OLEO-006

Optimization of the formulation and process of oleogels for food using Response Surface Methodology (RSM)

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Abstract

Edible oleogels are a promising technology for the food industry as a substitute for saturated and hydrogenated fats. This involves structuring oils that are naturally liquid at room temperature using edible gelators to form a three-dimensional network. An oleogelator is a structuring agent enabling self-assembly of a solid phase dispersed in an oily liquid phase forming an oleogel. The latter can be described as a thermoreversible semi-solid lipid matrix with viscoelastic properties. The design of oleogels is the subject of numerous experiments to develop a range of versatile products in several food areas, always with the aim of structuring the food matrix. They are used as a substitute for conventional concrete fats. They can be found in the manufacture of muffins, meat products, bakery products and margarines. Indeed, they are the most promising alternative for replacing fats in margarines to make them healthier, without altering their techno-functional characteristics. Moreover, such a food matrix offers an ecological advantage, notably by reducing the importation of fats (coprah, cocoa, palm oil), and thus aims to reduce deforestation, pollution and carbon footprint. The aim of this study is to formulate oleogels for food use with a mixed oleogelator system (soy lecithin, Monomuls L12®, Geleol® and rice bran waxe (RBW)), using response surface methodology (RSM). For this research, we decided to formulate the oleogels with rice bran wax for its ability to stabilize the gel network, its edible property, and its wide application in food products. Rapeseed oil was chosen mainly for its nutritional qualities. First, a mixture design highlighting the optimal proportions of the different constituents is produced. This is followed by an experimental plan aimed at studying the different physico-chemical parameters (concentration of the gelling agent, percentage of added water and oleogel cooling ratel) influencing the structuring of the oleogel network.

Materials & Methods

Protocols

Fatty acid profiles *were* determined by GC-FID. Fatty acids were methylated according to the Ackman method (1998).

Lipid profiles were obtained by TLC-FID Iatroscan MK5.

Thermic profiles were obtained using DSC with a temperature ramp at a rate of 5°C/min (Cassel, 2002).

Hardness of oleogels were measured by universal testing machine (AGS-X, Shimadzu) and texture-compression method (Gaudino *et al*., 2019).

Oil holding capacity (OHC) were measured by a centrifugation step (15 min, 14000 g) to destabilize the structured emulsion (Palla *et al*., 2017).

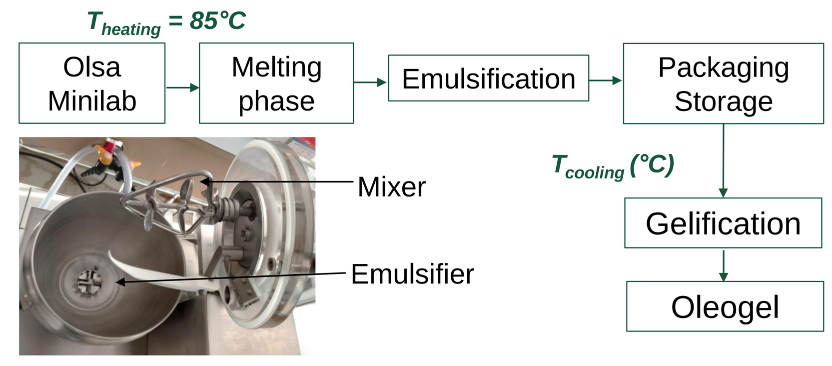
Rheological measurements of oleogels were performed using a rheometer (Discovery HR-20, TA instruments ; cone and plate geometry, 55 mm cone diameter) according to the Ashkar *et al.* method (2019).

Formulation of oleogels

Oleogels were formed from rapeseed oil containing 10% of blended oleogelators (soy lecithin, Monomuls L12®, Geleol® and rice bran waxe (RBW)).

Oleogels were obtained by melting the system at 85°C and stored at room temperature.

Oleogels and emulsion-oleogels from the design experiments were formulated with Olsa minilab (1000 rpm, 30 min).



Optimization by RSM

Mixture design of quatery-component mixture without constraint (Scheffe matrix).

Equation of mixture model:

$$Y = \sum_i^4 \beta i\, Xi + \sum_{i\neq j}^4 \sum_{j=2}^4 \beta_{ij} X_i X_j + \sum_{i\neq j}^4 \sum_{i\neq k}^4 \sum_k^4 \beta_{ijk} X_i X_j X_k + \cdots$$

Experimental design based on the composition of the mixture obtained by mixture design: 5% soy lecithin, 15% Monomuls L12®, 65% Geleol® , 15% RBW.

Equation of quadratic model:

$$Y = \beta_0 + \sum_{i=j}^{3} \beta i\, Xi + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{3-1} \sum_{j=2}^{3} \beta_{ij} X_i X_j$$

Where Y is the response, X_i and X_j are the parameters, and β are the regression coefficients.

Experimental domain and levels of distribution of variables

Factors	Levels
Gelators (%)	6 ; 9 ; 12 ; 15 ; 18
Water (%)	0 ; 8.33 ; 16.67 ; 25 ; 33.33 ; 41.67 ; 50
T°C Cooling (°C)	-20 ; -7 ; 4

Rheology behavior, hardness, oil holding capacity were measured and analyzed by Software NemrodW®.

Results

Physicochemical characterization

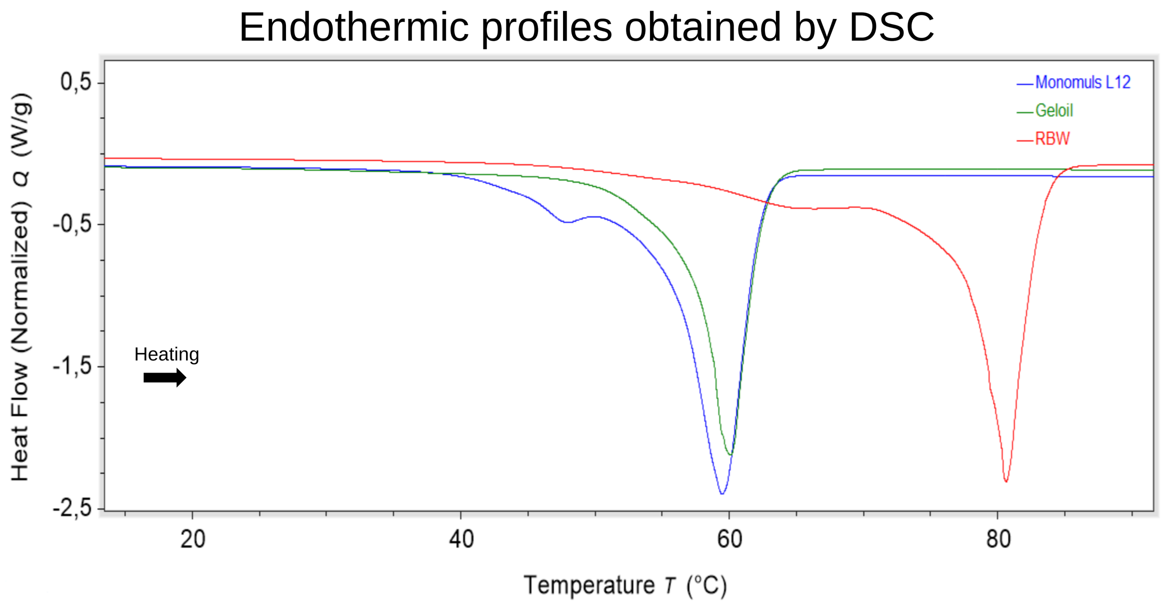
Fatty acid profiles of oleogelators

Fatty acid	Monomuls L12®	Geleol®	Soy lecithin
C10:0	-	-	-
C12:0	99.09 ± 0.04	-	-
C14:0	0.29 ± 0.00	0.38 ± 0.00	0.08 ± 0.00
C16:0	0.17 ± 0.03	46.77 ± 0.01	17.57 ± 0.06
C17:0	-	-	0.09 ± 0.00
C18:0	0.12 ± 0.01	52.16 ± 0.02	3.97 ± 0.00
C20:0	-	-	0.27 ± 0.00
C22:0	-	-	0.40 ± 0.01
C24:0	-	-	0.25 ± 0.00
Σ SFA	99.67	98.93	22.17
C16:1 n-7	-	0.15 ± 0.00	0.13 ± 0.00
C18:1 n-7	-	-	23.61 ± 0.02
C18:1 n-9	0.13 ± 0.03	-	0.57 ± 0.02
Σ MUFA	0.13	0.15	24.31
C18:2 n-6	-	-	49.00 ± 0.1
C18:3 n-3	-	-	3.80 ± 0.1
Σ PUFA	0.00	0.00	58.96

Lipid composition obtained by TLC-FID

Neutral lipid (%)	Monomuls L12®	Geleol®	Soy lecithin
Free fatty acid	-	-	9.71 ± 0.19
Monoacylglycerol	96.13 ± 0.85	39.00 ± 5,66	-
Diacylglycerol	3.87 ± 0.85	33.54 ± 2,26	3.55 ± 0.13
Triacylglycerol	-	1.98 ± 0,20	24.10 ± 0.83
Polar lipid (%)	-	25.23 ± 7,58	62.64 ± 0.79

Endothermic profiles obtained by DSC



Mixture design

Scheffé matrix for 4 components

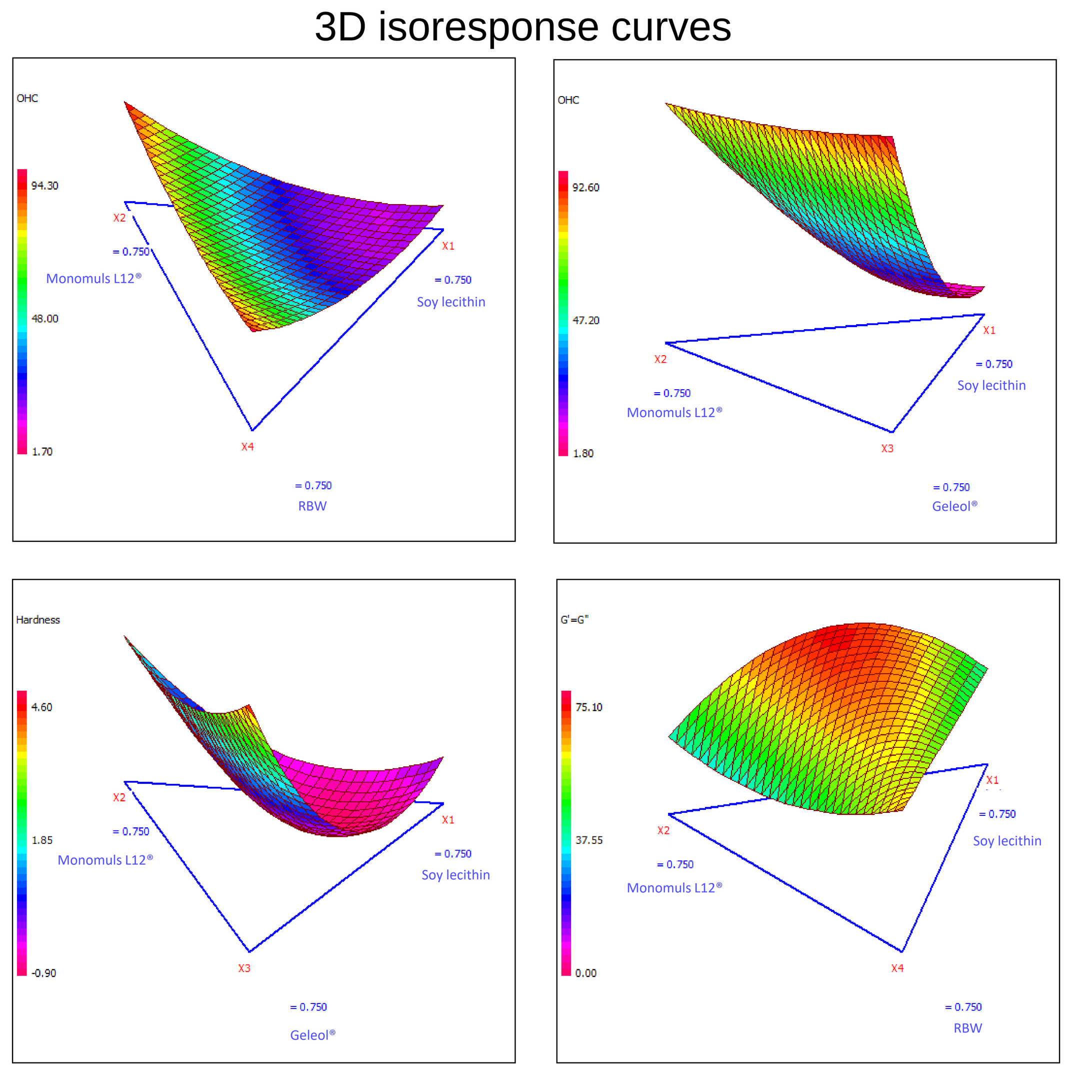
Mixture	Soy lecithin	Monomuls L12®	Geleol®	RBW
E1	1.000	0.000	0.000	0.000
E2	0.000	1.000	0.000	0.000
E3	0.000	0.000	1.000	0.000
E4	0.000	0.000	0.000	1.000
E5	0.500	0.500	0.000	0.000
E6	0.500	0.000	0.500	0.000
E7	0.500	0.000	0.000	0.500
E8	0.000	0.500	0.500	0.000
E9	0.000	0.500	0.000	0.500
E10	0.000	0.000	0.500	0.500
E11	0.333	0.333	0.333	0.000
E12	0.333	0.333	0.000	0.333
E13	0.333	0.000	0.333	0.333
E14	0.000	0.333	0.333	0.333
E15	0.625	0.125	0.125	0.125
E16	0.125	0.625	0.125	0.125
E17	0.125	0.125	0.625	0.125
E18	0.125	0.125	0.125	0.625

Effects and interactions

Name	OHC (%)	Hardness (N)	G'=G" (°C)
β1	4.12	0.32	-0.24
β2	88.33 ***	4.38 *	27.43 *
β3	97.58 ***	4.38 *	43.89 **
β4	98.62 ***	2.94 *	60.69 **
β1-2	-86.01	-9.01	33.11
β1-3	-60.89	-8.23	150.94 *
β2-3	19.35	1.11	-2.04
β1-4	-100.07 *	-5.81	199.64
β2-4	-86.59	-10.94	61.74
β3-4	-27.99	0.67	22.53
β1-2-3	-475.572	-3900	860.16 *
β1-2-4	-34.28	0.90	726.91
β1-3-4	-329.97	-2739	-488.67
β2-3-4	-143.16	-25.59	-634.66

Significance : ***= 99.9 % ; **= 99.0 % ; *= 95.0 %

3D isoresponse curves

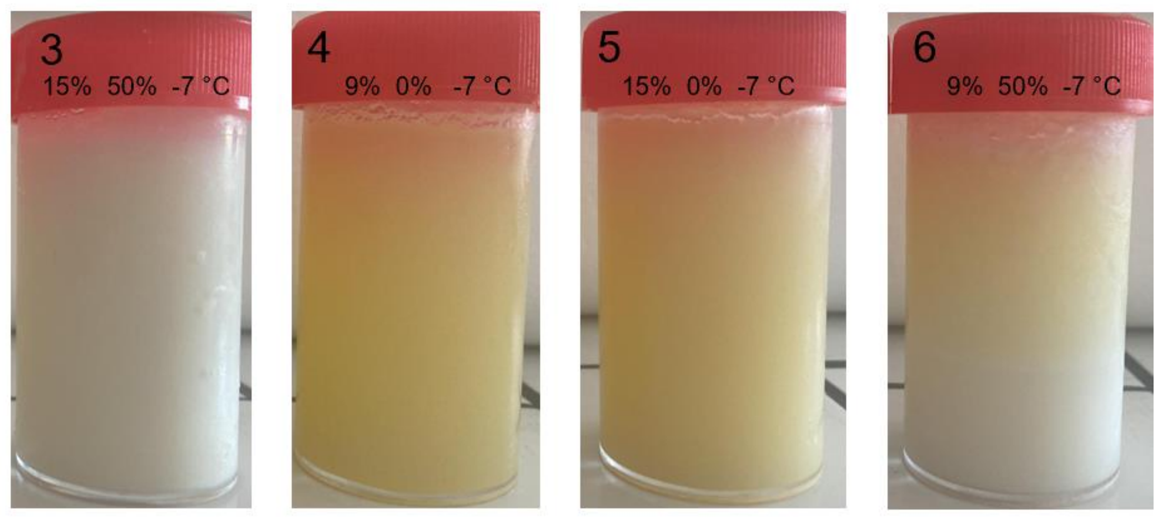


Experimental design

Doehlert matrix for 3 variables

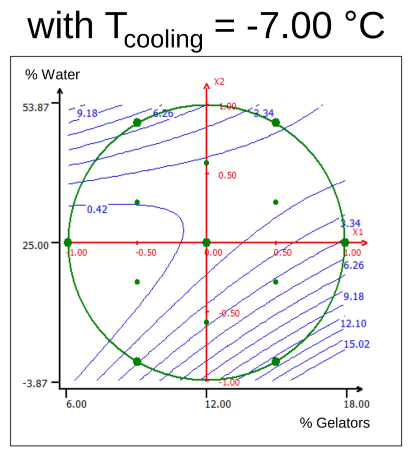
Experiment	Gelator (%)	Water (%)	$T_{cooling}$ (°C)
E1	18.00	25.00	-7.00
E2	6.00	25.00	-7.00
E3	15.00	50.00	-7.00
E4	9.00	00.00	-7.00
E5	15.00	00.00	-7.00
E6	9.00	50.00	-7.00
E7	15.00	33.33	4.00
E8	9.00	16.67	-20.00
E9	15.00	16.67	-20.00
E10	12.00	41.67	-20.00
E11	9.00	33.33	4.00
E12	12.00	8.33	4.00
E13	12.00	25.00	-7.00
E14	12.00	25.00	-7.00
E15	12.00	25.00	-7.00
E16	12.00	25.00	-7.00

Photos of oleogels and emulsion-oleogels

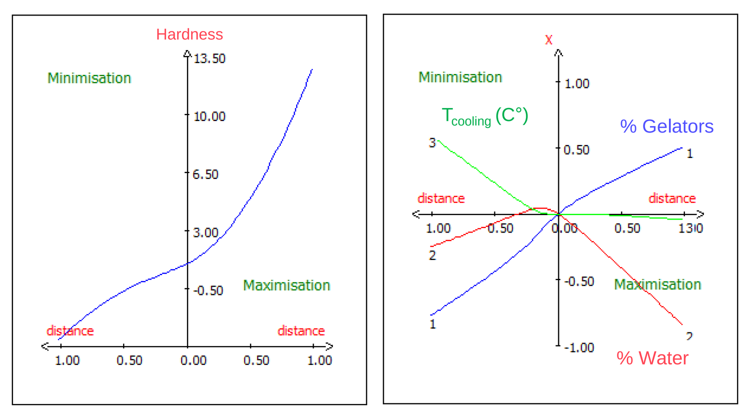


Isoresponse curves and variable maximization

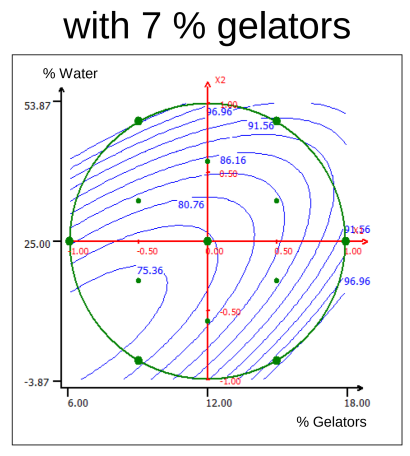
Hardness variation with $T_{cooling}$ = -7.00 °C



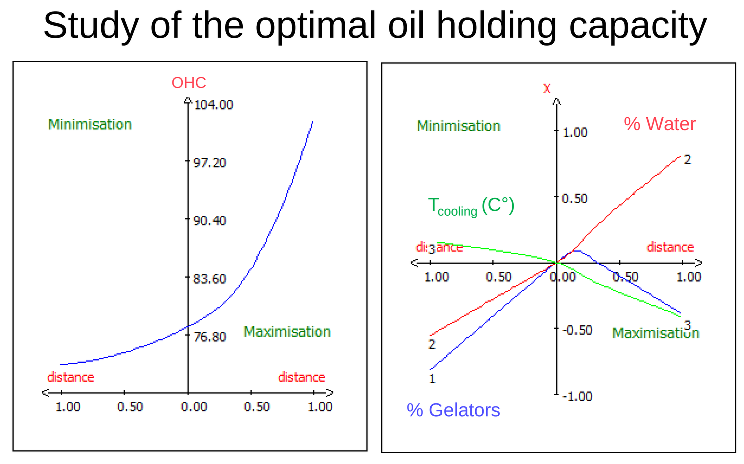
Study of the optimal pathway for hardness



OHC variation with 7 % gelators



Study of the optimal oil holding capacity



Discussion

Mixture design :

Geleol®, Monomuls L12® and RBW increase OHC.

Geleol®, Monomuls L12® provide the most hardness.

RBW increases temperature of G'=G" unlike lecithin.

→ An optimized rapeseed oil oleogel with 10% blended oleogelator: 5% soy lecithin, 15% Monomuls L12®, 65% Geleol® , 15% RBW.

Experimental design :

Oleogel formulation using a mixture design and DOE leads to the optimal conditions in a few experiments, due to the knowledge of the main effects and interactions between constituents and process parameters.

Conclusion

Nowadays, formulations of new solid fat mimetic systems such as oleogels allow us to consider solutions in order to substitute exotic fat used in food products (coprah, palm oil, kernel oil, etc). This study highlights the feasibility to control the textural behavior by using specific low and high molecular weight oil gelator and / or the process parameters. Based on different preparation conditions of oleogels, high polyunsaturated oil such as rapeseed oil may be incorporated in gel network, such as spreadable fats. Extensive research are needed to further clarify the process-structure-function relationship of these mimetic fats in comparison with the native lipid fraction in food products.

References

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