SMP (°C)	31.8–47.1	47.0–50.4	43.2–47.1
MP85 (°C)	18.2–50.0	46.6–52.1	38.9–50.0
MP90 (°C)	28.7–50.8	48.0–52.8	40.1–50.8
MP95 (°C)	30.2–51.9	49.6–53.7	40.7–51.9
Consistency (MPa)	1.5–293.4	69.9–603	9.0–67.6

SMP, slip melting point; MP85, melting point at 85% melted crystals; MP90, melting point at 90% melted crystals; MP95, melting point at 95% melted crystals.

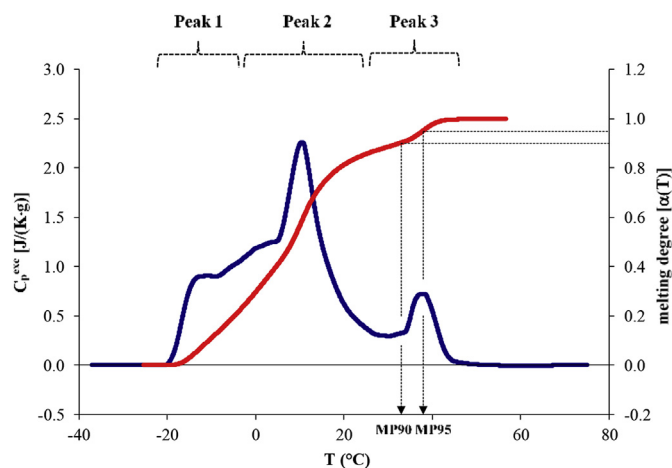


Fig. 1. Differential Scanning Calorimetry melting profile of a chemically interesterified sample of canola-tallow blend.

in non-interesterified blends and/or formed during interesterification. Peak 3 represents the high-melting species associated with saturated TAGs deriving from tallow. In this complex scenario, i.e. a mixture of crystals with different thermal stability, it is difficult to define a sample specific melting point to find a correlation with the SMP. For this reason, the integral form of the DSC traces was taken into account (Fig. 1), i.e. the overall degree of the advance of melting process as a function of temperature ($\alpha(T)$), and melting points as a function of given percentages of melted crystals (85, 90, and 95%) were calculated (MP85, MP90, and MP95; Table 1). In all cases, as already observed for SMP, interesterification reactions caused a decrease in the melting points of structured lipids compared to tallow and the non-interesterified blends. These changes in melting points are in accordance with previous studies (Li et al., 2018; Morselli Ribeiro, Ming, Silvestre, Grimaldi, & Gonçalves, 2017; Wirkowska-Wojdyła, Bryś, Górska, & Ostrowska-Ligeża, 2016). As regards the melting percentage that better correlates melting point with SMP, highly significant ($p < 0.001$) Pearson correlations were found between SMP and all the determined melting points. However, the correlation between SMP and MP95 ($r = 0.892$; Fig. 2) was considered the best one, since the lower bias was obtained (8.7 °C vs 30.0 and 18.9 °C for MP85 and MP90, respectively). In any case, it has to be noticed that the DSC temperature scan rate was higher than that of the SMP method and this difference may generate, in some cases, further uncertainty.

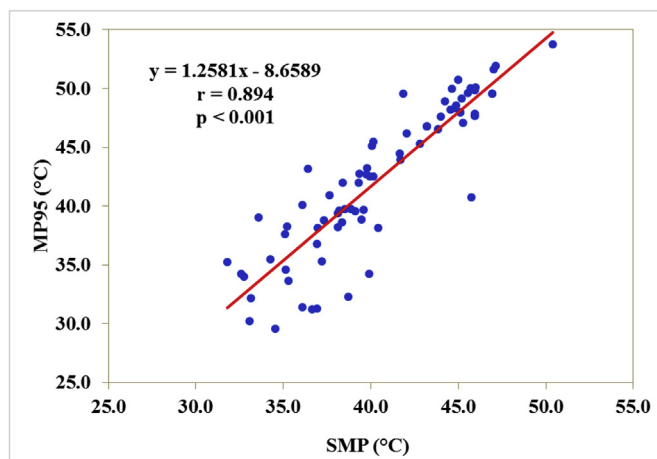


Fig. 2. Correlation between slip melting point (SMP) and melting point at 95% melted fat (MP95) of structured lipids produced by chemical or enzymatic interesterification of tallow with different vegetable oils.

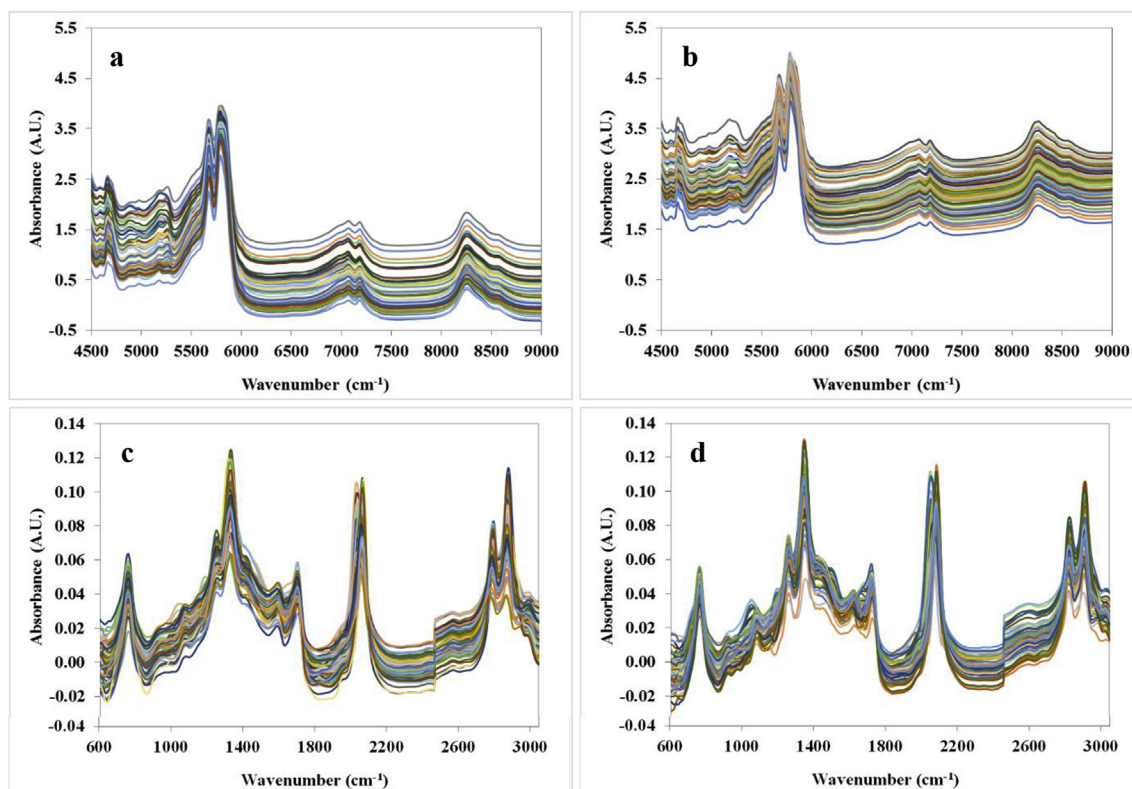


Fig. 3. Reduced spectra of structured lipids produced by chemical or enzymatic interesterification of tallow with different vegetable oils: a) FT-NIR spectra of melted samples; b) FT-NIR spectra of solid samples; c) FT-IR spectra of melted samples; d) FT-IR spectra of solid samples.

Consistency of the samples was calculated as “yield value” (MPa) and the obtained ranges are listed in Table 1. As expected, the consistency of tallow was quite higher than both interesterified lipids and non-interesterified blends. Therefore, consistency of blends increased with the increasing amount of tallow. Interesterified lipids tended to show lower consistency values compared to their corresponding blends before the reactions, probably due to higher amounts of tri-unsaturated TAGs produced by interesterification. In addition, differences in polymorphic structure and aggregation behavior, which lead to alteration in the structure of tallow crystal network, can change the consistency (Silva et al., 2009).

3.2. IR spectral profiles of structured lipids

The reduced (without non-informative wavenumber regions) FT-NIR and FT-IR spectra of melted and solid interesterified lipids and non-interesterified blends are shown in Fig. 3. In FT-NIR spectra, absorption bands between 6055 and 5345 cm^{-1} appeared to be highly significant. This region is mainly related to the first overtone of C-H stretching in fatty acid molecules (Blanco, Beneyto, Castillo, & Porcel, 2004). Despite the high values of absorbance observed in both melted and solid samples, signal saturation was not reached, while it appeared in the discarded spectral region (i.e. 4497–3600 cm^{-1}). The absorption peak in the 5345–4562 cm^{-1} region is ascribable to the combination band of O-H and C=O stretching of ester groups (RCOOR). The region 7397–6661 cm^{-1} corresponds to the first overtone of the O-H bond of mono- and diglycerides that might be produced as intermediates and by-products during interesterification reactions (Blanco et al., 2004; Chang et al., 2005). FT-NIR spectra of solid samples showed higher absorbance values and baseline trend in comparison to melted samples, probably due to scattering effects caused by the fat crystals (Chang et al., 2005) and to the longer pathlength used (8 mm vs 1 mm).

For all FT-IR spectra, more attention was paid to the fingerprint region (1500–800 cm^{-1}). This region includes C-O-C vibration in

esters, C-H bending and stretching vibrations, and the second overtone of C=O and -OH in fatty acid structure (Chang et al., 2005; Moh, Tang, Man, & Lai, 1999). Melted and solid sample spectra were more similar than in the case of FT-NIR region, because scattering effects are less important in FT-IR region (Doyle, 1995). Moreover, the very little amount of sample used for FT-IR spectra collection and the absence of a temperature control, made melted samples partially solidify during measurements, thus decreasing differences with respect to previously crystallized samples.

3.3. Prediction of physical parameters from infrared spectra with partial least square analysis

The capability of predicting melting properties and consistency of interesterified fats from IR spectra was investigated by constructing PLS models. All regression models were developed using both FT-NIR and FT-IR spectra of solid and melted samples individually. The detailed PLS results are shown in Tables 2 and 3 in terms of number of LVs, coefficients of determination in calibration (R^2_{cal}) and cross-validation (R^2_{cv}), RMSEC and RMSECV. For each response variable, the best models (reported in bold in Tables 2 and 3) were chosen based on lower number of LVs, higher R^2 , and lower errors. In general, the regression models were characterized by a low number of LVs (from 4 to 10) and limited errors compared to the values of the response. Better results were usually obtained using FT-NIR data of solid samples. Even if during FT-IR analyses of melted samples a partial solidification could occur due to the lack of temperature control, models calculated with spectral data of melted samples were similar to or even better than those based on data of solid samples. Actually, as already commented, scattering effects are less important in FT-IR, making composition of samples more important than their state for physical properties prediction.

The best PLS model for SMP was obtained with the FT-NIR spectra of solid samples after first derivative transformation. The limited errors

Table 2

Statistical parameters of developed PLS models for the prediction of melting and consistency properties of structured lipids by FT-NIR data acquired both on melted and solid samples. The best models are reported in bold.

Response	Melted samples						Solid samples					
	Pretreatment	LVs	RMSEC	R ² _{cal}	RMSECV	R ² _{cv}	Pretreatment	LVs	RMSEC	R ² _{cal}	RMSECV	R ² _{cv}
SMP (°C)	SNV	10	1.6	0.86	2.3	0.72	SNV	7	1.6	0.86	2.0	0.80
	MSC	10	1.6	0.86	2.4	0.72	MSC	7	1.7	0.85	2.1	0.78
	d1	6	2.0	0.79	2.6	0.68	d1	5	1.3	0.91	1.6	0.88
	d2	10	1.4	0.90	2.1	0.78	d2	3	1.9	0.82	2.0	0.80
MP85 (°C)	SNV	9	3.8	0.78	4.9	0.63	SNV	9	2.5	0.90	3.4	0.83
	MSC	9	3.8	0.77	4.9	0.65	MSC	8	2.3	0.86	3.7	0.79
	d1	6	4.3	0.71	5.4	0.55	d1	6	2.7	0.88	3.4	0.83
	d2	10	2.6	0.89	3.7	0.76	d2	6	2.8	0.88	3.8	0.80
MP90 (°C)	SNV	10	2.8	0.84	4.2	0.64	SNV	8	2.4	0.89	3.3	0.81
	MSC	10	2.8	0.84	3.9	0.69	MSC	10	2.1	0.91	3.0	0.83
	d1	6	3.6	0.74	4.6	0.59	d1	6	2.4	0.89	2.8	0.84
	d2	9	2.5	0.87	3.4	0.78	d2	4	2.8	0.84	3.5	0.78
MP95 (°C)	SNV	10	2.4	0.85	3.4	0.73	SNV	10	2.0	0.90	2.7	0.84
	MSC	9	2.8	0.8	3.6	0.68	MSC	8	2.4	0.85	3.0	0.79
	d1	10	2.4	0.85	3.2	0.74	d1	6	2.3	0.86	2.9	0.78
	d2	10	2.5	0.84	3.4	0.71	d2	7	2.2	0.88	2.9	0.79
Consistency (MPa)	SNV	10	17.2	0.87	40.7	0.25	SNV	No significant models				
	MSC	7	17.2	0.87	38.9	0.35	MSC	7	11.9	0.94	18.3	0.86
	d1	4	14.3	0.81	24.6	0.41	d1	10	10.4	0.95	25.6	0.68
	d2	4	16.3	0.88	36.3	0.44	d2	1	32.5	0.53	36.9	0.40

SMP, slip melting point; MP85, melting point at 85% melted crystals; MP90, melting point at 90% melted crystals; MP95, melting point at 95% melted crystals; SNV, Standard Normal Variate; MSC, Multiplicative Scatter Correction; d1, first derivative; d2, second derivative; LVs, latent variables; RMSEC, root mean square error of calibration; R²_{cal}, determination coefficient of calibration; RMSECV, root mean square error of cross-validation; R²_{cv}, determination coefficient of cross-validation.

and the high determination coefficients prove that it is possible to predict SMP of structured lipids by means of FT-NIR spectroscopy.

All the models constructed for the prediction of melting points based on FT-NIR spectra were satisfactory. On the contrary, FT-IR models calculated using solid sample data showed lower R²_{cv} (0.58–0.67) and higher RMSECV (3.6–5.1 °C), thus being not satisfactory. The lower performances of these models can be due to the very limited amount of sample used for spectra acquisition, possibly not representing the real structure of crystallized lipids. Actually, the best models for melting point prediction were calculated using FT-NIR spectra of solid samples acquired in transmission mode. In this case, a

higher amount of sample compared to FT-IR analysis was used, being thus more representative of the whole fat.

Similarly, only FT-NIR spectra collected on solid samples provided good prediction models for consistency. In particular, the model based on MSC pre-treated data provided high determination coefficients (0.94 and 0.86 in calibration and cross-validation, respectively) with RMSEC and RMSECV of 11.9 and 18.3 MPa, respectively.

The best models were also re-calculated using only the wave-numbers selected by the Martens uncertainty test, in order to obtain simpler and more robust models (Table 4). This procedure did not allow choosing a very limited number of variables, but, in any case, a

Table 3

Statistical parameters of developed PLS models for the prediction of melting and consistency properties of structured lipids by FT-IR data acquired both on melted and solid samples. The best models are reported in bold.

Response	Melted samples						Solid samples					
	Pretreatment	LVs	RMSEC	R ² _{cal}	RMSECV	R ² _{cv}	Pretreatment	LVs	RMSEC	R ² _{cal}	RMSECV	R ² _{cv}
SMP (°C)	SNV	8	1.7	0.85	2.5	0.70	SNV	5	2.7	0.63	3.3	0.47
	MSC	7	1.8	0.83	2.6	0.66	MSC	5	2.7	0.61	3.3	0.50
	d1	6	1.7	0.84	2.3	0.73	d1	7	1.8	0.83	2.5	0.68
	d2	5	1.8	0.83	2.2	0.75	d2	9	1.4	0.90	2.4	0.70
MP85 (°C)	SNV	9	3.1	0.85	5.0	0.59	SNV	5	5.3	0.55	6.2	0.41
	MSC	7	3.6	0.80	4.8	0.65	MSC	5	5.4	0.54	6.3	0.35
	d1	6	3.4	0.82	4.6	0.68	d1	10	3.0	0.85	5.1	0.58
	d2	5	3.7	0.78	4.5	0.70	d2	5	4.4	0.70	5.2	0.56
MP90 (°C)	SNV	9	2.6	0.86	4.3	0.65	SNV	5	4.4	0.61	5.2	0.45
	MSC	7	3.0	0.82	4.0	0.69	MSC	5	4.4	0.60	5.1	0.49
	d1	6	2.9	0.83	3.9	0.70	d1	9	2.7	0.85	4.6	0.60
	d2	4	3.3	0.78	3.9	0.71	d2	5	3.7	0.72	4.5	0.60
MP95 (°C)	SNV	8	2.3	0.86	3.4	0.71	SNV	5	3.7	0.65	4.5	0.51
	MSC	7	2.4	0.85	3.3	0.71	MSC	5	3.7	0.65	4.5	0.49
	d1	3	3.1	0.75	3.4	0.71	d1	10	2.1	0.88	3.6	0.67
	d2	4	2.9	0.79	3.4	0.72	d2	4	3.5	0.68	3.9	0.63
Consistency (MPa)	SNV	3	41.9	0.22	45.3	0.12	SNV	2	44.5	0.14	48.3	0.03
	MSC	3	42.0	0.22	45.9	0.08	MSC	4	41.6	0.25	47.5	0.07
	d1	3	40.2	0.28	44.6	0.15	d1	1	44.2	0.15	48.6	0.05
	d2	2	40.3	0.28	44.1	0.17	d2	1	45.0	0.18	48.1	0.01

SMP, slip melting point; MP85, melting point at 85% melted crystals; MP90, melting point at 90% melted crystals; MP95, melting point at 95% melted crystals; SNV, Standard Normal Variate; MSC, Multiplicative Scatter Correction; d1, first derivative; d2, second derivative; LVs, latent variables; RMSEC, root mean square error of calibration; R²_{cal}, determination coefficient of calibration; RMSECV, root mean square error of cross-validation; R²_{cv}, determination coefficient of cross-validation.

Table 4

Statistical parameters of PLS models constructed with selected FT-NIR and FT-IR variables for the prediction of melting and consistency properties of structured lipids.

Response	Spectroscopy	Samples	Pretreatment	LVs	RMSEC	R ² _{cal}	RMSECV	R ² _{cv}
SMP (°C)	FT-NIR	melted	d2	8	1.5	0.88	2.03	0.79
	FT-NIR	solid	d1	5	1.3	0.91	1.68	0.85
	FT-IR	melted	d2	4	1.9	0.81	2.09	0.78
	FT-IR	solid	d2	8	1.4	0.90	1.85	0.83
MP85 (°C)	FT-NIR	melted	d2	9	2.9	0.87	3.87	0.78
	FT-NIR	solid	SNV	8	2.6	0.89	3.19	0.84
	FT-IR	melted	d1	4	3.8	0.77	4.19	0.72
	FT-IR	solid	d1	10	3.1	0.85	3.80	0.78
MP90 (°C)	FT-NIR	melted	d2	6	2.7	0.85	3.51	0.76
	FT-NIR	solid	d1	4	2.5	0.87	2.82	0.85
	FT-IR	melted	d1	3	3.8	0.71	4.08	0.67
	FT-IR	solid	d1	5	3.7	0.72	4.16	0.66
MP95 (°C)	FT-NIR	melted	d1	8	2.5	0.84	3.07	0.76
	FT-NIR	solid	SNV	7	2.4	0.86	2.83	0.80
	FT-IR	melted	SNV	7	2.3	0.86	2.78	0.81
	FT-IR	solid	d1	4	3.6	0.66	3.80	0.63
Consistency (MPa)	FT-NIR	melted	d1	10	14.9	0.90	23.63	0.75
	FT-NIR	solid	MSC	9	11.7	0.94	13.97	0.91

SMP, slip melting point; MP85, melting point at 85% melted crystals; MP90, melting point at 90% melted crystals; MP95, melting point at 95% melted crystals; SNV, Standard Normal Variate; MSC, Multiplicative Scatter Correction; d1, first derivative; d2, second derivative; LVs, latent variables; RMSEC, root mean square error of calibration; R²_{cal}, determination coefficient of calibration; RMSECV, root mean square error of cross-validation; R²_{cv}, determination coefficient of cross-validation.

significant reduction was obtained. Indeed, the number of FT-NIR selected variables was 1169 and 1168 respectively for melted and solid sample (vs a total of 4505 wavenumbers), while 496 and 488 variables were chosen from FT-IR spectra of melted and solid samples, respectively (vs a total of 1907 wavenumbers). The construction of PLS models using the selected variables provided a general slight improvement in prediction ability of the models, lowering the number of LVs, reducing RMSECV and increasing R²_{cv}. The best improvement was obtained for consistency prediction. The best performances of FT-NIR spectroscopy applied to solid samples were confirmed.

There is limited information in the literature regarding the estimation of lipid physical properties by using IR spectroscopy. However, the results of this research are in agreement with a study about the monitoring of lipase-catalyzed interesterification of vegetable fats (Chang et al., 2005). The authors demonstrated that FT-NIR analysis of the interesterified products in solid form exhibited higher correlations with conventional methods with respect to FT-NIR spectroscopy applied to liquid samples or FT-IR spectroscopy of both solid and melted fats.

4. Conclusions

In this study, the application of FT-NIR and FT-IR spectroscopy for the prediction of SMP, MP, and consistency of various interesterified lipids was investigated. The use of PLS regression analysis coupled with different spectral data pre-treatments provided satisfactory models for the predictions of the physical properties, thus confirming the formulated hypothesis. The work represents a proof of concept that IR spectroscopy can be used for structured fat characterization, thus providing producers with rapid and non-destructive techniques as good alternatives to the traditional analytical methods.

Future developments should be focused on the collection of a higher number of FT-NIR spectra of liquid samples at different interesterification stages, in order to improve the developed models and propose in-line applications for industrial processing.

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Conflicts of interest

Declarations of interest: none.

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References

- AOCS (1989). Method Cc 3-25. Slip melting point, AOCS standard open tube melting point. *Official methods and recommended practices of the AOCS* (3rd ed.). Champaign: The American Oil Chemists' Society.
- Barone, G., Del Vecchio, P., Fessas, D., Giancola, C., & Graziano, G. (1993). The deconvolution of multistate transition DSC curves of biological macromolecules: Bovine serum albumin and bovine seminal ribonuclease. *Thermochimica Acta*, 227, 185–195.
- Bhattacharyya, S., Bhattacharyya, D. K., & De, B. K. (2000). Modification of tallow fractions in the preparation of edible fat products. *European Journal of Lipid Science and Technology*, 102, 323–328.
- Blanco, M., Beneyto, R., Castillo, M., & Porcel, M. (2004). Analytical control of an esterification batch reaction between glycerine and fatty acids by near-infrared spectroscopy. *Analytica Chimica Acta*, 521, 143–148.
- Bryś, J., Wirkowska, M., Górska, A., Ostrowska-Ligeza, E., & Bryś, A. (2014). Application of the calorimetric and spectroscopic methods in analytical evaluation of the human milk fat substitutes. *Journal of Thermal Analysis and Calorimetry*, 118, 841–848.
- Cascant, M. M., Breil, C., Fabiano-Tixier, A. S., Chemat, F., Garrigues, S., & de la Guardia, M. (2018). Determination of fatty acids and lipid classes in salmon oil by near infrared spectroscopy. *Food Chemistry*, 239, 865–871.
- Chang, T., Lai, X., Zhang, H., Søndergaard, I., & Xu, X. (2005). Monitoring lipase-catalyzed interesterification for bulky fat modification with FT-IR/NIR spectroscopy. *Journal of Agricultural and Food Chemistry*, 53, 9841–9847.
- De Graef, V., Vereecken, J., Smith, K. W., Bhaggan, K., & Dewettinck, K. (2012). Effect of TAG composition on the solid fat content profile, microstructure, and hardness of model fat blends with identical saturated fatty acid content. *European Journal of Lipid Science and Technology*, 114, 592–601.
- Doyle, W. M. (1995). Near-IR and mid-IR process analysis—a critical comparison. *Advances in Instrumentation and Control*, 50, 433–441.
- Engelmann, J. I., Silva, P. P., Igansi, A. V., Pohndorf, R. S., Cadaval, T. R. S., Jr., Crexi, V. T., et al. (2018). Structured lipids by swine lard interesterification with oil and esters from common carp viscera. *Journal of Food Process Engineering*, 41, e12679.
- Foca, G., Ferrari, C., Ulrici, A., Ielo, M. C., Minelli, G., & Fiego, D. P. L. (2016). Iodine value and fatty acids determination on pig fat samples by FT-NIR spectroscopy: Benefits of variable selection in the perspective of industrial applications. *Food Analytical Methods*, 9, 2791–2806.
- Gertz, C., & Behmer, D. (2014). Application of FT-NIR spectroscopy in assessment of used frying fats and oils. *European Journal of Lipid Science and Technology*, 116, 756–762.
- Hocevar, L., Soares, V. R., Oliveira, F. S., Korn, M. G. A., & Teixeira, L. S. (2012). Application of multivariate analysis in mid-infrared spectroscopy as a tool for the

- evaluation of waste frying oil blends. *Journal of the American Oil Chemists' Society*, 89, 781–786.
- Kowalska, M., Zbikowska, A., & Kowalski, B. (2014). Enzymatically modified fats based on mutton tallow and rapeseed oil suitable for fatty emulsions. *Journal of the American Oil Chemists' Society*, 91, 1703–1710.
- Li, Y., Zhao, J., Xie, X., Zhang, Z., Zhang, N., & Wang, Y. (2018). A low trans margarine fat analog to beef tallow for healthier formulations: Optimization of enzymatic interesterification using soybean oil and fully hydrogenated palm oil. *Food Chemistry*, 255, 405–413.
- Martin, D., Reglero, G., & Señoráns, F. J. (2010). Oxidative stability of structured lipids. *European Food Research and Technology*, 231, 635–653.
- Moh, M. H., Tang, T. S., Man, Y. C., & Lai, O. M. (1999). Rapid determination of peroxide value in crude palm oil products using Fourier transform infrared spectroscopy. *Journal of Food Lipids*, 6, 261–270.
- Morselli Ribeiro, M. D., Ming, C. C., Silvestre, I. M., Grimaldi, R., & Gonçalves, L. A. G. (2017). Comparison between enzymatic and chemical interesterification of high oleic sunflower oil and fully hydrogenated soybean oil. *European Journal of Lipid Science and Technology*, 119, 1500473.
- Oliveira, P. D., Rodrigues, A. M., Bezerra, C. V., & Silva, L. H. (2017). Chemical interesterification of blends with palm stearin and patawa oil. *Food Chemistry*, 215, 369–376.
- Özdemir, İ. S., Dağ, Ç., Özinaç, G., Suçoran, Ö., Ertaş, E., & Bekiroğlu, S. (2018). Quantification of sterols and fatty acids of extra virgin olive oils by FT-NIR spectroscopy and multivariate statistical analyses. *LWT-Food Science and Technology*, 91, 125–132.
- Pereira, J. M. G., Sanchez, J. L., de Lima, P. C., Possebon, G., Tanamati, A., Tanamati, A. A. C., et al. (2018). Industrial hydrogenation process monitoring using ultra-compact Near-Infrared Spectrometer and chemometrics. *Food Analytical Methods*, 11, 188–200.
- Rodríguez, A., Castro, E., Salinas, M. C., López, R., & Miranda, M. (2001). Interesterification of tallow and sunflower oil. *Journal of the American Oil Chemists' Society*, 78, 431–436.
- Silva, R. C., Cotting, L. N., Poltronieri, T. P., Balcão, V. M., de Almeida, D. B., Goncalves, L. A., & Gioielli, L. A. (2009). The effects of enzymatic interesterification on the physical-chemical properties of blends of lard and soybean oil. *LWT-Food Science and Technology*, 42, 1275–1282.
- Wirkowska-Wojdyła, M., Bryś, J., Górska, A., & Ostrowska-Ligeza, E. (2016). Effect of enzymatic interesterification on physicochemical and thermal properties of fat used in cookies. *LWT-Food Science and Technology*, 74, 99–105.