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Design of Roll-In Margarine Analogous by Partial Drying of Monoglyceride-Structured Emulsions

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Design of roll-in margarine analogous by partial drying of monoglyceride-structured emulsions

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Graphical Abstract

Monoglyceride-structured emulsion



- 47.6% water
- Soft



Partial gentle drying

Partially-dried emulsion



- 20% water
- Plastic and laminable



Baking trials

Puff pastry



- Comparable to roll-in-margarine puff pastry

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Legend Graphical Abstract

The application of a gentle drying procedure at 30 °C was used to turn soft monoglyceride-structured O/W emulsions into plastic and laminable systems. The latter showed a water content and rheological properties analogous to those of a conventional roll-in margarine and similar performances in baking trials of puff pastry.

For Peer Review

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4 1 **Title: Design of roll-in margarine analogous by partial drying of monoglyceride-structured**
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6 2 **emulsions**

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10 3 **Running Title: Novel monoglyceride-emulsions for margarine replacement**

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26
27
28 9 **Abstract**

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31 10 A novel process is proposed to turn soft gelled emulsions containing 4 or 9 g/100 g saturated
32
33 11 monoglyceride (MG4 and MG9) and 52.4 g/100 g water into a fat material with the typical water content
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35 12 (20 g/100 g) and rheological properties of roll-in margarines. A gentle drying procedure at 30 °C was
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37 13 found to allow partial water removal from the emulsions, without causing phase separation. As compared
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39 14 to the initial emulsions, the partially dried systems (MG4-dried and MG9-dried) showed a more solid-
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41 15 like appearance and a microstructure with oil droplets tightly packed into the MG-network. Calorimetric
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43 16 (DSC) and crystal organization (XRD) analyses showed that drying modified neither the amount of
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45 17 crystallized material nor induced MG transition toward a different lamellar organization. Moreover, the
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47 18 MG9-dried emulsion showed rheological properties ($G' = 4.6 \times 10^5$ Pa, critical stress = 634 Pa)
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49 19 comparable to those of commercial roll-in margarine and was successfully used in baking trials of puff
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51 20 pastry.
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3 21 **Practical applications:** The last years have seen an increasing demand of strategies for the nutritional
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5 22 improvement of lipid-containing foods, due to the emerging health concern related to the consumption
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7 23 of high quantities of saturated and trans fatty acids. However, the unique technological and sensory
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9 24 properties of fats make this task very challenging, especially considering the production of laminated
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11 25 products requiring the use of plastic fat materials with peculiar rheological properties. The results
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13 26 obtained in this study are very promising, as they show that the MG9-dried fat can be used as a trans-
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15 27 free alternative to traditional laminating margarine.
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20 28 Key-words: fat substitution/monoglyceride/rheological properties/laminated products/puff pastry
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23 29 Abbreviations: MG, monoglycerides
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27 30 **1 Introduction**

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29 31 Food fats, including animal fats (e.g. butter and lard), tropical oils (e.g. palm oil, palm kernel oil and
30
31 32 coconut oil) as well as margarine and shortenings containing them, are multi-purpose ingredients used
32
33 33 to modulate food structure (aeration, lightness), rheological properties (plasticity, texture), and sensory
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35 34 characteristics (taste, colour, flavour, crispiness, creaminess) [1]. They have the common characteristic
36
37 35 to be spreadable at room temperature thanks to the presence of a fat crystal network made of
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39 36 triacylglycerols [2]. In this context, saturated and trans fatty acids play a determining role being
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41 37 crystalline at room temperature. Despite unique fat technological functionalities, the last years have seen
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43 38 an increasing demand for strategies for the nutritional improvement of lipid-containing foods. This is due
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45 39 to the emerging health concern related to the consumption of high quantities of saturated and trans fats.
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47 40 The latter are well known to be associated with an increased risk of diet-related diseases and pathological
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49 41 conditions, including cardiovascular diseases, obesity and type II diabetes [3,4]. The World Health
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51 42 Organization (WHO) recommends the amount of total, saturated and trans fats to be less than 30% and
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43 10% of the total energy intake, respectively [5]. At the same time, the European Commission in 2019
44 imposed a limitation of trans fats to 2 g per 100 g of total fats [6].

45 In this context, the most challenging fats to be substituted are those used to produce laminated products,
46 such as puff pastry and croissants, called roll-in fats or laminating fats [7]. They mainly include
47 margarines that are water-in-oil emulsions containing at least 80 g/100 g fat, of which more than 50% is
48 represented by saturated and/or trans fatty acids [8,9]. Upon lamination, these roll-in-fats are shaped into
49 several thin sheets which inter-lie among an equal number of dough layers. Laminated products owe their
50 peculiar physical and sensory properties to this laminated structure: during baking, in fact, dough water
51 evaporates, causing the expansion of the dough layers, which bake separately, due to the alternate fat
52 layers [10]. Roll-in-fats should present specific characteristics, as described by Blake and Marangoni
53 [11]. They need to be plastic enough to withstand the lamination process without losing continuity. To
54 this aim, their rheological properties should be similar to the dough ones and their melting temperature
55 higher than that of the lamination process, to avoid fat melting and prevent dough layers from coming in
56 contact. Moreover, it should be underlined that the presence of water in margarine is required for optimal
57 lubrication, plasticity and leavening [12]. Water is entrapped in the continuous matrix of fat crystals as
58 tiny droplets, presenting a diameter of about 1 μm , which accounts for $5\text{-}10 \times 10^9$ droplets per mL of
59 product [13]. Although finely dispersed, water droplets are combined loosely enough for the emulsion to
60 break easily upon melting of the crystalline continuous phase, which favours puff during product baking
61 [14].

62 Different Authors proposed roll-in-fat mimetics with low saturated fat content [15–20]. However, these
63 strategies resulted in fat materials which are not comparable to margarines, since not containing water
64 [21].

65 An alternative strategy could be based on the use of MG-structured emulsions, which have actually
66 shown good performances as fat substitutes in different baked goods, including short dough pastry [22],

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3 67 sweet bread [23], cookies [24]; ice-cream [25]. The use of MG is not new and ternary gelled systems
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5 68 containing saturated monoglycerides were firstly proposed by Marangoni and co-workers in 2007 [26–
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7 69 28]. At high water content, the system appears as a liquid emulsion in which MG crystalline bilayers
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10 70 surround and stabilize oil droplets. Increasing the MG content, the MG walls extend from one droplet to
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12 71 the next one, leading to a continuous solid network, which generates a gel-like material with the
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14 72 rheological features typical of spreadable fats. The final gel structure is affected by several compositional
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16 73 and processing factors, such as MG and other ingredient type and concentration, pH, temperature and
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18 74 application of shear. In any case, it exists a defined range of compositional variables in which the system
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20 75 equilibrium is not assured and phase separation could occur [27,29,30]. It should be noted that it is not
21
22 76 possible to prepare systems simulating margarine rheological properties and fat/water ratio by simply
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24 77 increasing the MG content. In fact, the relative increase in MG requires more water and a concomitant
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26 78 decrease in the oil content to form a water-continuous phase in which the MG interact giving a stable gel
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28 79 [27,28]. In this regard, Blake and Marangoni [11] affirm that to ensure proper hydration and sufficient
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30 80 oil-droplet encapsulation, the water content of these emulsions must not be lower than 30 g/100 g. To
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32 81 improve the rheological properties of MG emulsions, waxes were added but the final water content (35–
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34 82 40 g/100 g) was in any case higher than that expected in margarine [11].
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40 83 Based on these considerations, in this work, a novel process is proposed to turn soft MG gelled emulsions
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42 84 into fat materials with the typical water content (20 g/100 g) and rheological properties of roll-in
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44 85 margarines. In particular, we propose to apply a gentle drying to remove part of the water from the
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46 86 aqueous network surrounding oil droplets in MG emulsions, without disrupting their ternary structure.
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48 87 The partially dried structured emulsions were analyzed for microstructure, calorimetric (DSC), crystal
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50 88 organization (XRD) and rheological properties. Finally, the best performing sample was selected and
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52 89 used in baking trials of puff pastry.
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90 2 Materials and Methods

91 2.1 Materials

92 Myverol™ saturated monoglyceride (MG) were kindly supplied by Kerry Ingredients and Flavour
93 (Bristol, UK), palmitic, stearic acid, NaOH were purchased from Sigma Aldrich (Milan, Italy),
94 ingredients for puff pastry were purchased in a local market; commercial margarines were selected
95 among those typically used for the industrial preparation of laminated baked goods and kindly provided
96 by local food companies.

97 2.2 Structured emulsion preparation

98 MG structured emulsions were prepared according to Calligaris, Da Pieve, Arrighetti, and Barba [31].
99 Briefly, the oil phase was composed of MG (4 and 9 g/100 g), a co-surfactant mixture (0.8 and 1.8 g/100
100 g) of palmitic and stearic acid (weight ratio 1:1) and sunflower oil (47.6 and 41.6 g/100 g). The water
101 phase (52.4 g/100 g) was composed of 1 mM NaOH (pH 11) in deionized milli-Q water to promote the
102 partial ionization of the co-surfactant mixture and obtain a properly swollen phase. The samples were
103 prepared by mixing the water solution and the oil phase previously heated at 78 °C in a water bath and
104 homogenizing by using a high-speed homogenizer DI 25 (Ika-Werke, Staufen, Germany) at 59,000g for
105 1 min. Finally, the mixture was cooled at 4 °C in an ice bath and then stored at 4 °C for 24 h before usage.
106 The obtained structured emulsions were called MG4 and MG9.

107 2.3 Structured emulsion drying

108 The drying process was conducted according to the method patented by our research group [32]. The
109 structured emulsions were spread in a thin layer (3.0 ± 0.5 mm), as measured by a CD-15APXR digital
110 calliper (Absolute AOS Digimatic, Mitutoyo Corporation, Kanagawa, Japan) and dried at 30, 40 and 50
111 °C using a professional oven (Air-o-steam, 10 GN 1/1, Electrolux, Pordenone, Italy), with an airflow set
112 at the medium level. The drying process was continued until the structured emulsions reached a lipid

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3 113 phase weight concentration of 80 g/100 g, which was determined by weighting the samples at defined
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5 114 time intervals. The partially dried structured emulsions were called MG4-dried and MG9-dried.
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8 115 2.4 *Puff pastry preparation*

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11 116 Puff pastry was prepared using commercial laminating palm margarine (Control) and the MG9-dried
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13 117 sample (36.9 g/100 g). Plain flour (47.7 g/100 g) was mixed with fine salt (0.7 g/100 g) and water (14.7
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15 118 g/100 g) using a domestic mixer (Kenwood Chef KVC3110S, Milan, Italy) until obtaining homogeneous
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17 119 dough (250 g). The latter was placed on a paper-lined sheet pan dusted with flour, covered, and left to
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19 120 rest for 30 min at 4 °C. Then, the dough was rolled into a square of 45×45 cm. Similarly, the commercial
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21 121 margarine and the MG9-dried sample were shaped into squares of about 31×31 cm, and puff pastry was
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23 122 produced as described by Patient [12], with 2 h rest at 4 °C between subsequent folding steps. Puff pastry
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25 123 was finally rolled up to 3-mm thickness and cut into 4×5 cm rectangles, which were baked at 180 °C for
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27 124 9 min (Air-o-steam, 10 GN 1/1, Electrolux, Pordenone, Italy) and cooled at 20 °C before analyses.
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32 125 2.5 *Analytical determinations*

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34 35 126 2.5.1 *Image acquisition*

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38 127 Sample images were acquired using an image acquisition cabinet (Immagini & Computer, Bareggio,
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40 128 Italy) equipped with a digital camera (EOS 550D, Canon, Milano, Italy). The digital camera was placed
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42 129 on an adjustable stand positioned 45 cm above a black or white cardboard base where the samples were
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44 130 placed. The light was provided by 4 100 W frosted photographic floodlights, in a position allowing
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46 131 minimum shadow and glare. Images were saved in jpeg format resulting in 3456×2304 pixels.
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51 132 2.5.2 *Optical microscopy*

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53 133 Samples were placed on a glass slide, covered with a cover slide and observed using a Leica DM 2000
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55 134 optical microscope (Leica Microsystems, Heerbrugg, Switzerland). The images were taken at 200×
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135 magnification using a Leica EC3 digital camera and elaborated with the Leica Suite Las EZ software
136 (Leica Microsystems, Heerbrugg, Switzerland).

2.5.3 Differential scanning calorimetry

The calorimetric analysis was carried out using a TA4000 differential scanning calorimeter (Mettler-Toledo, Greifensee, Swiss) connected to a GraphWare software TAT72.2/5 (Mettler-Toledo, Greifensee, Swiss). Heat flow calibration was achieved using indium (heat of fusion 28.45 J/g). Temperature calibration was carried out using hexane (m.p. $-93.5\text{ }^{\circ}\text{C}$), water (m.p. $0.0\text{ }^{\circ}\text{C}$) and indium (m.p. $156.6\text{ }^{\circ}\text{C}$). Samples were prepared by carefully weighing 15–20 mg of the sample in 160 μL aluminium DSC pans, closed with hermetic sealing. An empty pan was used as a reference. Samples were heated under nitrogen flow (0.5 mL/min) from 20 to $80\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C}/\text{min}$. The start of the melting transition was taken as on-set (T_{on}) points of transition, that are the points at which the extrapolated baseline intersects the extrapolated tangent of the calorimetric peak in the transition state. Results were normalized to account for the weight variation of the samples. Total peak enthalpy was obtained by integration. The program STAR ever. 8.10 (Mettler-Toledo, Greifensee, Swiss) was used to plot and analyze the thermal data.

2.5.4 X-ray diffraction

X-ray diffraction patterns were recorded at the X-ray Diffraction beamline 5.2 at the Synchrotron Radiation Facility Elettra located in Trieste (Italy). The X-ray beam emitted by the wiggler source on the Elettra 2 GeV electron storage ring was monochromatized by a Si(1 1 1) double crystal monochromator, focused on the sample and collimated by a double set of slits giving a spot size of $0.2\times 0.2\text{ mm}$. A drop of the sample was lodged into a nylon pre-mounted cryoloop 20 micron for crystallographic experiments (0.7–1.0 mm) (Hampton Research HR4-965, Aliso Viejo, CA, USA). Sample temperature was controlled using a 700 series cryo-cooler (Oxford Cryosystems, Oxford, UK) with an accuracy of $1\text{ }^{\circ}\text{C}$. Analyses were performed at $20\text{ }^{\circ}\text{C}$. Data were collected at a photon energy of 8.856 keV ($\lambda = 1.4\text{ \AA}$), using a 2M

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3 158 Pilatus silicon pixel X-ray detector (DECTRIS Ltd., Baden, Switzerland). Bidimensional patterns
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5 159 collected with Pilatus were calibrated by means of a LaB6 standard and integrated using the software
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8 160 FIT2D [33] obtaining a powder-like pattern for every sample experiment. The angular range (two theta)
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10 161 of observed diffraction ring spanned from 1.3° to 21° , corresponding to interplanar distances d from 60
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12 162 Å to 3.9 Å and to reciprocal lattice spacings q from 0.1 \AA^{-1} to 1.62 \AA^{-1} .

16 163 2.5.5 Rheology

18 164 The viscoelastic properties (moduli G' and G'') of the samples were tested using an RS6000 Rheometer
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20 165 (Thermo Scientific RheoStress, Haake, Germany), equipped with a Peltier system for temperature
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22 166 control. Measures were performed using a parallel plate geometry at 15°C with a gap of 1.0 mm.
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24 167 Oscillatory sweep tests to identify the linear viscoelastic region (LVR) were performed increasing stress
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26 168 from 0.1 to 3,000 Pa at 1 Hz frequency. Critical stress (Pa) was identified as the strain value
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28 169 corresponding to a 10% drop in G' value.
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33 170 2.5.6 Colour

35 171 The puff pastry surface colour was measured using a tristimulus Chromameter-2-Reflectance
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37 172 colourimeter (Minolta, Osaka, Japan) with a CR-300 measuring head, standardized against a white tile,
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39 173 and data were expressed in L^* , a^* and b^* scale.
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44 174 2.5.7 Leavening capacity

46 175 The leavening capacity of puff pastry was determined by measuring the volume gain (%) before and after
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48 176 baking (cm^3g^{-1}) by using the rapeseed displacement method [34].
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52 177 2.5.8 Sensory analysis

54 178 A group of 13 judges was used for the sensory evaluation of puff pastry samples. Judges were not trained
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56 179 on sensory analysis of puff pastry but they were experts in the use of the selected sensory method. Control
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3 180 puff pastry prepared with commercial margarine and the sample prepared with the MG9-dried emulsion
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5 181 were evaluated. Judges were asked to evaluate the intensity of firmness, crispiness and oiliness of the
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8 182 puff pastry samples, which were identified by 3-digit random codes. The selected descriptors were
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10 183 evaluated on a 1-9 point hedonic scale, in which 1 corresponded to “extremely low descriptor intensity”,
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12 184 and 9 to “extremely high descriptor intensity” [35].
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15 185 2.5.9 Data elaboration

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18 186 All determinations were expressed as the mean \pm standard error of at least three repeated measurements
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20 187 from two experiment replicates. Statistical analysis was performed by using R v. 3.0.2 (The R Foundation
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22 for Statistical Computing). Student’s t-test was used to determine statistically significant differences
23 188 between means ($p < 0.05$).
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27 190 The kinetics constants of the drying processes (k , h^{-1}) were obtained by fitting the drying data, expressing
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29 the moisture weight percentage as a function drying time (t , h), by using the model proposed by Lewis
30 191 [36] (eq. 1):
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$$33 \frac{X - X_e}{X_0 - X_e} = \exp(-kt) \quad (\text{eq. 1})$$

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36 193 where X , X_e and X_0 are the moisture content (g/100 g) at any time, equilibrium and initial, respectively.
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39 194 Data fitting was performed by using TableCurve2D software (Jandel Scientific, ver. 5.01). The goodness
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197 **3 Results and Discussion**

198 *3.1 Structured emulsion drying*

199 Water-in-oil emulsions containing 47.6 g/100 g water and 4 or 9 g/100 g monoglycerides were prepared
200 and characterized. Taking into consideration the MG content, the samples were named as MG4 and MG9,
201 respectively. As expected and in agreement with the literature, the obtained systems were self-standing
202 white emulsions, as well visible from sample images and micrographs reported in Figure 1. This peculiar
203 structure is due to the self-assembling of saturated monoglycerides, which form walls surrounding oil
204 droplets [26–28,31]. The latter resulted smaller in the case of the emulsion containing 9 g/100 g MG, due
205 to the higher amount of MG available for the stabilization of the increased surface area associated with
206 smaller oil droplets [31].


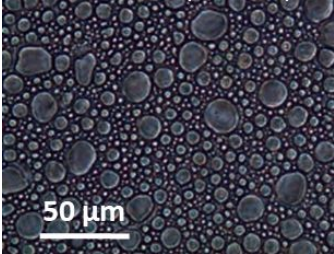

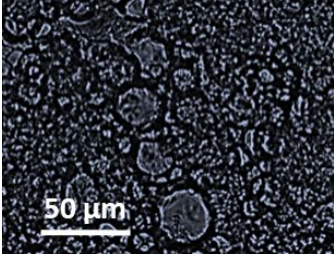

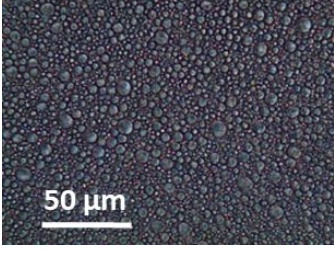

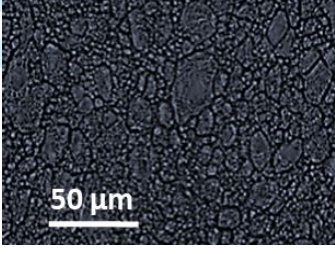
| Sample | Appearance | Micrographs |
|-----------|---|--|
| MG4 |  |  |
| MG4-dried |  |  |
| MG9 |  |  |
| MG9-dried |  |  |

Figure 1. Appearance and microscopic images of structured emulsions containing 4 and 9 g/100 g monoglycerides before (MG4, MG9) and after drying (MG4-dried, MG9-dried).

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209 These systems were dried in a thin layer at 30, 40 and 50 °C to partially remove water and obtain systems
210 with 80 g/100 g lipid content, analogous to that of traditional margarine [21]. As previously mentioned,
211 it was not possible to prepare systems containing such lipid ratio by simply following the emulsion
212 preparation procedure. In this case, in agreement with the literature, a non-homogeneous liquid system
213 was obtained, in which the lipid and water phase were separated [11].

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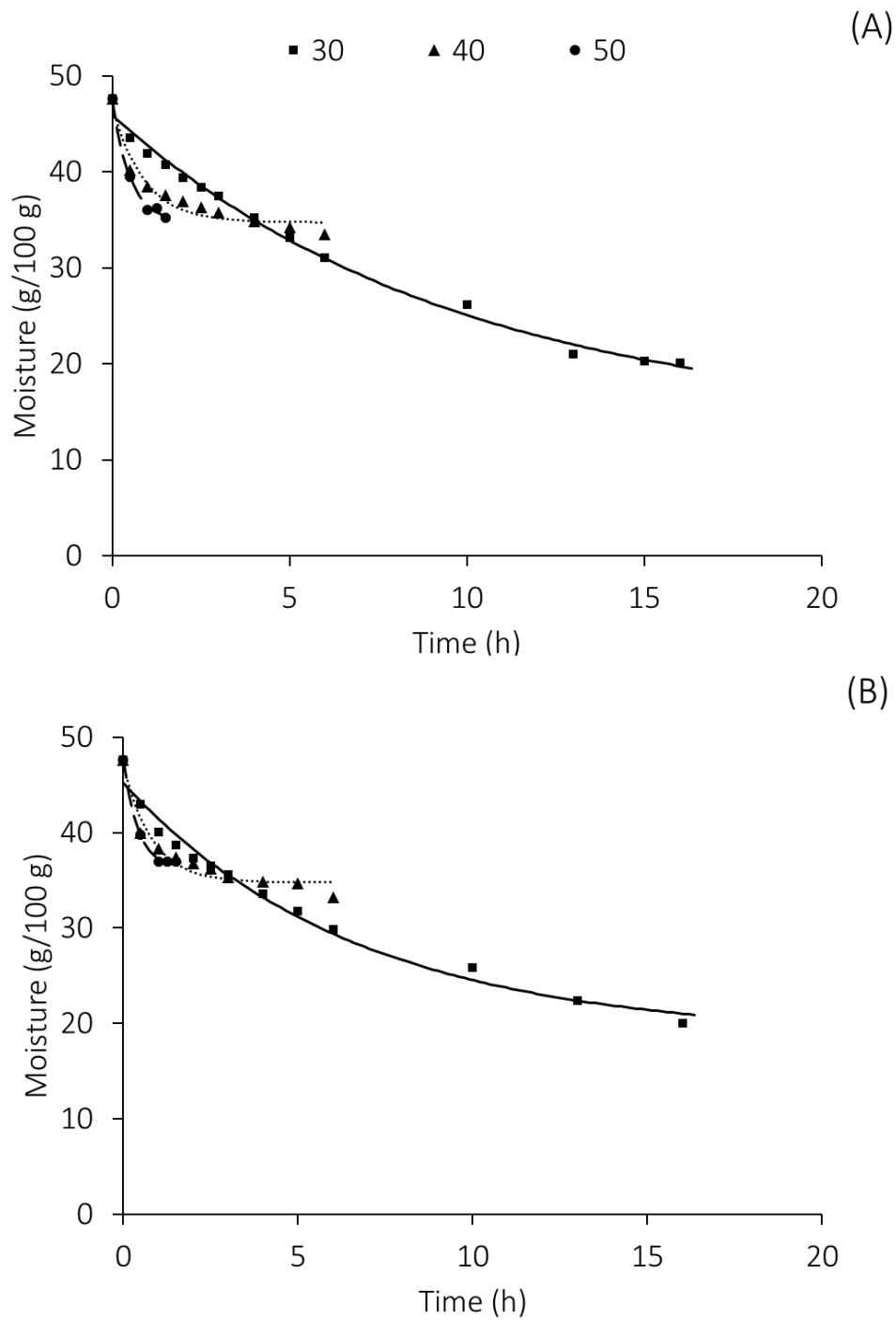


Figure 2. Moisture of structured emulsions containing 4 g/100 g (A) and 9 g/100 g (B) monoglycerides as a function of drying time at 30, 40 and 50 °C (symbols). Fitting curves of drying model are also reported (lines).

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3 218 Figure 2 reports the moisture (g/100 g) of the emulsions as a function of drying time at the different
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5 219 temperatures. During drying, water content showed an exponential decrease, with an initial fast decrease-
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8 220 phase followed by a tendency to reach a plateau. Experimental data were fitted to a classical exponential
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10 221 decay model developed for thin-layer drying [36] to obtain the kinetic constants reported in Table 1. The
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12 222 model well-explained experimental data, as shown by the R^2 values. Moreover, independently on the
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14 223 MG content, as expected, the increase in drying temperature provoked an increase in the drying rate,
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17 224 resulting in higher kinetic constant values (k , Table 1). However, it was not possible to take the samples
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19 225 at the desired 20 g/100 g moisture value at both 40 and 50 °C. At these temperatures, independently on
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21 226 the MG content, the systems broke down and leaked oil at moisture values of 33 and 35 g/100 g,
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24 227 respectively, corresponding to a lipid content of 67 and 65 g/100 g. These results show that a drying
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26 228 temperature higher than 30 °C is associated with the destruction of the MG network responsible for
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28 229 emulsion structuration. By contrast, gentle drying at 30 °C allowed obtaining emulsions with 80 g/100 g
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31 230 lipid phase after about 16 h. It must be underlined that a further water removal at 30 °C from both MG4
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33 231 and MG9 sample resulted in emulsion break-down and oil leaking. These results suggest that the stability
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35 232 of the samples during drying was affected by both the drying rate and the water removal extent. In this
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38 233 regard, it is known that water is required to induce MG self-assembling into a supra-molecular
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40 234 organization able to encapsulate oil and water among the MG lamellae [27,28]. Moreover, as evidenced
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42 235 in the literature [27], the temperature should be strictly controlled during both emulsification and cooling
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45 236 phase to properly structure the gel. In particular, the increase in temperature during emulsification has
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47 237 been reported to affect the hydration state of the MG, decrease the electrostatic charge magnitude and
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49 238 also induce changes in the mesomorphic phase, leading to a greater tendency to aggregation and thus
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51 239 phase separation [27]. This evidence supports the hypothesis that also during drying, an accurate
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54 240 optimization of temperature and thus of water removal rate, is required. Based on the acquired results, a
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56 241 slow drying rate seems to allow the reorganization of the MG network surrounding oil droplets, while
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3 242 preventing phase separation. By contrast, an increase in drying rate probably induced MG aggregation,
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5 243 thus favouring system break-down.
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8 244 Based on these results, the temperature of 30 °C was selected to partially dry the structured emulsions
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10 245 MG4 and MG9 until reaching a water content of 20 g/100 g, comparable to that of conventional
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12 246 margarine. Upon drying, the MG concentration of the emulsions initially containing 4 and 9 g/100 g MG
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14 247 reached a concentration of 6.1 and 13.7 g/100 g, respectively. The obtained samples, called MG4-dried
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17 248 and MG9-dried, are shown in Figure 1. As compared to the initial MG4 and MG9 emulsions, the partially
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19 249 dried systems showed a more solid-like appearance and a microstructure with oil droplets tightly packed
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22 250 into a network consisting of MG (Figure 1). The oil droplets present in the original structure were
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24 251 deformed after drying, evolving from a spherical shape to a polygonal one. These results agree with
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26 252 literature studies in which the emulsion-template method is used for oil structuring. This approach is
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29 253 based on complete water evaporation from highly concentrated oil-in-water emulsions, which results in
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31 254 the trapping of the oil in a physical network of biopolymers including polysaccharides and proteins or
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33 255 their combination, originally forming the oil-water interface [37–40].
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35 256 Differential scanning calorimetry measurements were carried out on the emulsions before and after
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38 257 drying to identify the effects of drying on the melting temperature and the enthalpy of the transition.
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40 258 Figure 3 shows the heating curves of the emulsions before and after drying.
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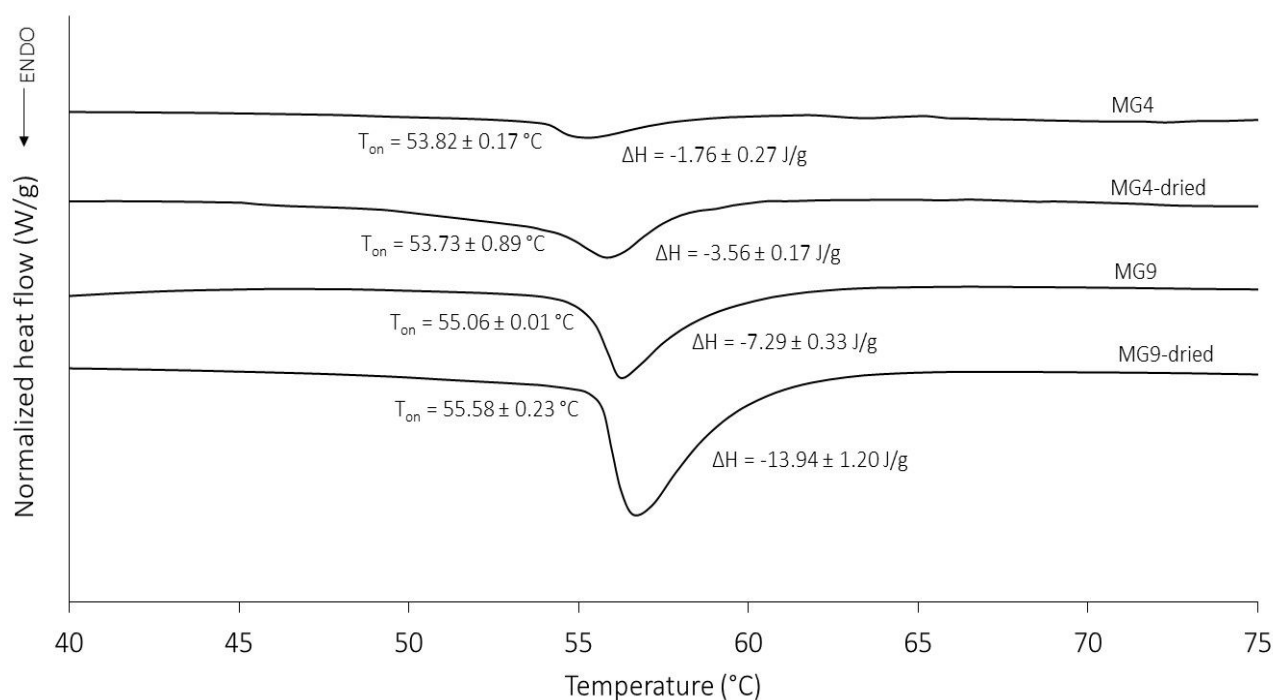


Figure 3. Calorimetric melting curves of structured emulsions before (MG4, MG9) and after (MG4-dried, MG9-dried) drying. Onset melting temperature (T_{on}) and melting enthalpy (ΔH) are also reported.

All systems showed one endothermic peak corresponding to the disruption of the network among MG lamellar bilayers, followed by the melting of the crystalline MG [30]. The melting enthalpy (ΔH) expressed per g of emulsion resulted well correlated with the MG and co-surfactant content ($R^2 = 0.993$), being proportional to the quantity of crystallised material in the matrix [26,27,30]. By contrast, the melting enthalpy per g of saturated fatty acids was not significantly different in the MG4 and MG9 emulsions (data not shown), neither was affected by drying ($p \geq 0.05$). Moreover, no significant differences between sample melting temperature (T_{on}) before and after drying ($p \geq 0.05$) were observed. These results could be associated with the fact that drying did not significantly modify the amount of crystallized material in the samples.

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3 272 Synchrotron XRD diffraction patterns were also acquired to obtain information on the effect of drying
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5 273 on MG crystal packing in the emulsions. The patterns, reported in Figure 4, resulted similar to those
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8 274 reported in the literature for analogous samples [27,28,30,31]. The diffraction signal superimposes onto
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10 275 two large amorphous halos centred respectively about $d = 23 \text{ \AA}$ ($q = 0.27 \text{ \AA}^{-1}$) and $d = 4.42 \text{ \AA}$ ($q = 1.4$
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12 276 \AA^{-1}). Two lamellar forms appear to coexist, whose lower angle visible peaks correspond to average
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14 277 interplanar distances of $d = 62 \text{ \AA}$ ($q = 0.1 \text{ \AA}^{-1}$) and $d = 48 \text{ \AA}$ ($q = 0.13 \text{ \AA}^{-1}$), respectively (Figure 4). All
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17 278 other stakes around 4 \AA are characteristic of MG high-angle diffraction patterns, the most intense being
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19 279 at 4.54 and 4.12 \AA . All the samples presented similar patterns in the wide angle region, due to the in-
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21 280 plane chain ordering of MG crystals in the $L\beta$ phase [28,31]. Based on the fact that there were no
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24 281 differences in the d-spacing of the samples in the wide-angle region, it can be concluded that they
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26 282 presented the same in-plane molecular ordering [31]. In the small angle region, the diffraction signals of
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28 283 the two lamellar phases appear to be much more intense with respect to the amorphous phase in sample
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31 284 MG9 than in the sample MG4. In both cases, no structural differences were noted before and after drying,
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33 285 and no transition toward a different lamellar organization occurred upon drying.
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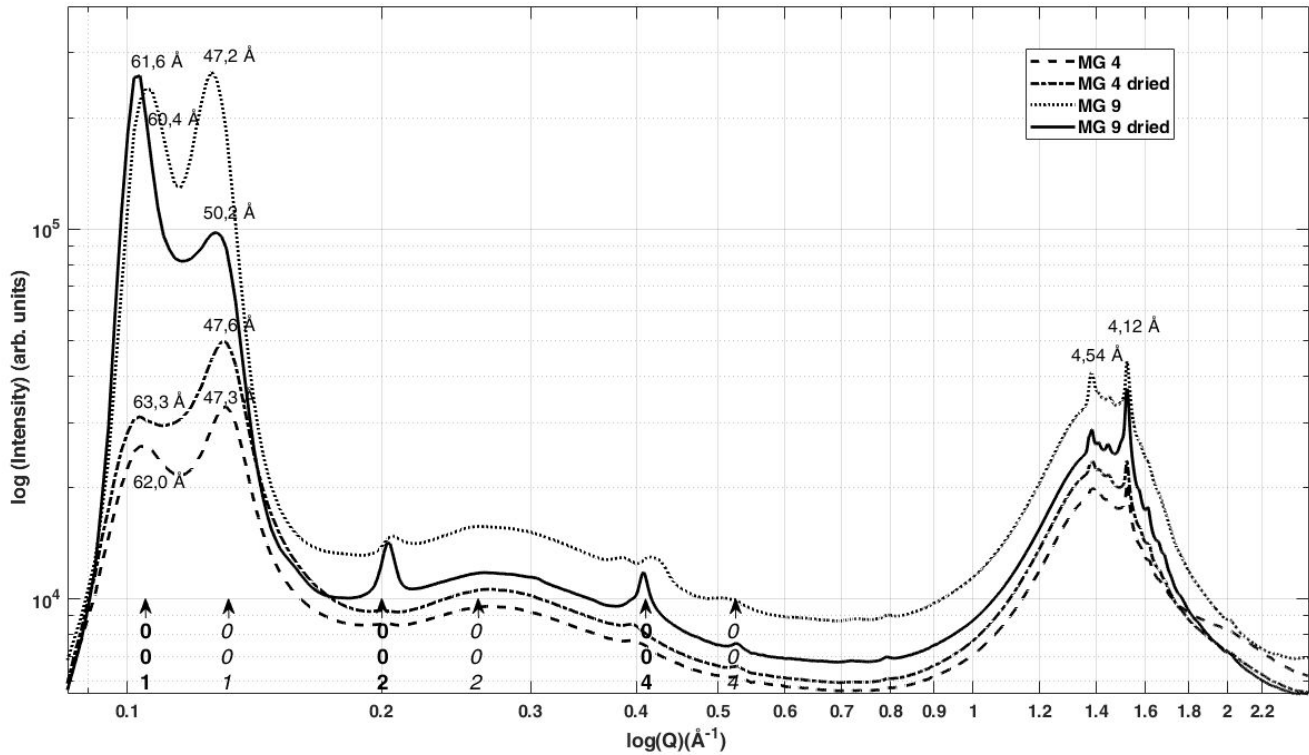
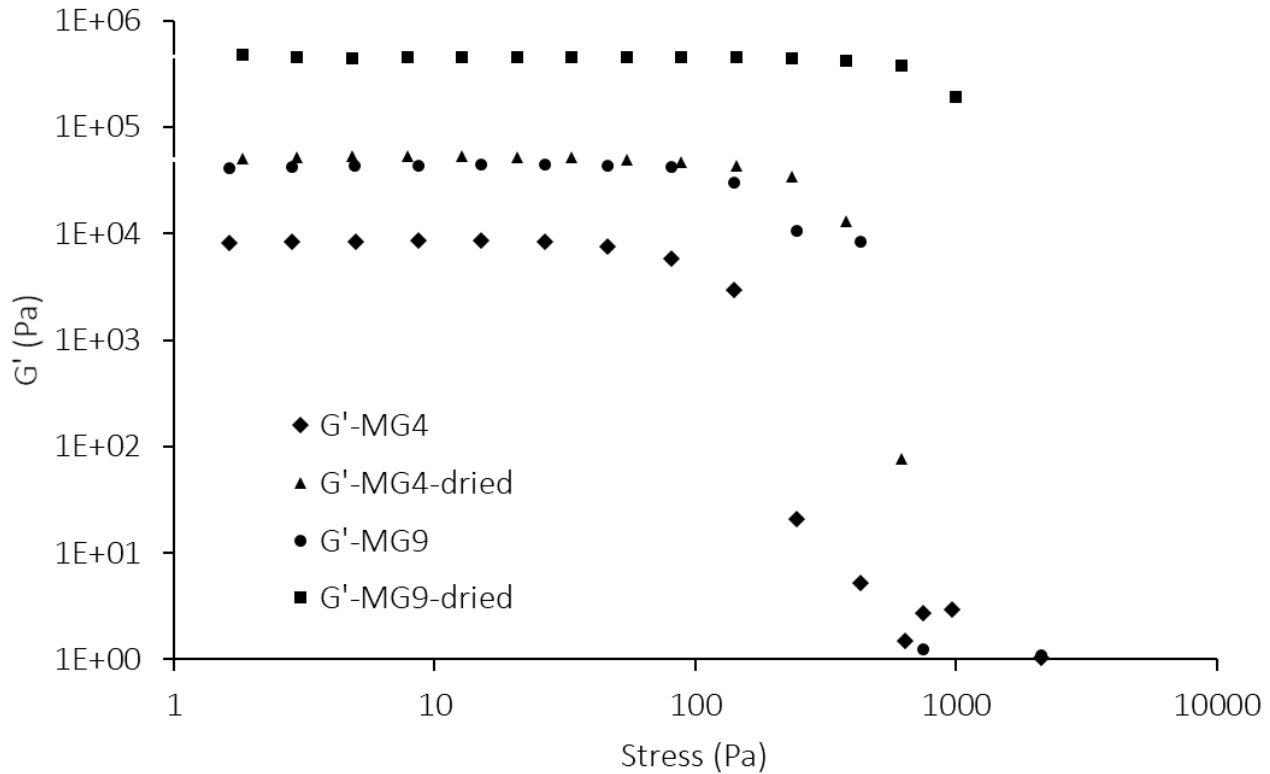


Figure 4. Powder X-ray diffraction spectra of structured emulsions before (MG4, MG9) and after (MG4-dried, MG9-dried) drying. Patterns plotted as a function of reciprocal lattice spacing q , where $q = 2\pi/d = (4\pi/\lambda) \cdot \sin\theta$, d is the lattice spacing, λ is the X-ray wavelength and 2θ is the Bragg scattering angle, represented as log-log plots opportunely scaled and shifted for clarity.

Finally, the rheological characteristics of the samples before and after drying were studied (Supplementary Figure 1; Table 2).



Supplementary Figure 1. Amplitude sweep test of structured emulsions before (MG4, MG9) and after (MG4-dried, MG9-dried) drying. Error bars of triplicate measurements were typically not larger than the symbols and were left out for clarity.

In agreement with the literature, the emulsions before drying presented a gel-like behaviour ($G' > G''$), due to the elasticity of crystalline MG network, with critical stress and G' values increasing with the MG content [27,30]. As expected, the elastic modulus (G') and critical stress of the emulsion containing 9 g/100 g MG resulted significantly higher than that of the MG4 sample, due to the higher amount of solid fat content [11]. Drying led to a significant increase in both G' and the critical stress of the MG4 and MG9 emulsions (Table 2). This agrees with literature data showing that a lower water amount increases the packing of the MG, generating a system showing enhanced structural properties [11]. The values of

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3 308 G' and critical stress have been previously indicated as key parameters for comparing the rheological
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5 309 properties of MG structured emulsions with those of traditional solid fats [11]. Thus, rheological
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8 310 properties of dried MG emulsions were compared to those of three commercial laminating fats with 20
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10 311 g/100 g water content. In agreement with literature data [41,42], the latter gave G' and critical stress
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12 312 values in the range $8.2\text{-}26.7\times 10^5$ Pa and $263.7\text{-}995.4$ Pa, respectively. With reference to these ranges, the
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14 313 MG4-dried sample showed critical stress and G' values about 2 and 10 times lower, respectively. By
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17 314 contrast, the MG9-dried emulsion showed rheological features comparable to those of the analyzed
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19 315 commercial laminating fats (Table 2). Such rheological features have been previously obtained in
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21 316 analogous MG structured emulsions by adding at least 15 g/100 g waxes or substituting sunflower oil
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24 317 with palm oil [11]. However, the first systems showed unpleasant waxy taste, while the seconds require
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26 318 the addition of saturated fatty acids.
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29 319 3.2 Dried structured emulsions as fat alternatives in puff pastry

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32 320 Based on its promising features, the MG9-dried sample was used in baking trials in the production of
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34 321 puff pastry and compared to a common roll-in laminating palm margarine showing a G' and critical stress
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36 322 of 15.7×10^5 and 995.4 Pa, respectively. Some of the preparation phases of the puff pastry using MG9-
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39 323 dried sample are reported in the Supplementary Figure 2.
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Supplementary Figure 2. Preparation phases of puff pastry using MG9-dried sample as laminating fat substitute.

During both puff pastry preparation and baking, the MG9-dried emulsion showed the typical features required to a laminating fat. Thanks to its plasticity, the MG9-dried sample was easily laminated into thin sheets between dough layers during the folding process, during which it did not melt, preventing the dough layers from touching. Therefore, upon lamination and folding, clearly defined and continuous dough and MG9-dried layers were visible, confirming the optimal rheological features of the MG9-dried sample. Finally, during baking, no evident oil leaking was observed, which indicates that the fat phase was retained between the dough layers. This allowed the typical physical leavening of puff pastry, as well-evident from the images reported in Figure 5.

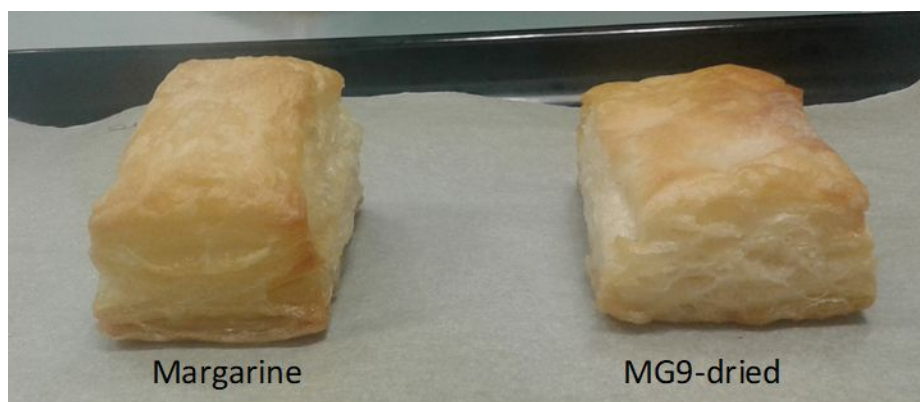


Figure 5. Image of puff pastry prepared with commercial laminating margarine and MG9-dried emulsion.

The puff pastry prepared with the MG9-dried sample displayed the flaky golden-brown appearance of puff pastry containing margarine. As shown in Table 3, the only observable difference was that MG9-dried puff pastry showed a lighter colour, as indicated by the lower absolute values of the colourimetric parameters a^* and b^* and a 16% lower leavening capacity. Moreover, it presented comparable instrumental firmness, which was also confirmed by the judges during sensory evaluation ($p \geq 0.05$). The latter also evidenced that the substitution of the commercial margarine with the MG9-dried fat did not affect puff pastry friability ($p \geq 0.05$) but resulted in an increased oiliness mouthfeel. It must also be noted that the judges did not highlight the presence of off-flavours or off-taste upon tasting the puff pastry samples. These findings are very promising, as they show that MG9-dried fat can be used as laminating fat replacement.

4 Conclusions

Results here reported face the timely challenge of developing substitutes of roll-in margarine able to deliver a nutritional improvement of laminated products conventionally rich in saturated and trans fatty acids. The process here proposed for the production of the margarine substitute requires simple unit operations (e.g heating, homogenization, cooling, drying), which are commonly applied in food

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3 354 industries, making its scaling up feasible both technically and economically. Based on the acquired
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5 355 results, drying temperature is the key factor to be controlled to obtain a well-structured margarine
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8 356 alternative. In fact, the desired 20 g/100 g water content, typical of margarine, is only obtained by
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10 357 applying a gentle and gradual drying at 30 °C. Under these conditions, the MG structure entrapping both
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12 358 water and oil is maintained, avoiding phase separation. The resulting system showed good performances
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15 359 in both lamination and baking of puff pastry, making it an optimal candidate for the substitution of
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17 360 margarine in the industrial production of laminated products with improved nutritional quality. It is not
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19 361 excluded that by changing the starting emulsion formulation (e.g. oil type, other ingredients in the water
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22 362 phase) it would be possible to further improve the range of MG-based margarine analogues.

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28
29
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35 367 The authors have declared no conflicts of interest.

36 37 38 39 368 **Permission statements**

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41 369 The manuscript *does not* contain experiments using animals.

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43 370 The manuscript *does not* contain human studies.

44 45 46 47 371 **References**

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Table 1. Model parameter estimates for the drying process at 30, 40 and 50 °C of structured emulsions containing 4 (MG4) and 9% (MG9) monoglycerides.

| Sample | Temperature (°C) | k (h ⁻¹) | R ² |
|------------|------------------|------------------------|----------------|
| MG4 | 30 | 0.103 ± 0.009 | 0.996 |
| | 40 | 1.119 ± 0.220 | 0.952 |
| | 50 | 2.018 ± 0.288 | 0.997 |
| MG9 | 30 | 0.150 ± 0.024 | 0.982 |
| | 40 | 1.207 ± 0.234 | 0.953 |
| | 50 | 2.464 ± 0.315 | 0.997 |

Table 2. Rheological parameters of structured emulsions before (MG4, MG9) and after (MG4-dried, MG9-dried) drying.

| Sample | G' (×10 ⁵ Pa) | Critical stress (Pa) |
|------------------|----------------------------|---------------------------|
| MG4 | 0.085 ± 0.012 ^c | 22.6 ± 3.3 ^d |
| MG9 | 0.438 ± 0.029 ^b | 86.0 ± 4.6 ^c |
| MG4-dried | 0.533 ± 0.098 ^b | 139.4 ± 6.4 ^b |
| MG9-dried | 4.565 ± 0.212 ^a | 633.9 ± 25.5 ^a |

^{a, b, c, d} In the same column, means indicated by different letters are statistically different (p<0.05)

Table 3. Leavening capacity, firmness, colour and sensory attributes of puff pastry prepared with commercial roll-in margarine and MG9-dried emulsion.

| Roll-in fat | Colour | | | Leavening capacity | Firmness (kN) | Sensory score | | |
|------------------|--------------|--------------|--------------|--------------------|---------------|---------------|------------|-----------|
| | L* | a* | b* | | | Firmness | Friability | Oiliness |
| Margarine | 82.84 ± 0.61 | -1.22 ± 0.12 | 24.22 ± 0.93 | 12.3 ± 1.2 | 1.1 ± 0.2 | 5.0 ± 0.8 | 5.9 ± 1.6 | 4.5 ± 1.2 |
| MG9-dried | 85.66 ± 1.08 | -0.50 ± 0.14 | 15.91 ± 0.76 | 10.4 ± 0.5 | 0.8 ± 0.1 | 4.9 ± 1.9 | 4.9 ± 2.3 | 7.3 ± 1.0 |