Textural and rheological properties of soybean oil organogels structured with polyglycerol and propylene glycol esters during storage

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SUMMARY: Organogels have emerged as an alternative to the intake of saturated fats. Organogels of soybean oil (SBO) structured with polyglycerol esters (PGE) or propylene glycol esters (PPGE) at different concentrations (0.5, 1.0, 2.0, 3.0, or 4.0%) were formulated. Both emulsifiers at 4% (w/w) concentrations were able to form solid-like organogels and showed thixotropy and low mechanical resistance when compression forces were applied. However, the SBO/PGE (4%) organogels presented lower values for flow curves and micrographs showed a more organized network compared to the SBO/PPGE at 4%. However, higher flow curve values, larger crystals, and mechanical resistance on compression were observed after a two-month storage period of SBO/PPGE compared to SBO/PGE organogels. Both organogels have the potential to be used for diverse food applications although the SBO/PGE was more stable throughout storage.

KEYWORDS: *Fatty acids; Hardness; Organogels; Polyglycerol ester; Propylene glycol ester; Saturated thermal stability*

RESUMEN: *Propiedades texturales y reológicas de organogeles de aceite de soja estructurados con ésteres de poliglicerol y propilenglicol durante el almacenamiento.* Los organogeles surgieron como una alternativa a la ingesta de grasas saturadas. Se formularon organogeles de aceite de soja (SBO) estructurados con ésteres de poliglicerol (PGE) o ésteres de propilenglicol (PPGE) a diferentes concentraciones (0,5, 1,0, 2,0, 3,0 y 4,0%). Ambos emulsificantes fueron capaces de formar organogeles sólidos con un 4% (p/p) y mostraron tixotropía y baja resistencia mecánica cuando se aplicaron fuerzas de compresión. Sin embargo, los organogeles SBO/PGE (4%) presentaron valores más bajos de curvas de flujo y las microfotografías mostraron una red más organizada en comparación con el SBO/PPGE al 4%. Sin embargo, se observaron valores de curva de flujo más altos, cristales más grandes y resistencia mecánica a la compresión después de dos meses de almacenamiento en el SBO/PPGE en comparación con los organogeles de SBO/PGE. Ambos organogeles tienen potencial para ser usados en la industria alimentaria aunque el organogel SBO/PGE fue más estable durante almacenamiento.

PALABRAS CLAVE: *Ácidos grasos saturados; Dureza; Estabilidad Térmica; Ester de poliglicerol; Ester de propilenglicol; Organogeles*

1. INTRODUCTION

Fats are a vital part of the human diet, not only due to their sensory attributes but also for providing essential fatty acids and energy (Dorni *et al.,* 2018). The food industry currently uses processed, fractionated, or interesterified fats with high contents of saturated fatty acids (SFA). A high intake of SFA is associated with increased levels of blood cholesterol and a high mortality rate from cardiovascular diseases (Hunter *et al.,* 2009). The World Health Organization (WHO) recommends that the total daily intake of SFA should not exceed 10% of the total caloric intake and diets should contain higher levels of polyunsaturated fatty acids (PUFAs) n-3 and linoleic acid (n-6) (WHO, 2008). Therefore, efforts have been made to replace SFA with sources rich in PUFAs (Wang, 2018) with little success due to the technological properties that SFAs provide to foods. PUFAs are mostly liquid at room temperature and may not have the desired functionality compared to solid shortenings such as creaming, high viscosity, and enhanced flavor, odor, and texture in bakery products (Buitimea-Cantúa *et al.,* 2017; Abramovič *et al.,* 2018). Because of this, the organogel technology for structuring PUFA-rich oils was developed as a viable alternative to considerably reduce saturated and *trans* fats, and recently have been utilized for the manufacturing of an array of lipid-based products (Chaves *et al.,* 2018).

Organogels impart the desired functionality to foods without generating *trans* fatty acid (TFA) and with reduced SFA contents (da Silva *et al.,* 2018a). Oleogelation has several advantages compared to hydrogenation and interesterification, the most relevant being that no biochemical processes are involved (Sellami *et al.,* 2012; Dinç *et al.,* 2014).

During the preparation of organogels, one or more structuring agents can be used to produce a change in the physical properties of the vegetable oil that facilitate the formation of semi-solid or solid plastic materials. The vegetable oils from safflower, rice bran, sunflower, canola, high-oleic sunflower and soybean, and cod liver oil have been successfully structured into organogels (Rocha *et al.,* 2013; Lopez-Martinez *et al.,* 2015; Sintang *et al.,* 2017a, b; Palla *et al.,* 2017; Yang *et al.,* 2018; da Silva *et al.,* 2018a; Wijarnprecha *et al.,* 2018). The quite inexpensive and highly available soybean oil has the ad-vantage of containing a relatively high proportion of polyunsaturated fatty acids, which are known to decrease serum cholesterol and cardiovascular diseases (Chou *et al.,* 2018). Several investigations have demonstrated the feasibility of producing different functional organogels with diverse structurants such as carnauba (*Copernica cerifera*), sugarcane (*Saccharum officinarum*), candelilla (*Euphorbia cerifera*), sunflower (*Helianthus annuus*), rice (*Oryza sativa*) bran, and monoglycerides (Marangoni, 2012; Rocha *et al.,* 2013; Patel *et al.,* 2015; Lim *et al.,* 2017; Öğütcü and Yılmaz 2014; Chaves *et al.,* 2018; da Silva *et al.,* 2018b; Buitimea-Cantúa *et al.,* 2020). The organogels formulated with different vegetable oils (oil phases) produced different crystallization behaviors and consequently formed organogels with different thermal stability, rheological and textural properties (Marangoni, 2012; Rocha *et al.,* 2013; Öğütcü and Yılmaz 2014; Lim *et al.,* 2017; Cotabarren *et al.,* 2019; Buitimea-Cantúa *et al.,* 2020).

Other researchers have focused on the influence of diverse structurant agents such as waxes and emulsifiers added in small concentrations (<10%, w/w) on the mechanical, rheological, and textural properties of organogels (Pernetti *et al.,* 2007; Rocha *et al.,* 2013; Sintang *et al.,* 2017b). Among the emulsifiers used for producing organogels are sorbitan tristearate and mono- and diacylglycerols (Ojijo *et al.,* 2004; Hughes *et al.,* 2009; Rocha-Amador *et al.,* 2014; López-Martínez *et al.,* 2015; Sintang *et al.,* 2017a; Palla *et al.,* 2017; Fayaz *et al.,* 2017; Cotabarren *et al.,* 2019). In particular, organogels formulated with monoglycerides increase their stability, change their microstructural crystal network and produce plastic structures typical of hardstock fats that impart the desired functionality to foods without TFA and with low SFA contents (Dassanayake *et al.,* 2011; López-Martínez *et al.,* 2015; Palla *et al.,* 2017; Fayaz *et al.,* 2017; Cotabarren *et al.,* 2019). Polyglycerol esters are emulsifiers which are commonly used in the food industry (Curschellas *et al.,* 2013) and they could be a new alternative for the production of organogels. López-Martínez *et al.* (2015) reported that the utilization of a mixture of monoglycerides in safflower oil developed mixed self-assembled structures that resulted in organogels with improved rheological properties compared to the use of pure monoglycerides. Recently, Cotabarren *et al.* (2019) concluded that organogel mixtures of

monoglyceride and phytosterols produced by extrusion-based 3D printing showed crystals in organogels of irregular, elongated, fibrillar, or needle-like shapes. Meng *et al. (*2019) utilized sodium stearoyl lactylate as a gelling agent at concentrations of 7. 9, 11, and 13% (w/w) with sunflower oils to structure organogels and concluded that higher concentrations of the oleogelator resulted in a denser crystalline network, which provided stronger mechanical strength and enhanced the ability to retain the oil phase.

An organogel is a self-assembled or crystalline particle structure formed by the entanglement of one or more structurant units such as crystals, fibrillar networks, or suspended polymer strands (Sawalha *et al.,* 2011; Sintang *et al.,* 2017a; Sintang *et al.,* 2017b). The structuring mechanisms involved in these systems can be divided into a dispersion of the fat phase as crystallized or uncrystallized solid particles or self-assembled complex structures, which are held together by specific supramolecular interactions (Pernetti *et al.,* 2007). It is essential to optimize and design the textural and rheological properties when developing a new organogel. However, during storage organogels may change their rheological properties and appearance (phase separation) due to oil exudation, which are major causes of rejection (Sintang *et al.,* 2017a; Sintang *et al.,* 2017b). This study was planned to evaluate the textural and rheological properties of soybean oil organogels structured with polyglycerol or propylene glycol esters at different concentrations during two months of storage at room temperature. Both structurants are considered GRAS by the FDA and are derived from mono and diglycerides, acetylated mono and dyglycerides, phosphated mono and diglycerides, and esters of propilenglycol, sorbitan, phosphate, sucrose, polyglycerol lactate, and lecithin (Hasenhuettl, 1997). The polyglycerol esters and propylene glycol esters are used as emulsifiers in foods, in amounts not greater than that required to produce the intended physical or technical effect.

2. MATERIALS AND METHODS

2.1. Materials

Refined soybean oil (SBO) was bought at a local supermarket (Monterrey, N.L., Mexico). The structurants used were: 1) A mixture of mono-diglycerides and polyglycerol esters (Polyglycerol Esters of Fatty Acids) or PGE (Fusion point = 55-61 °C) (Admulse MSPG-40) and 2) Propylene Glycol Esters of Fatty Acids or PPGE (Fusion point = 55-60 °C) (Admulse MEPG-AL). The structurants were kindly provided by ADIPLEX, S.A. de C.V (Monterrey, Nuevo León, Mexico).

2.2. Preparation of organogels

The preparation of organogels consisted of a standard methodology described by Rocha *et al.* (2013), in which samples were prepared by heating soybean oil to 80 °C under continuous stirring. When the temperature of 80 °C was reached, the structurant was added at different concentrations (0.5, 1.0, 2.0, 3.0, or 4.0% w/w) and mixed until complete dissolution. The mixture was kept under agitation for about 3 min to assure complete melting. The resulting blends of soybean oil with PEG or PPGE were stored at 20 °C for 24 h to enhance the formation of gels and kept at this temperature for two months. The organogels were identified as SBO/PEG (soybean oil with polyglycerol esters) and SBO/PPGE (soybean oil with propylene glycol esters).

2.3. Visual appearance

After 24 hours of storage of the organogels, a visual assessment was performed. Organogels were subjectively classified into five types: 1, 2, 3, 4, and 5, corresponding to liquid, viscous liquid, high-flowing semisolid gel, low flowing semisolid gel, and a totally solid gel which maintained its structure and hardness, respectively (García *et al.,* 2013).

2.4. Thermal stability

The thermal stability of organogels was determined by a cyclization process described by Garcia *et al.* (2013). Briefly, samples of 30 mL of each organogel were placed in 50-mL beakers and then subjected to sequential temperature variations according to the following conditions: 25 °C for 24 h for complete crystallization, followed subsequently by 5 °C for 24 h, 25 °C for 24 h, 5 °C for 48 h, 35 °C for 24 h, 25 °C for 24 h, 35 °C for 48 h and 5 °C for 48 h. Finally, the sample was stored at 25 °C for 24 h according to conditions specified in Table 1. After each storage condition, samples were immediately tested and classified according to the visual subjective appearance (type 1, 2, 3, 4, or 5). According to results

TABLE 1. Thermal stability of soybean oil organogels structured with polyglycerol esters (PGE) or propylene glycol esters (PPGE) tested sequentially at different temperatures and times[*]

Organogels	Esters (%)	Temperature /Time								
		25 °C /24 h	5 °C /24 h	25 °C /24 h	5 °C /48 h	35 °C /24 h	25 °C /24 h	35 °C /48 h	5 °C /48 h	25 °C /24 h
SBO/PGE	0.5	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a
	1	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a
	2	3±0 b	2±0 b	2±0 b	2±0 b	2±0 b	2±0 b	2±0 b	2±0 b	2±0 b
	3	4±0 c	3±0 c	3±0 c	3±0 c	3±0 c	3±0 c	3±0 c	3±0 c	3±0 c
	4	5±0 d	4±0 d	4±0 d	4±0 d	4±0 d	4±0 d	4±0 d	4±0 d	4±0 d
SBO/PPGE	0.5	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a
	1	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a	1±0 a
	2	3±0 b	2±0 b	2±0 b	2±0 b	2±0 b	2±0 b	2±0 b	2±0 b	2±0 b
	3	4±0 c	3±0 c	3±0 c	3±0 c	3±0 c	3±0 c	3±0 c	3±0 c	3±0 c
	4	5±0 d	4±0 d	4±0 d	4±0 d	4±0 d	4±0 d	4±0 d	4±0 d	4±0 d

[*]Subjectively rated according to Garcia *et al.* (2013) in type 1 (totally liquid), 2 (viscous liquid), 3 (high-flowing semisolid gel), 4 (low-flowing semisolid gel), and 5 (solid gel). Mean value ± SD (n=3). Tukey tests were employed for comparison of means ($p < 0.05$). Different lowercase letters within each column indicate significant differences ($p < 0.05$). The number of panelists who evaluated the physical status of the samples was three. SBO; soybean oil, PGE; polyglycerol esters, PPGE; propylene glycol esters.

of thermal stability, type-5 organogels stable under the cyclization conditions tested herein were stored at 25 ºC for 2 months. Both the visual appearance and thermal stability of the organogels were used as the main criteria to select the optimal concentration of SBO/PEG or SBO/PPGE.

2.5. Instrumental color measurements

The color of the SBO, PEG, PPGE, and their respective organogels were analyzed after 24 h at 25 °C. The color measurements based on the system CIEL*C*h (L = luminosity from zero (black) to 100 (white); +*a* = red, -*a* = green, +*b* = yellow, and -*b* = blue) were obtained with a Hunter Lab colorimeter (MiniScan PLUSXE, Hunter Lab, Reston, VA, U.S.A.) (da Silva *et al.*, 2018b) with slight modifications. The equipment was calibrated with standards provided by the supplier. E values were calculated by using the following equation: $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$.

2.6. Hardness (compression/extrusion)

The hardness of solid-like SBO/PGE and SBO/PPGE organogels structured with 4% concentration (w/w) were evaluated by compression/extrusion measurements using the texture analyzer Stable Micro Systems model TA-XT2i (Godalming-UK). 40 mL of organogels were conditioned in 50-mL glass containers of 35 mm internal diameter and 22 mm height. The glass containers were kept for 24 h at 20 °C for stabilization and after this period compressed with a 15-mm acrylic cylinder (25 mm diameter and 35 mm height) with a head cross speed of 1.0 mm/s (Rocha *et al.,* 2013). All determinations were performed in triplicate.

2.7. Microstructure

The organogels were placed on a glass slide and covered with a coverslip. Then, organogels were conditioned at 20 °C for 24 h and examined under constant temperature. The morphologies of the crystals of SBO/PGE and SBO/PPGE organogels (4% w/w) were viewed under a polarized light microscope (Olympus System Microscope model BX 50, Olympus America Inc., Center Valley, PA, USA) equipped with the digital camera Olympus EX300 (Olympus America Inc., Center Valley, PA, USA). Photographs were taken in different fields and visuals, and the resulting images were evaluated using the software Image Pro-Plus 7.0.1 for Windows by Media Cybernetics (Bethesda, MD, USA) with a magnification of 4x (Rocha *et al.,* 2013).

2.8. Rheological properties: Flow curve

The rheological properties were assessed using a Rheometer (Anton Paar, Graz, Austria). The flow

curves were acquired with sand-blasted rough plate geometry of 5 cm wide, a roughness of 5-7 μm, and a gap of 300 μm. The temperature throughout the analyses was maintained constant at 25 °C with shear rates ranging from 0 to 300 s⁻¹ (Rocha *et al.,* 2013). All determinations were made in triplicate and the models adjusted according to the Power Law, which classifies fluids according to their behavioral index (n) into: Newtonian ($n = 1$ and $τ0 = 0$), pseudoplastic ($0 < n < 1$) or dilating ($1 < n < ∞$).

2.9. Statistical analysis

The results were evaluated by analysis of variance (ANOVA) and Tukey tests were employed for comparison of means ($p < 0.05$). Data were reported as means and standard deviations. All statistical analyses were performed using the software JMP 5.0.1 (SAS Institute, Cary, NC, USA).

3. RESULTS AND DISCUSSION

3.1. Visual appearance and thermal stability

The SBO/PGE and SBO/PPGE organogels formulated with different concentrations and kept at different storage temperatures showed changes in stability. Their visual appearance, gel consistency, and stability were affected by the concentration of structurants (Table 1). As expected, the stability and consistency increased with a higher concentration of structurants for both the SBO/PGE and SBO/PPGE organogels. Gels formulated with 0.5% showed a total liquid consistency. However, both structurants supplemented at 2% (w/w) yielded high flowing organogels with semisolid features (type 3).

Among the experimental organogels, the SBO/PGE and SBO/PPGE gels formulated with 4% (w/w) were entirely solid and stable (Type 5) at 25 °C compared to their counterparts prepared with lower concentrations of structurants. Interestingly, both structurants kept forming solid-like organogels when added at 4% and stored at a higher temperature (35 °C). These organogels had a slightly lower consistency (type 3) and did not show any indication of liquid phase separation. The consistency of all organogels decreased 1-point unit after 24 h of storage. As the concentration of structurant decreased, the consistency/stability of organogels also decreased, particularly those formulated with concentrations of 0.5 and 1.0%. These organogels yielded liquid gels

rated as Type 1. The higher stability in SBO/PGE and SBO/PPGE organogels formulated with a concentration of 4% (w/w) were attributed to the chemical composition of these pure structurants (Polyglycerol Esters or PEG and propylene glycol esters or PPGE). These structurants can potentially mimic triacylglyceride crystallization through molecular self-assembly, leading to the formation of the more stable three-dimensional gel network. Similarly, Öğütcü and Yilmaz (2014) reported that a 3% addition of monoglycerides in olive oil-based organogels yielded stable gels, whereas the candelilla wax could not create stable gels at the same concentration. Therefore, the results herein clearly indicate the potential for the use of SBO/PGE and SBO/PPGE for the production of gels with semi-liquid consistency at concentrations lower than 3% (w/w). PEG and PPGE structurants at concentrations of 0.5, 1.0, 2.0, or 3.0% w/w, showed total liquid and semi-liquid consistencies and negatively affected the thermal stability of organogels (Tables 1 and 2). Furthermore, a preliminary study was carried out to select the optimal storage of organogels. Organogels stored for two months showed particle aggregation and thus negatively affected the consistency. The best organogels were produced for the assessment of the microstructure, hardness, and rheological properties after 24 hours and two months of storage.

3.2. Color parameters

The color parameters of the organogels (SBO/PGE and SBO/PPGE) formulated with 4% PGE or PPGE are summarized in Table 2. The results indicate that the luminosity and yellowish coloration were not significantly affected by the two different polyglycerols. However, a significant difference in *ΔE* values was obtained in the organogels formulated with SBO/PPGE. The *ΔE* values of SBO/PPGE organogels indicated a greater color difference caused by the structurant type.

The luminosity, greenness and yellowish values in organogels formulated with 4% SBO/PGE were $L = 24.49$; $a = 0.70$, $b = 3.94$; whereas in SBO/PPGE counterparts $L = 24.48$; $a = 0.72.$, $b = 3.79$ (Table 2). The observed differences can be attributed to the addition of higher proportions of soybean oil. The values of *b* parameter ($b =$) (yellowish) in soybean oil can be attributed to the presence of chlorophyll derivatives (pheophytin A) which are responsible

TABLE 2. Color parameters L, a, b, and ΔE and maximum force of soybean oil organogels structured with polyglycerol esters (PGE) or propylene glycol esters (PPGE) at 4.0% (w/w) after storage at 25 °C for 24 hours and two months. *

Parameter	Organogels	
	SBO/PGE	SBO/PPGE
Color		
L	24.49 ± 0.28 a	24.48 ± 0.34 a
a	0.70 ± 0.10 a	0.72 ± 0.99 a
b	3.94 ± 0.29 a	3.79± 0.31 a
ΔE	73.55 ± 0.45 b	78.62 ± 0.73 a
Hardness (N)		
24 h	0.06 ± 0.01 aA	0.06 ± 0.01 aA
2 months	0.06 ± 0.01 bA	0.08 ± 0.01 aB

* Mean value ± standard deviations (n=3). Tukey tests were employed for comparison of means ($p < 0.05$). Different letters within each row and uppercase letter in column per treatment and determination denote significant differences ($p < 0.05$). L= luminosity (100 = lightness and 0 = darkness), +a = increasing red and -a = increasing green, +b = increasing yellow and -b = increasing blue, and ΔE value = $[(DL^2) + (Da^2) + (Db^2)]^{1/2}$. SBO; soybean oil, PGE; polyglycerol esters, PPGE; propylene glycol esters. N; Newton.

for imparting green-yellow colorations (Fraser and Frankl, 1985). On the other hand, the SBO-free PGE presented higher luminosity values (L=27.64). The structurants showed higher luminosity because the PGE was devoid of chlorophyll. Among all organogels, the SBO/PGE containing 2, 3 or 4% presented the lowest color values (data not shown). Thus, the addition of PGE for the production of SBO/PGE organogels enhanced luminosity values.

3.3. Hardness

The concentration of 4% SBO/PGE or SBO/PPGE was selected as the best to form structured organogels that could withstand prolonged storage at room temperature. These organogels presented characteristics of ideal thermal stability. The organogel texture values measured as hardness (N) at 24 hours and after 2 months of storage at room temperature are summarized in Table 2. These results showed that higher concentrations of SBO/PPGE and SBO/PEG produced organogels with similar maximum force at 24 hours. However, both SBO/PGE and SBO/PPGE organogels stored for 24 hours showed lower mechanical resistance compared to counterparts stored for 2 months. Interestingly, the organogels SBO/

PPGE (4%, w/w) after 2 months of storage showed a higher mechanical resistance (0.080 N) compared to counterparts formulated with SBO/PGE (0.065 N). The major textural changes occurred after 24 h of storage. After organogels were prepared, the crystals gradually rearranged, allowing growth formation, which consequently altered the texture. The rearrangement increased oil exudation (apolar liquid phase) from the fat crystals and also enhanced phase separation (post-hardening phenomena) (Hughes *et al.,* 2009). Moreover, the SBO/PPGE organogel formulated with a concentration of 4% showed two different crystal morphologies, consisting of larger fat crystal networks and spherulite crystals which were more evenly distributed compared to crystals formed in the SBO/PGE organogels. Likewise, the presence of two different morphologies of crystal explains the highest hardness and shear stress values observed for the SBO/PPGE organogel (Figure 1 A-B). This behavior is attributed to the different chemical compositions of the structurants. PEG is a mixture of mono-diglyceride and polyglycerol esters whereas PPGE consisted of propylene glycol esters of fatty acids. These results showed that a higher concentration of SBO/PPGE (4%, w/w) than SBO/

A) SBO/PPGE (4x_24 h)   B) SBO/PPGE (4x _2 months)

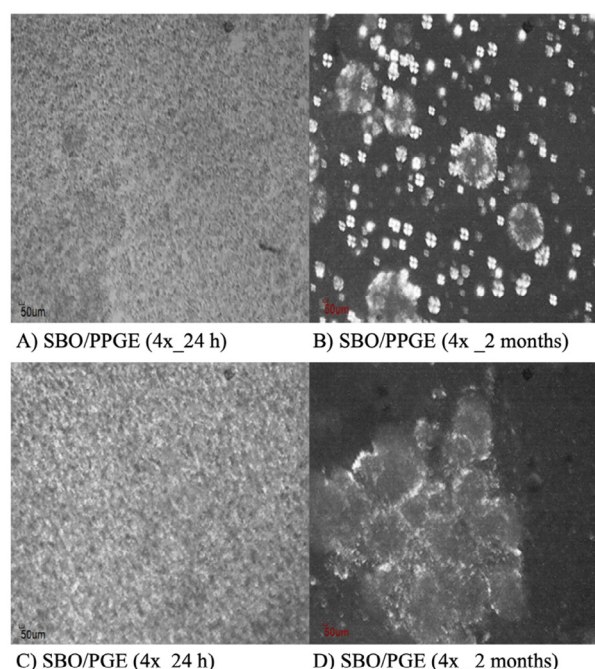C) SBO/PGE (4x_24 h)   D) SBO/PGE (4x _2 months)

FIGURE 1. Morphological image obtained by polarized light microscopy in SBO/PPGE (A and B) and SBO/PGE (C and D) organogel with 4% of structurants, with the magnification of 4x at 20 °C after 24 h and 2 months. SBO; soybean oil, PGE; polyglycerol esters, PPGE; propylene glycol esters.

PEG produced stronger organogels after 2 months of storage. Pernetti *et al.* (2007) demonstrated that both diacylglycerols and monoacylglycerols were needed to produce organogels with softer textures. Regardless of the type of emulsifier, the longer the chain length the greater the firmness of the gel. However, these SBO/PGE and SBO/PPGE at 4% organogels showed lower hardness compared to organogels prepared with sugarcane wax (4%) and soybean oil (1.65 N) (Rocha *et al.,* 2013). Limited information exists about the presence of SBO/PGE and SBO/PPGE organogels, and this research contributes to new valuable information on the effects of PEG and PPGE addition and storage time on the hardness and related properties of the structured organogels.

3.4. Rheological properties: Flow curve

The organogels flow curves determined after 24 hours and 2 months of storage at 25 °C are depicted in Figures 2 A and B. The curves can be used for qualitative comparisons among organogels. Both SBO/PGE and SBO/PPGE organogels showed a characteristic thixotropic behavior (Steffe, 1996; Rocha *et*

FIGURE 2. Flow curves of organogels A) SBO/PGE and B) SBO/PPGE with 4% of structurants after 24 h and 2 months. Mean value ± standard deviations (n=3) of SBO/PGE from 24 h (3.64) and 2 months (9.84); SBO/PPGE from 24 h (5.69) and 2 months (10.41). SBO; soybean oil, PGE; polyglycerol esters, PPGE; propylene glycol esters.

al., 2013). However, organogels prepared with SBO/PGE stored for 24 h showed considerably lower shear stress values (24.16 Pa at 10.40 s^{-1}) (Figure 2A). However, a significant portion of the observed changes in shear stress occurred during storage because flow curve values increased with storage time for all treatments. Higher shear stress values were observed in organogels prepared with SBO/PPGE (Figure 2B). Shear stress values increased with the shear rate for the SBO/PPGE (4%) organogels after 2 months of storage (64.63 Pa at 300 s^{-1} at 25 °C). Also, the SBO/PGE organogels presented a fast increase and decrease in shear stress at low shear rates which are a consequence of the easier disruption of the structural network (Riscardo *et al.,* 2005; Perrechil *et al.,* 2010). The shear stress values for SBO/PGE organogels at 2 months storage were 78.50 Pa at 10.40 s^{-1}. Storage resulted in stronger structural deformational changes in gels kept for 2 months, likely due to the formation of stronger crystal network aggregates.

The observed negative effects of storage for 8-10 weeks on the structure of organogels formulated in combination with monoglycerides and phytosterols have been previously described by Sintang *et al.* (2017a). Similar results related to shear stress (62.2 at 3 s^{-1} at 25 °C) were obtained by Rocha *et al.* (2013), who used sugarcane wax (4%) to structure organogels. Recently, Buitimea-Cantúa *et al.* (2020) reported that organogels elaborated with refined carnauba wax (5.5%) increased when the shear rate increased (110 at 3 s^{-1}) from 0 to 50 1/s and this effect was higher in organogels stored for 2 months (300 at 3 s^{-1}). Results herein demonstrated that the combination of SBO/PGE or SBO/PPGE added at different ratios could provide an array of new organogels with desired rheological properties which can last up to two months in storage at 25 °C. All organogels showed pseudoplastic flow characteristics.

3.5. Microstructure

Polarized light microphotographs of the SBO/PGE and SBO/PPGE organogels at 4% of concentration and stored for 24 h or 2 months are depicted in Figure 1. The micrographs show that the crystal networks of the SBO/PPGE organogels at 24 hours of storage tended to be smaller, more uniform, smoother, and more evenly distributed (Figure 1A) compared to the crystal arrangements of the SBO/PGE counterparts (Figure 1C).
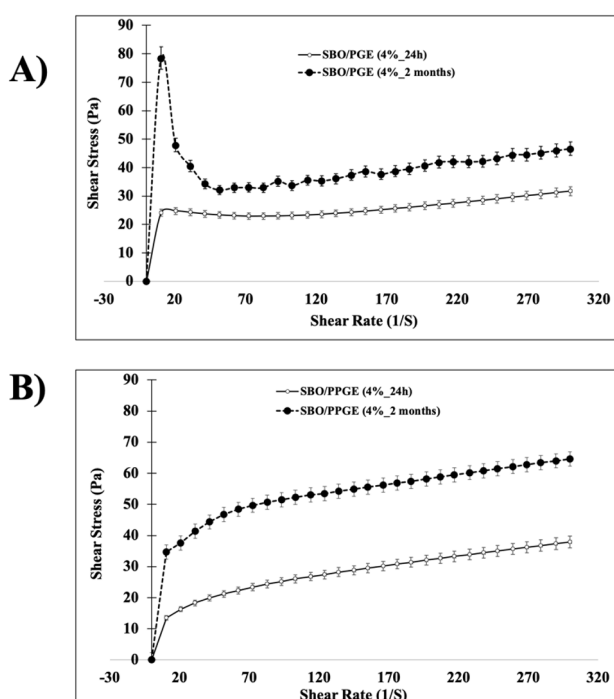
A significant portion of the organogel crystal structure changed after 2 months of storage at 25 °C because these gels had larger crystal aggregations (Figures 1B and D). The structure formed by the SBO/PGE organogels (spherulite-crystals) (Figure 1D) is an indication of weaker intermolecular interactions such as Van der Waals interactions and London dispersion forces (Sintang *et al.,* 2017a). Different complex phenomena took place after two-months' storage of solid-like organogels produced with 4% of PGE or PPGE. Post-crystallization events included polymorphic transitions from less stable to more stable polymorphs, the appearance of new crystalline particles, sintering, and Ostwald ripening (Johansson and Bergenståhl, 1995; Ojijo *et al.,* 2004). These phenomena yielded the formation of larger crystal clusters instead of smaller counterparts, thereby leading to a weaker gel (Ribeiro *et al.,* 2015; Tanaka *et al.,* 2007). These observations were previously documented by Doan *et al.* (2017) and recently by Buitimea-Cantúa *et al.* (2020) in organogels structured with refined carnauba wax.

This might explain the observed higher mechanical resistance at the beginning of the compression/extrusion tests. It is important to visualize the morphology and crystal networks because they reflect the spatial distribution of crystals that influences their rheological properties (Marangoni and Rousseau, 1996; Blake *et al.,* 2014).

4. CONCLUSIONS

The structurants PGE and PPGE were able to form semi-solid/solid-like organogels with soybean oil at 25 °C when used at 4%. The SBO/PGE organogel showed a more organized crystal network (smaller and more uniform crystals which were evenly distributed) compared to the crystals of the SBO/PPGE counterpart. The SBO/PGE organogel was softer and presented lower mechanical resistance compared to the SBO/PPGE counterpart. However, the prolonged storage of two months affected the structure of organogels formulated with either SBO/PGE or SBO/PPGE. These organogels presented larger crystal networks and higher shear stress values, which significantly affected hardness. These negative effects were more pronounced in organogels structured with SBO/PGPE. Therefore, both structurants were effective for the formation of organogels with concentrations higher than 4%, and

with technological properties that can be applied in lipid-based food products.

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