

Interesterification of rapeseed oil with anhydrous milk fat and its stearin fraction

II. Modifications of melting properties

J.-M.GIET¹, M.AGUEDO², E.HANON², S.DANTHINE¹, M.PAQUOT³, G. LOGNAY⁴,
A.THOMAS⁵, M. VANDEBOL⁶, P. THONART⁷, **Jean-Paul WATHELET**², C. BLECKER¹

Department of Chemistry and Bio-Industries, ¹Lab. of Food Technology, ²Lab. of General and Organic Chemistry, ³Lab. of Industrial Biological Chemistry, ⁴Lab. of Analytical Chemistry, ⁵Lab. of Numerical Molecular Biophysics, ⁶Lab. of Animal and Microbial Biology, ⁷Lab. of Bio-Industry. Faculté Universitaire des Sciences Agronomiques, Gembloux, Belgium.

Introduction

Chemical and/or physical modification of oils and fats are commonly used by food industry to widen their range of applications (1,2). Lipase-catalysed interesterification of anhydrous milk fat (AMF) and various vegetable oils is now a well documented procedure (3-7). The purpose of this technique is to produce original structured fats with properties different from a simple blending, that may be used as spreads or introduced into pastry. The new fats contain higher amounts of polyunsaturated fatty acids (PUFA) than butter, which provides health benefits (8,9).

To our knowledge only a few authors associated AMF fractionation with blending and interesterification (10,11), although this combination may be used to increase the ratio of vegetable oil in blends and thus the PUFA content of the product.

The compositional changes occurring during the lipase-catalysed interesterification of AMF/rapeseed oil (RO) and AMF stearin fraction (AMFSF)/RO blends were described in the first part of this study. In the present and second part are reported the resulting changes in physical properties, especially the melting behaviour through solid fat content (SFC), dropping point (DP) and fusion profiles by differential scanning calorimetry (DSC).

Materials and methods

AMF fractionation. See the first part of this work.

Dropping point. DP was measured with a MP90 apparatus (Mettler-Toledo, Zurich Switzerland) with a 1 °C/min heating rate.

Solid fat content. SFC was measured on Minispec MQ20 pulse-NMR equipment (Bruker, Karlsruhe, Germany) according to the 2.150 (serial) IUPAC method.

Differential scanning calorimetry. DSC was carried out using a Q1000 apparatus (T.A. Instruments, New Castle, Delaware, USA). Samples (2 mg in SFI aluminium pan) were melted completely 10 min at 80 °C, cooled to –80 °C, kept isothermal for 30 min and heated at 15 °C/min to 80 °C.

Results

Dropping Point.

Dropping points of the fats and the blends before and after 6 hours of interesterification are reported in Table 1. Blends contained 30% (w/w) (RO).

	<i>fats</i>	<i>NIE blends 30% RO</i>	<i>IE blends 30% RO</i>
AMF	33.6 ± 0.2	31.7 ± 0.0	29.9 ± 0.1
AMFSF	38.8 ± 0.1	36.3 ± 0.1	32.3 ± 0.0

Table 1. DP (°C) of the fats, of the non-interesterified (NIE) blends and interesterified (IE) blends.

Adding 30% RO to the hard fats caused a decrease of their DPs of about 2 °C in both cases. A further decrease was observed after enzymatic interesterification, with a higher amplitude in the case of the blend containing AMFSF.

SFC.

Fig. 1 illustrates the change in SFC observed at various temperatures consequently to interesterification. Plotting delta(SFC) emphasizes the amplitudes of SFC variations (inset); higher variations were observed in the case of AMFSF/RO.

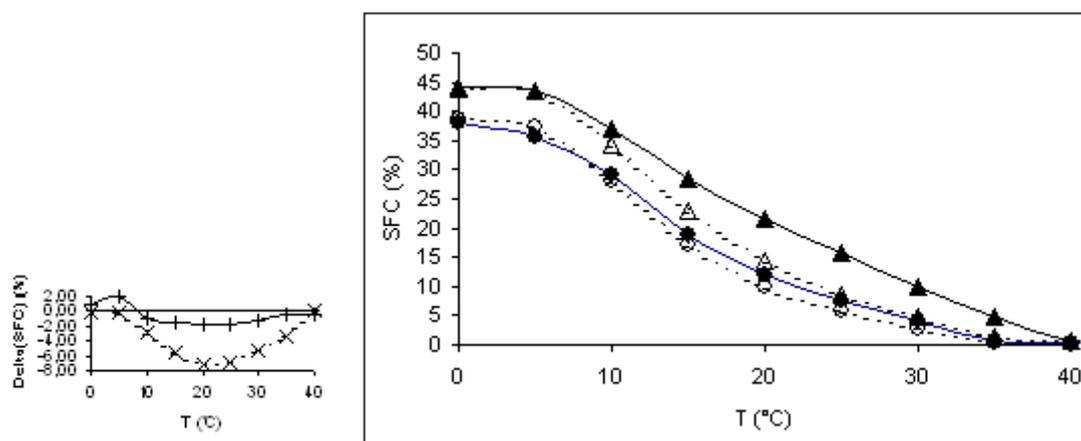


Figure 1. SFC at various temperatures for NIE (▲) and IE (△) AMFSF/RO blends and for NIE (●) and IE (○) AMF/RO blends. Inset: Delta(SFC) is the difference between NIE and IE blends for AMF/RO (+) and AMFSF/RO (X).

DSC.

The complex triglyceride composition of AMF and AMFSF gave rise to complex DSC profiles. Blending these fats with RO modified their DSC profiles by notably causing the apparition of an oil-specific peak around $-25\text{ }^{\circ}\text{C}$. The changes occurring in DSC profiles with interesterification are illustrated on Fig. 2.

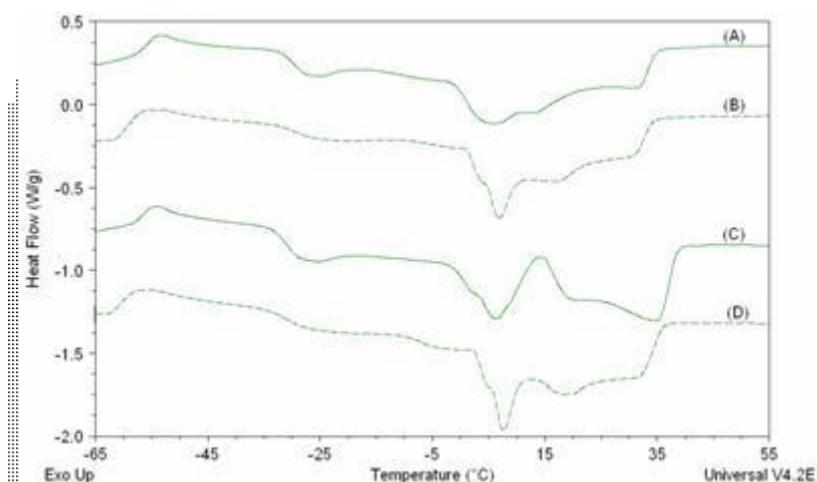


Figure 2. DSC profiles of NIE (A) and IE (B) AMF/RO blends and of NIE (C) and IE (D) AMFSF/RO blends.

For both blends, the peak around $-25\text{ }^{\circ}\text{C}$ almost totally disappeared after 6 hours of reaction, indicating the progressive restructuring of low-melting TAG species. In the case of AMF/RO, interesterification caused the sharpening of the main melting peak (around $5\text{ }^{\circ}\text{C}$) resulting in at least two convoluted peaks. Other modifications of lesser amplitude were also observed. In the case of AMFSF/RO, a sharpening of the main melting peak was associated with a strong peak's temperature shift along with a very significant reorganization in the high melting region of the profile, i.e. above $20\text{ }^{\circ}\text{C}$; the end of fusion temperature in that case is shifted by about $5\text{ }^{\circ}\text{C}$ to lower temperatures.

Conclusions

The observed physical changes after interesterification were the consequences of TAG restructuring; disappearing of low melting TAGs was observed together with an overall decrease of solid content.

As shown by the melting properties of the interesterified fat blends, new fats with original properties can be obtained. Enzymatic interesterification is a choice mild and solvent-free process enabling to produce tailored food fats fitting the consumers' concerns for healthy, practical and palatable products.

References

1. Gunstone F.D., Padley F.B. Lipids technologies and applications. 1997. CRC Press, New-York, NY, USA.
2. Akoh C.C., Min D.B. Food lipids: chemistry, nutrition, and biotechnology. 2002. 2nd Ed., CRC Press, New-York, USA.
3. Aguedo M., Hanon E., Danthine S., Paquot M., Lognay G., Thomas A., Vandebol M., Thonart P., Wathélet J.-P., Blecker C. Enrichment of anhydrous milk fat in polyunsaturated fatty acid residues from linseed and rapeseed oil through enzymatic interesterification. *J. Agric. Food Chem.* 2008. 56:1757-1765.
4. Zhang H., Mu H., Xu X. Monitoring lipase-catalyzed butterfat interesterification with rapeseed oil by Fourier transform near-infrared spectroscopy. *Anal. Bioanal. Chem.* 2006. 386:1889–1897.
5. Rousseau D., Marangoni A.G. Tailoring the textural attributes of butter fat/canola oil blends via *Rhizopus arrhizus* lipase-catalysed interesterification. 1. Compositional modifications *J. Agric. Food Chem.* 1998. 46:2368-2374.
6. Marangoni A.G., Rousseau D. Chemical and enzymatic modification of butterfat and butterfat-canola oil blends. *Food Res. Int.* 1998. 31:595-599.
7. Balcão V.M., Malcata F.X. Lipase catalysed modification of milkfat. *Biotechnol. Adv.* 1998. 16:309-341.
8. Rodriguez-Cruz M., Tovar A.R., del Prado M., Torres N. Molecular mechanisms of action and health benefits of polyunsaturated fatty acids. *Rev. Invest. Clin.* 2005. 57:457-72.
9. Hooper L., Thompson R.L., Harrison R.A., Summerbell C.D., Ness A.R., Moore H.J., Worthington H.V., Durrington P.N., Higgins J.P.T., Capps N.E., Riemersma R.A., Ebrahim S.B.J., Smith G.D. Risks and benefits of omega 3 fats for mortality, systematic cardiovascular disease, and cancer: review. *BMJ.* 2006. 332:752-760.
10. De B.K., M. Hakimji, A. Patel, D. Sharma, H. Desai, T. Kumar. Plastic fats and margarines through fractionation, blending and interesterification of milk fat, *Eur. J. Lipid Sci. Technol.* 2007. 109:32-37.
11. Pal D.K., Bhattacharyya D.K., Ghosh S. Modifications of butter stearin by blending and interesterification for better utilization in edible fat products. *JAOCS.* 2001. 78:31-36.