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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, and safflower oils separately, 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.

Keywords: calorimetry; chemometrics; consistency; infrared spectroscopy; slip melting point.

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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 square 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 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 et al., 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 IFESTOS 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, Cp^{exc} [J/(K·g)]. Thanks to this treatment, the area beneath the recorded peaks directly corresponds to the relevant transition enthalpy, $\Delta H_{overall}$. Accordingly, the degree of the overall melting process as a function of temperature, α(T) (ranging from 0 to 1), was obtained by the following equation:

$$\alpha(T) = \frac{\int_{T_0}^{T} Cp^{exc} dT}{\Delta H_{overall}} \qquad \text{[Eq. 1].}$$

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):

$$C = \frac{KW}{P^{1.6}} \qquad \text{[Eq. 2]}$$

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 transflectance mode (1 mm pathlength) by a fiber optic reflection probe (1.5 m length) inserted directly in the lipid. A spectral range of 12500-3600/cm was used, with 8/cm 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

151 over the range of 4000-700/cm, at 4/cm resolution, by using a single reflection ZnSe ATR cell
152 (MIRacle^{TM}, PIKE Technologies, Inc., Madison, WI) and 32 scans for both samples and
153 background. Measurements were replicated twice on samples prepared as already reported for
154 FT-NIR analyses. Melted samples were poured on the ATR cell by means of a pipette, while
155 solid fats were spread on the ATR crystal by means of a spatula.
156
157 *2.6. Data analysis*
158 FT-IR and FT-NIR data are complex so, to extract useful information, multivariate analysis
159 techniques were applied by means of The Unscrambler X software (v. 10.4.1, CAMO Process
160 A/S, Oslo, Norway). Four data matrices with 71 samples including tallow (2), interesterified
161 lipids (60), and non-interesterified blends (9) were constructed with FT-NIR and FT-IR spectra of
162 both melted and solid samples. The following wavenumber ranges were selected in order to keep
163 the most informative and less noisy segments of the spectra:
164 - FT-NIR: 9002-4497/cm
165 - FT-IR: 3051-2599 and 2052-597/cm.
166 For all matrices, the replicated spectra were averaged prior to the application of various pre-
167 processing techniques including smoothing (moving average, segment size: 7), standard normal
168 variate (SNV), multiplicative scatter correction (MSC), first (d1) and second (d2) derivatives
169 (Savitzky-Golay, 11 smoothing points). The partial least square regression (PLS) analysis was
170 applied to each pre-treated data matrices in order to predict the physical properties of
171 interesterified lipids. Due to the limited number of samples, models were validated only by an
172 internal cross-validation procedure, considering 5 randomly created cancellation groups. The best
173 models were selected based on the following figures of merit: determination coefficient (R^2), root
174 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 et al., 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 vegetables 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 in non-interesterified blends and/or formed during interesterification. Peak 3 represents the high-melting species associated with saturated TAGs

199 deriving from tallow. In this complex scenario, i.e. a mixture of crystals with different thermal
200 stability, it is difficult to define a sample specific melting point to find a correlation with the
201 SMP. For this reason, the integral form of the DSC traces was taken into account (Fig. 1), i.e. the
202 overall degree of the advance of melting process as a function of temperature ($\alpha(T)$), and melting
203 points as a function of given percentages of melted crystals (85, 90, and 95%) were calculated
204 (MP85, MP90, and MP95; Table 1). In all cases, as already observed for SMP, interesterification
205 reactions caused a decrease in the melting points of structured lipids compared to tallow and the
206 non-interesterified blends. These changes in melting points are in accordance with previous
207 studies (Li et al., 2018; Morselli Ribeiro, Ming, Silvestre, Grimaldi, & Gonçalves, 2017;
208 Wirkowska-Wojdyla, Bryś, Górska, & Ostrowska-Ligęza, 2016). As regards the melting
209 percentage that better correlates melting point with SMP, highly significant ($p < 0.001$) Pearson
210 correlations were found between SMP and all the determined melting points. However, the
211 correlation between SMP and MP95 ($r = 0.892$; Fig. 2) was considered the best one, since the
212 lower bias was obtained (8.7 °C *vs* 30.0 and 18.9 °C for MP85 and MP90, respectively). In any
213 case, it has to be noticed that the DSC temperature scan rate was higher than that of the SMP
214 method and this difference may generate, in some cases, further uncertainty.
215 Consistency of the samples was calculated as ‘‘yield value’’ (MPa) and the obtained ranges are
216 listed in Table 1. As expected, the consistency of tallow was quite higher than both interesterified
217 lipids and non-interesterified blends. Therefore, consistency of blends increased with the
218 increasing amount of tallow. Interesterified lipids tended to show lower consistency values
219 compared to their corresponding blends before the reactions, probably due to higher amounts of
220 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 appeared to be highly significant. This region is mainly related to the first overtone of C-H stretching in fatty acid molecules (Blanco et al., 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). The absorption peak in the 5345-4562/cm region is ascribable to the combination band of O-H and C=O stretching of ester groups (RCOOR). The region 7397-6661/cm 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, Beneyto, Castillo, & Porcel, 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). 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

244 control, made melted samples partially solidify during measurements, thus decreasing differences
245 with respect to previously crystallized samples.
246
247 *3.3. Prediction of physical parameters from infrared spectra with partial least square analysis*
248 The capability of predicting melting properties and consistency of interesterified fats from IR
249 spectra was investigated by constructing PLS models. All regression models were developed
250 using both FT-NIR and FT-IR spectra of solid and melted samples individually. The detailed PLS
251 results are shown in Tables 2 and 3 in terms of number of LVs, coefficients of determination in
252 calibration (R^2cal) and cross-validation (R^2cv), RMSEC and RMSECV. For each response
253 variable, the best models (reported in bold in Tables 2 and 3) were chosen based on lower
254 number of LVs, higher R^2, and lower errors. In general, the regression models were characterized
255 by a low number of LVs (from 4 to 10) and limited errors compared to the values of the response.
256 Better results were usually obtained using FT-NIR data of solid samples. Even if during FT-IR
257 analyses of melted samples a partial solidification could occur due to the lack of temperature
258 control, models calculated with spectral data of melted samples were similar to or even better
259 than those based on data of solid samples. Actually, as already commented, scattering effects are
260 less important in FT-IR, making composition of samples more important than their state for
261 physical properties prediction.
262 The best PLS model for SMP was obtained with the FT-NIR spectra of solid samples after first
263 derivative transformation. The limited errors and the high determination coefficients prove that it
264 is possible to predict SMP of structured lipids by means of FT-NIR spectroscopy.
265 All the models constructed for the prediction of melting points based on FT-NIR spectra were
266 satisfactory. On the contrary, FT-IR models calculated using solid sample data showed lower R^2_{cv}
267 (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 wavenumbers 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 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 R^2_{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

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Declarations of interest: none

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392 **Legends to Figures**

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

395

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

399

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

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Table 1. Minimum-maximum ranges and standard deviation (s.d.) values 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

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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.

	Melted samples						Solid samples					
Response	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; R^2_{cal}, determination coefficient of calibration; RMSECV, root mean square error of cross-validation; R^2_{cv}, determination coefficient of cross-validation.

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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.

	Melted samples						Solid samples					
Response	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; R^2_{cal}, determination coefficient of calibration; RMSECV, root mean square error of cross-validation; R^2_{cv}, determination coefficient of cross-validation.

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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; R^2_{cal}, determination coefficient of calibration; RMSECV, root mean square error of cross-validation; R^2_{cv}, determination coefficient of cross-validation.

Fig. 1

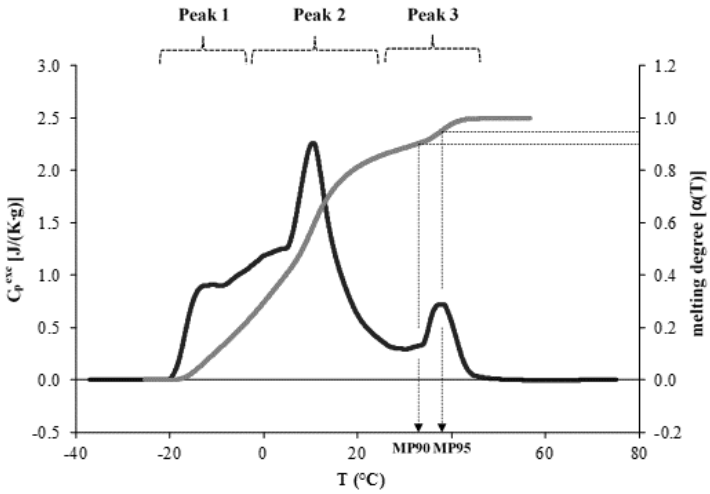


Fig. 1. Color version for online only

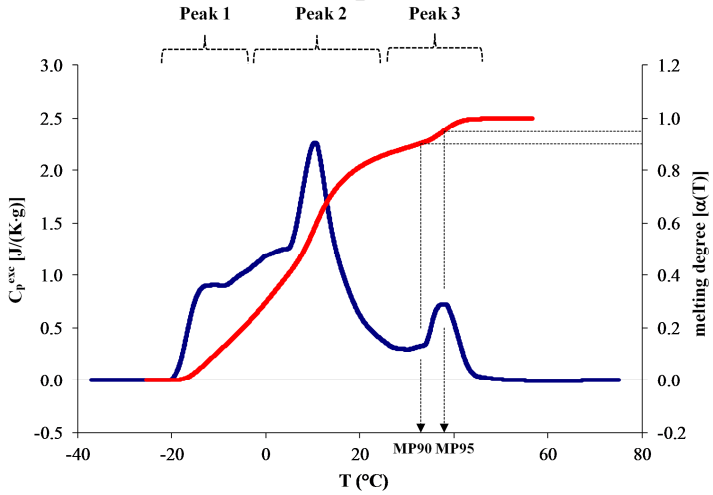
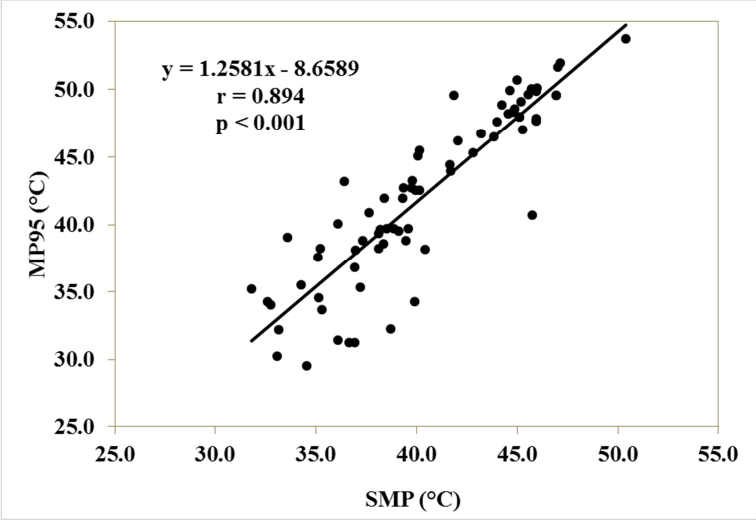


Fig. 2.



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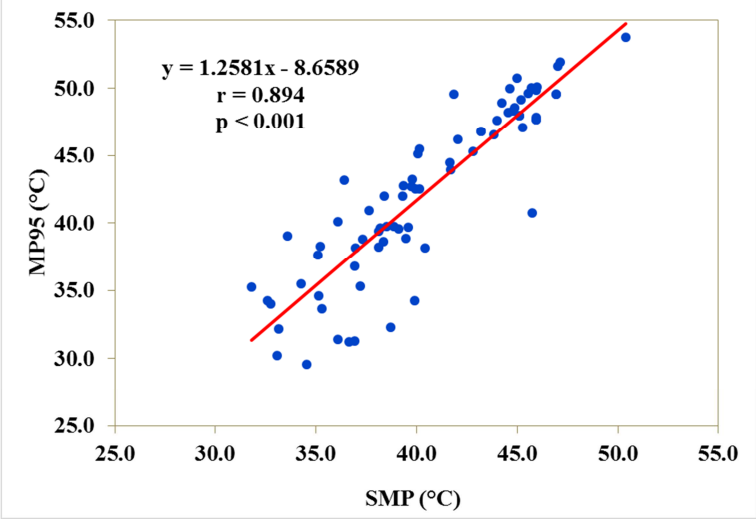

Fig. 3

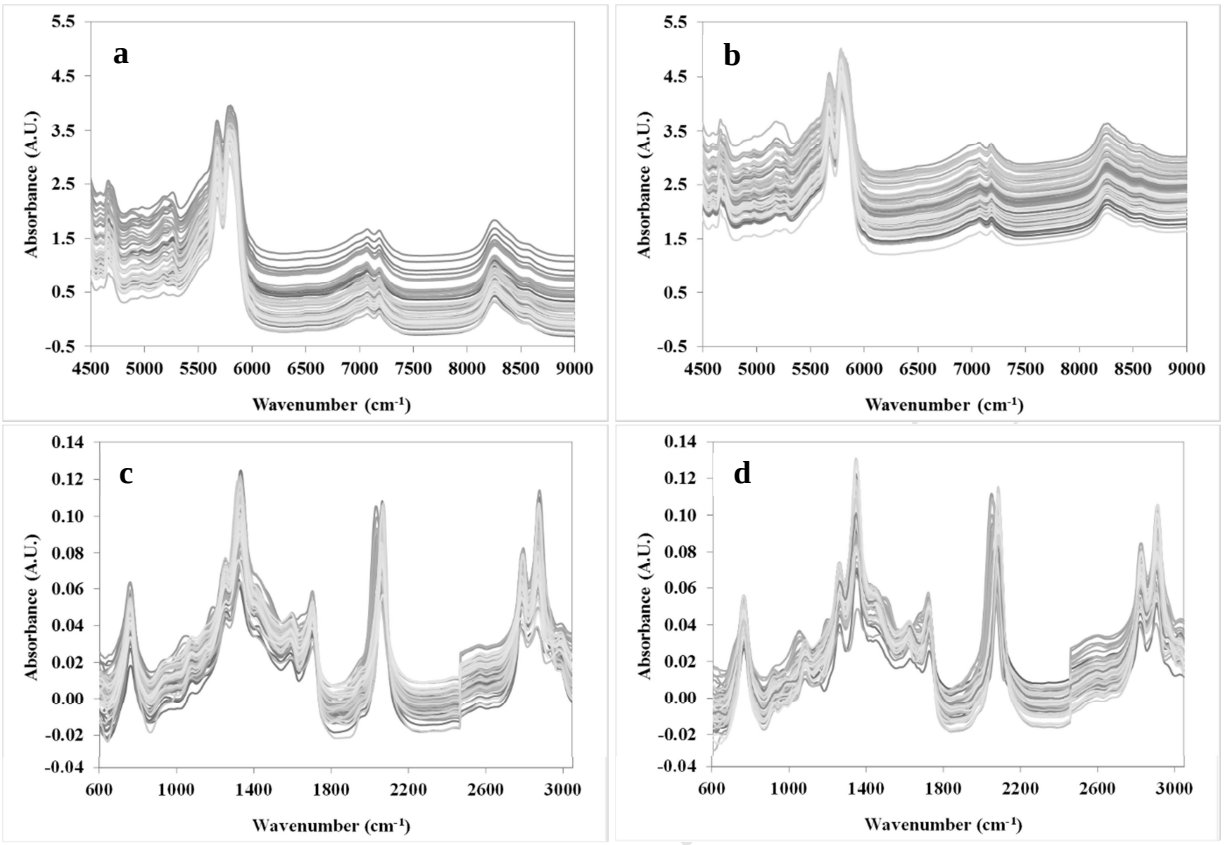

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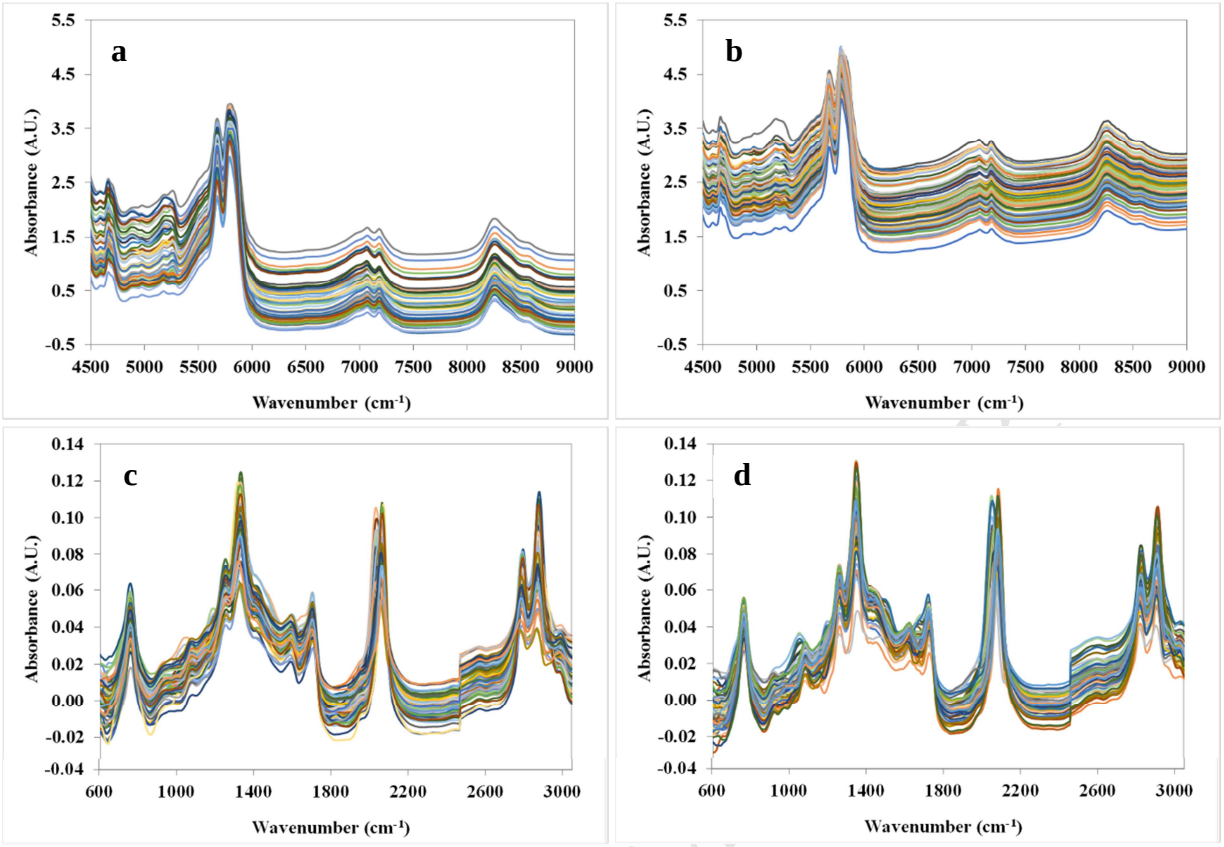
Fig. 3. Color version for online only



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Highlights

- Chemical and enzymatical interesterification of tallow with three vegetable oils.
- Determination of slip melting point, melting points and consistency of structured fats.
- Collection of FT-IR and FT-NIR spectra on melted and solid samples.
- Good potential of IR spectroscopy in the prediction of fat physical properties.

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