Predicting puff pastry margarine performances based on LAOS output

A. Chakraborty[a], C. Blecker[a], V. Van Hoed [b], P. Barthelemy[b], R. Detry [b], S. Danthine [a]

[a]Gembloux Agro-Bio Tech TERRA University of Liège Avenue de la Faculté d'Agronomie 2B, Gembloux 5030, Belgium; E-mail: achakraborty@uliege.be

[b] Industrialaan 25 Puratos nv Zone Maalbeek, 1702 Groot-Bijgaarden, Belgium.

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Corresponding author: Arpita Chakraborty (achakraborty@uliege.be, arpitac7@gmail.com)

Abstract

Laminated pastries rely heavily on the unique viscoelastic and plastic properties of margarine. Traditional methods for predicting such properties, such as solid fat content (SFC), hardness, small amplitude oscillatory rheology, and subjective sensory tests (thumb test), often lack the sensitivity to detect subtle variations in margarine possessing similar characteristics. SFC primarily focuses on solid fat content, hardness measurement with cone provides a single-point assessment and identifying linear viscoelastic region cannot adequately describe the non-linear behavior which is crucial for lamination processes involving significant deformations. Additionally, subjective sensory tests are highly operator-dependent and prone to variability and inconsistency.

This study introduces Large Amplitude Oscillatory Shear (LAOS) as an approach to characterize the viscoelastic properties of same composition lamination margarines. LAOS, a powerful nonlinear rheological technique, enables precise differentiation of margarines produced with minor variations in processing conditions and maturation temperatures, even when traditional methods fail to detect significant viscoelastic differences.

Results demonstrate that LAOS effectively captures the subtle viscoelastic variations between margarines, correlating strongly with their baking performance. This study emphasizes the crucial role of nonlinear rheology, specifically LAOS, in accurately predicting the behavior of lamination margarines and optimizing their performance in baking applications.

1. Introduction

Margarine, a versatile ingredient in the food industry, extends its application in spreads, baking products, and cooking processes (Patel et al., 2016). Margarines used explicitly for baking croissants or puff pastry, require significant functional properties. These margarines are generally known as roll-in, lamination, or sheeting margarine. The final products are prepared by laminating and folding consecutive layers of fat and dough (Detry et al., 2021a). The primary function of lamination margarine in puff pastry baking is establishing barriers between each layer and separating dough layers, facilitating optimal rising. While baking, water within the system evaporates as steam, leading to the expansion of dough layers. Lamination margarine allows fat to deform and adopt a new shape under stress, without breaking and by attaining a continuous structure. The ability to not break and continue to form an undisrupted structure when stress is applied is the main functionality required for lamination step.

Generally, during puff pastry lamination, at first the base dough is prepared which is allowed to mix until the gluten development starts. After allowing a resting phase, the dough is laminated first into a sheet upon which the laminated fat is introduced. Subsequent steps involve creating layers with the help of a laminating roller and folding. During this step, the product experiences higher strain which helps in creating thin alternate layers of dough and lamination fat. In most of the cases, where puff pastry is prepared manually an overnight resting is allowed before to rest the dough at 4-6°C. This allows the dough to relax before the final lamination. This step is mainly followed to avoid any overworking and melting of the fat layer. However, in recent developments of continuous process the entire process with final lamination and baking is performed in a single day (Wickramarachchi et al., 2015). Several consequences can arise when the lamination process is not maintained well. For instance, it is possible to obtain a flat puff if the layers do not separate well during baking. Margarines processed inappropriately can result in uneven layers which can also lead to a flat puff because of the heterogeneous distribution of fat within the dough layers. The dimensions of the puff could shrink if an adequate resting time is not allowed (Cauvain, 2017; Pajin et al., 2011). The interplay between firmness and flexibility is crucial for achieving the desired rise and texture in the final baked product (Dobraszczyk & Morgenstern, 2003).

For the prediction of margarine's baking performances, industries use sensorial methods, such as the bakers pressing their thumb against the margarine to understand hardness, lumps, and stickiness. Further, they translate these properties concerning plastic or non-plastic margarine to try to predict baking performance (Cavillot et al., 2009). Besides, they also bend the margarine to specific shapes and look for cracks to evaluate accordingly (Gao et al., 2022a). As instrumental methods, hardness and solid fat content (SFC) are measurements widely used to relate fat crystallization at the micro-structural level with plastic properties. Properties like the spreadability of margarine can be correlated with its hardness. It is known that the product showing higher hardness results in less spreadability compared to the product showing lower hardness (Fallahasgari et al., 2023). Additionally, solid fat content also indicates the functionality of fat systems (Devi & Khatkar, 2016). In industry, SFCs are measured at different ranges of temperatures to predict the plastic nature of the fat system (Liu et al., 2010). SFC is known to provide knowledge on the melting behavior of fat systems. Hardness and SFC share an indirect correlation, and it is relatively imprecise due to the involvement of several other factors (Braipson-Danthine & Deroanne, 2004; Detry et al., 2021a; Narine & Marangoni, 1999). The hardness of the product is well connected with its mechanical properties; however, it is not a highly sensitive method that can directly indicate the functionality of different fat systems (Macias-Rodriguez & Marangoni, 2017a). Therefore, establishing a reliable and precise method to predict lamination margarine performance in baked goods beyond these subjective and instrumental methods remains challenging.

In general, rheological analysis provides an understanding of various critical factors of the end product, such as sensory, texture, and performance. Moreover, rheological studies concerning fat systems can provide in-depth knowledge of crystal network behavior and interaction forces associated with elastic and viscous properties of the matter (Macias Rodriguez, 2019). In the field of rheology, the study of the linear viscoelastic region (often referred to as SAOS - small amplitude oscillation shear) has been extensively explored in a strain-controlled oscillatory system. The linear rheological method allows a detailed investigation of the material's viscoelastic behavior under minor deformation conditions, providing valuable insights into its mechanical and structural characteristics (Doi et al., 1988; Ferry, 1980; Oldroyd, 1984). However, during the lamination process, puff pastry margarine undergoes large deformations which makes studying non-linear regions more relevant and essential. Regions experiencing high amplitude strain provide valuable insights regarding irreversible deformations (Yazar & Rosell, 2023). Non-linear viscoelastic studies are recommended for products that undergo large deformation. In relation to laminated products, studying non-linear viscoelastic regions was found relevant for dough as well as for fat systems (Macias-Rodriguez & Marangoni, 2018a; Yazar & Rosell, 2023). Lamination shortening and cake shortenings were compared under large deformation (Macias-Rodriguez et al., 2017).

Moreover, the effectiveness of non-linear region study in discriminating against the viscoelastic properties of two completely different compositions of margarines (all-purpose and lamination) have been established. The authors indicated that the non-linear region effectively revealed the early-stage deformation of all-purpose margarine, distinguishing it from lamination margarine. This finding led them to conclude that it was possible to differentiate between the two types of margarine using this instrumental method (Macias-Rodriguez & Marangoni, 2018). Due to their distinct intended applications, the margarines used in the abovementioned studies differed significantly in composition and processing conditions.

LAOS studies have never been reported for lamination margarine with the same formulations which is produced with slightly different processing conditions to predict their performance in baking performances of lamination margarines. Within the current scope of work, the main goal remains to conduct LAOS studies along with other physical and sensorial studies to predict the baking performances of three lamination margarines of the same composition but slightly different processing conditions (referred to as case study I). For the second part of the study (referred to as case study II), two margarines were selected and subjected to three different maturation temperatures (14°C, 18°C, 22°C). For this part, the aim was to investigate further if the method selected for predicting the baking quality of margarine still detects the differences within the margarines which are matured at three different temperatures, if there is any. In the end, puff pastries were baked to confirm the performances of margarine. Overall, the interest of this study lies in predicting the baking performances of margarines based on their physical (hardness, SFC) and sensorial (thumb test) properties together with the LAOS output. Additionally, complementary tests including cyclic triangular strain recovery test were performed to understand the LAOS output more clearly.

2. Theory/ Calculations

The success of lamination margarine in producing high quality puff pastry relies on a delicate balance between two key properties: viscoelasticity and plasticity. Viscoelasticity is characterized by the co-existence of solid and fluid depending on time frame (Donley et al., 2020). Plastic deformation and yielding are characterized by the shift of a material from solid-like to fluid-like forms based on the applied stress or strain. Plasticity is the capacity of a viscoelastic material to undergo permanent deformation (Jr & Rethwisch, 2020) allows the margarine to spread smoothly between dough layers, preventing tearing and ensuring a cohesive structure. The viscoelasticity and plasticity of a fat product depend on a few factors, such as composition and processing parameters, which can develop a range of fat crystal sizes and subsequently lead to a defined range of melting behavior. Certain post-processing handling conditions during maturation and storage time also play a significant role in determining the viscoelasticity and plasticity of the product (Gao et al., 2022a, 2022b).

Linear viscoelasticity region (LVR) is identified using small amplitude oscillation shear (SAOS), which applies oscillatory strains of small amplitudes. At low strain amplitudes, weak Van Der Waals forces maintain the material's structure. This structure recovers after strain removal. This is the linear viscoelastic region (Ferry, 1980; Flory, 1953). Here, the storage modulus dominates the loss modulus, indicating soft viscoelastic solid behavior. However, the Deborah number explains how material's behavior is time-dependent; solids can flow after a given time, and fluids can act as solids under rapid deformation (Reiner, 1964). It's the ratio of relaxation time to observation time. Additionally, identifying the yield stress is complex. No single method exists to pinpoint the yield point. It might be indicated by a drop in storage and loss modulus during an amplitude sweep, or it could be considered the crossover point or some other methods can be considered (Bonn et al., 2017; Dinkgreve et al., 2016; Moller et al., 2009; Møller et al., 2009).

Small and large amplitude oscillatory shear (LAOS) study helps in understanding the interconnection of steady flow viscosity ($\eta(\dot{\gamma})$), storage and loss moduli ($G'(\omega)$ & $G''(\omega)$)in the linear and non-linear viscoelastic behaviors (Dealy & Wissbrun, 2012). Generally, LAOS studies are performed in a strain-controlled environment, where the inputs are amplitude strain and frequency (γ_0, ω) and the outputs are stress waveforms needed to achieve the target strain. In strain-controlled LAOS deformation, the imposed strain takes the form of,

$$\gamma(t) = \gamma_0 \, sin \, \omega t \qquad (1)$$

resulting in a strain rate to achieve the target strain with a phase shift, which can be described with the following equation,

$$\dot{\gamma} = \gamma_0 \omega \, cos \, \omega t. \qquad (2)$$

LAOS outputs are visualized in the form of Lissajous-Bowditch (L-B) plots which can be described as forms of hysteresis when two simple harmonic motions are combined at right angles (Philippoff, 1966). Two types of L-B plots are generated out of LAOS studies, stress versus strain and stress versus strain rate which are generally used for interpreting the elastic and viscous nature of the product, respectively.

In the case of elastic or viscous Lissajous curves, it is recognized that when these curves reside within the linear region, they exhibit an elliptical shape (Dealy & Wissbrun, 2012; Pipkin, 2012). However, with increment of amplitude strain, these elliptical curves undergo clockwise shift and deformation, transitioning away from their initial elliptical form for the elastic properties. The deformation is also visually estimated with the enclosed area within the stress-strain plots. Generally, a shift from the y-axis indicates a phase lag between the stress and at that given strain. This shift may occur due to breakdown of the internal fat crystal network which reduces its ability to store energy elastically. This shift may also signify an increase in energy dissipation rather than energy storage. In the context of puff-pastry, high energy dissipation can contribute to stability of the margarine during the lamination phase. Higher energy dissipation can indicate that the material has good viscoelastic properties, allowing it to absorb energy during rolling and shaping without failure. Considering higher amplitude strain where nonlinear responses emerge, the material no longer behaves as a simple solid instead becoming more complex and may show strain softening or stiffening. In the context of nonlinear assessment of fat systems, particularly margarine, several establishment criteria have been put forth (Macias-Rodriguez & Marangoni, 2018a). When the enclosed area transforms from an elliptical to a more rectangular shape with an escalation in shear rate, it indicates an ideal plastic behavior (Ewoldt et al., 2010).

In contrast to the linear viscoelastic behavior observed in small amplitude oscillatory shear (SAOS), large amplitude oscillatory shear (LAOS) induces nonlinear viscoelastic behavior resulting in distorted, non-sinusoidal stress waveforms that are more challenging to interpret and model (Le et al., 2023). Apart from qualitative L-B shape-based interpretations, several studies have been performed to quantify the LAOS output.

Ways to analyze LAOS encompasses various methods such as Fourier transform rheology (Hyun et al., 2011; Wilhelm, 2002), determination of viscoelastic moduli (Ewoldt et al., 2008, 2010; Hyun et al., 2002) and stress decomposition techniques using Chebyshev polynomials (Cho et al., 2005; Ewoldt et al., 2008; Yu et al., 2009). Apart from quantifying certain characteristics by looking at the higher harmonics, the Sequence of Physical Processes (SPP) method was introduced by Rogers et al. (2011) which provides a quantitative framework for analyzing nonlinear rheological behavior. It offers advantages over Fourier Transform Chebyshev analysis, such as calculating transient moduli and visualizing material response through Cole-Cole plots. These plots reveal structural changes, making SPP valuable for understanding complex rheological behavior, especially in food systems. Time-resolved neutron scattering provides real-time molecular-scale measurements of structural changes under large amplitude oscillatory shear (LAOS) conditions, linking macroscopic rheology to microscopic structure and dynamics. Additionally, recent developments, including recovery rheology analysis coupled with LAOS enhance understanding of material behavior, particularly plastic performance. These advancements enable characterization of plastic, solid-like, and fluid-like characteristics at different strain amplitudes (K. Kamani et al., 2021; K. M. Kamani & Rogers, 2024).

Fourier transform rheology and Chebyshev polynomial decomposition are most used for quantifying the LAOS tests for analyzing nonlinear rheology of materials. These methods decompose distorted waveforms into sinusoidal basis functions to analyze harmonic intensities, where the onset of nonlinearity is indicated by increased significance of higher harmonics, especially the third. The ratio of third to first harmonic and sometimes fifth to 3^{rd} harmonic are used to define the intensity of nonlinear oscillatory shear responses.

Additionally, the method provides elastic and viscous Chebyshev coefficients, which can be used to calculate derivative and secant moduli and viscosities (Ewoldt et al., 2008). The author suggested measuring certain dimensionless indices for non-linear regions such as the S-factor and T-factor for elastic and viscous responses, respectively and described the interpretation of results as follows:

S-factor	Elastic responses	T-factor	Viscous responses
= 0	Linear elastic response	= 0	Linear viscous response
> 0	Intracycle strain stiffening	> 0	Intracycle strain thickening
< 0	Intracycle strain softening	< 0	Intracycle shear thinning

3. Materials and methods

Three margarines (M1, M2, and M3) were kindly provided by Puratos (Groot-Bijgaarden, Belgium). The three margarines have the same compositions, but their processing conditions vary slightly. For the first case study, margarines were stored at 18°C. For case study II, margarines (M1 & M2) were matured at three temperatures (14°C, 18°C, and 22°C) for four days and then moved to 18°C until analysis. M3 was not considered for case study II. For both cases, all analyses were conducted after a month of production. In addition, hardness was performed after 15 days of production for case study II.

3.1. Thumb test

Three experts from the company's trained panel participated in this test on company premises. Using the tactile evaluation technique with their fingers, they examined the margarine for specific textural attributes, including lumpiness, grittiness, and stickiness. They aimed to translate these characteristics into margarines' plastic behavior and further categorize them as high, medium and low plastic or very low plastic based on the observed characteristics.

3.2. Texture analysis

Hardness was measured using the texture analyzer SMS TA.ST2i/5 (Stable Micro Systems, Surrey, UK) with the help of a 45° steel cone probe. The pre-test speed was set at 0.5 mm/s, the test speed at 1mm/s and the post-test speed was run at 2mm/s. A penetration distance of 5mm was set. A temperature-controlled unit set at 18°C ± 0.5°C was used to maintain the temperature of the sample while performing these tests. Each test was performed in triplicates.

3.3. SFC

SFC was measured on the margarine using a pulsed NMR spectrometer (MiniSpec MQ20, Bruker, USA) at the storage temperature of 18°C in both case studies. Measurements were performed in triplicates.

3.4. Rheological test

Rheology tests were performed to investigate margarine's linear and non-linear viscoelastic regions. Oscillatory measurements were performed using a Modular Compact Rheometer

(MCR 302- Anton Paar, Austria). An air-cooled Peltier maintained the temperature of the plate. The probe of a 25mm diameter serrated parallel plate was used to avoid slippage of sample discs. Linear viscoelastic behaviors and strain recovery were performed using Rheoplus and nonlinear viscoelastic behaviors were determined using Rheocompass software. Raw data was collected in excel files and analyzed manually. Measurements were conducted in duplicates.

3.4.1. Sample preparation

Margarines were pierced with a 25mm diameter hollow cylinder to obtain the sample in cylindrical form. Then, the cylindrical margarine form was lightly pushed by a plunger from the other end to obtain a thickness of 2.0 ± 0.5mm, which was cut off using a wire cutter. Margarine sample discs had a dimension of approximately 25mm *2.5mm (diameter*thickness). The preparation of sample discs was carefully done in a temperature-controlled manner without any external disturbances.

3.4.2. Amplitude sweep – to identify LVR (Linear viscoelastic region)

Amplitude sweep was performed for a range of amplitude strain of 0.001-100% at a constant frequency rate of 3.6 rad/s (Macias-Rodriguez & Marangoni, 2018a) with thirty-one measuring points. This was performed primarily to identify the LVR. For this, a normal force of 3 N was set. For linear viscoelasticity, measurements were performed at 18°C. Each analysis was performed in triplicates.

3.4.3. Large amplitude oscillatory shear (LAOS)

For non-linear viscoelastic measurement, sample discs were carefully placed on the base, precisely covering the surface of the probe. After placing the sample disc, an axial load of 3 ± 0.5N was exerted on the sample. The margarine discs were then allowed to rest for 15 minutes. For the test, the program LAOS template was selected. Various intervals of amplitude strain were assessed on the margarine. Each interval was repeated ten times, and the last two data were selected for plotting the figures.

Ewoldt and his associates (2015) extensively examined potential factors leading to false results, including sample slip, gap setting, and filling between the sample, probe and base, as well as edge fracture. These factors were meticulously considered during sample preparation, placement and conducting the measurements, ensuring their careful management throughout the experiments.

3.4.4. Strain recovery

Margarines were exerted with cyclic triangular strain amplitude with intermediate intervals of zero shear stress. This was performed for the acquisition of strain recovery of margarines. For this test, only M1-18 and M2-18 were considered. Margarines dimensions were maintained at 25mm *2.5 ± 0.3mm (diameter*thickness). Tests were run at different strain amplitudes. The time interval of the test was chosen to closely match with the frequency of the LAOS (large amplitude oscillation shear) test. This helps to reproduce similar product behavior at different (low to high) strain amplitudes. After the cyclic triangular strain exertion, the strain was removed and shear stress zero was exerted. A sufficient recovery time was chosen to ensure steady state strain after stress removal. Two intervals of four consecutive cycles were run and the results are expressed for the last recovery. Except for the strain amplitude of 1.5 and 2%, all other strains were performed for M1 and M2 both. Additionally, 1.5 and 2% were performed for M1, to observe if more information can be obtained. The calculation of the recoverable and unrecoverable strain has been shown in Fig. 1. Further, the calculation of recoverable strain percentage has been expressed as the strain recovered by the total strain applied to margarine.

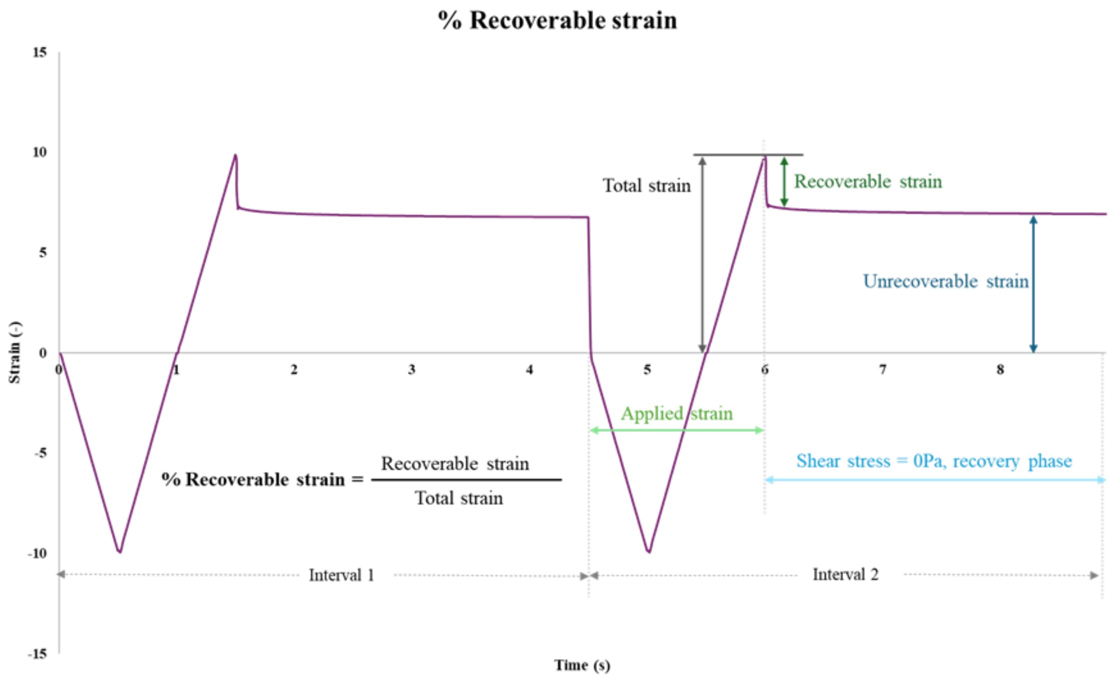


Figure 1. Recoverable strain acquisition.

3.5. Puff pastry baking

Margarines were a month old when used to bake puff pastry. Lamination and baking were performed in the pilot-baking center of Puratos (Groot-Bijgaarden, Belgium). The ratio of fat to flour in the dough was maintained at 60% lamination fat on a flour basis. The method of lamination and baking was similar to that mentioned by Detry et al., 2021a. After baking, the heights and volumes of the 6 puff pastries were measured.

4. Results and Discussions

Case study I

4.1. Sensorial and physical properties assessment (Thumb test, hardness, SFC)

A thumb assessment (Fig. 2a) was executed to predict the plastic characteristics of margarine across very low, low, medium, and high levels. As per the thumb test, M1 exhibited high plastic behavior, M2 exhibited notably very low plasticity and M3 showed medium plasticity. Interestingly, the thumb test could detect and distinguish distinct levels of plasticity that occurred due to the slight differences in the processing conditions of margarines. According to the hardness results, M1 is softer than M2 and M3 (Fig. 2b). M2, on average, is harder than M3 but not as much as M1. Additionally, M1 shows the lowest solid fat content (SFC) compared to M2 and M3 (Fig. 2b). The SFC of the margarines follow a similar trend as the hardness. The hardness and SFC of M1 is significantly different from M2 and M3. In contrast, thumb test indicated that M3 exhibited plastic properties like M1. Hardness, SFC and thumb test do not hold similar predictions because these tests are measuring different components of the product and not directly the viscoelastic properties. This suggests that the hardness, SFC and thumb test are not sufficient to measure the viscoelasticity of margarines and predict their baking performances.

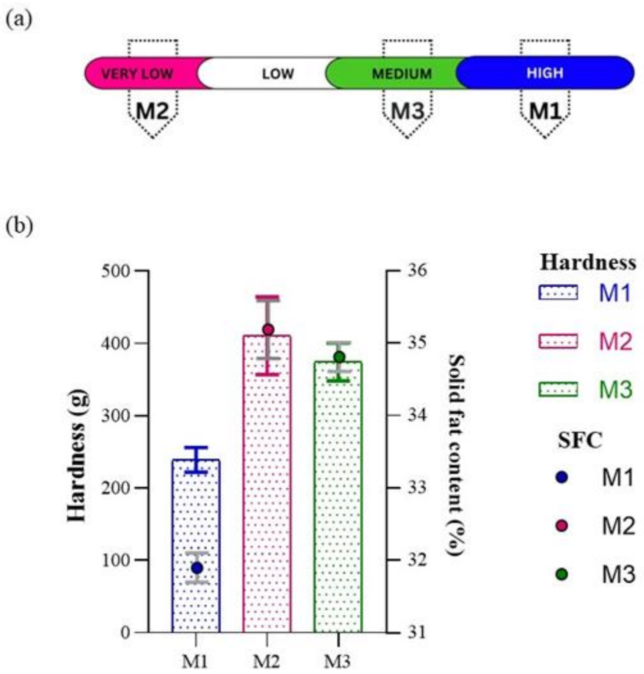


Figure 2. (a) Thumb test, & (b) Hardness and SFC of margarines (M1, M2, M3) produced with slightly different processing conditions. Measurements were performed at 18°C.

4.2. Rheological test

Amplitude sweep was conducted to identify the transitioning point from linear to non-linear viscoelastic region. Margarines were found to be in the linear region until the amplitude strain of 1x 10^{-2} %, and the non-linear region started at an amplitude of 1x 10^{-1} % (Fig. 3). These findings for laminated margarine also support the range of small amplitude oscillatory shear (SAOS) regimes mentioned in the literature (Macias-Rodriguez & Marangoni, 2017b).

The linear viscoelastic region (LVR) measurement output was further investigated in specific plots, such as storage or loss modulus against shear stress and shear stress against strain. The storage and loss modulus against shear stress (Fig. 4a) suggests all three margarines exhibit a sudden drop and back bending in both storage and loss modulus. Back bending for M2 was higher, whereas M3, and M1 showed the least back bending. Backward bending has been interpreted as product softening and "catastrophic failures" (Macias-Rodriguez & Marangoni, 2018b). When the shear stress was plotted against applied strain (Fig. 4b), an increase in stress with a steeper local slope followed by a drop was seen for M2 and a more plateaued slope for M1, followed by M3. In this context, it is reasonable to infer that the product exhibiting the least back bending and plateaued slope demonstrates comparatively superior viscoelastic properties, which are desirable functional properties for lamination application.

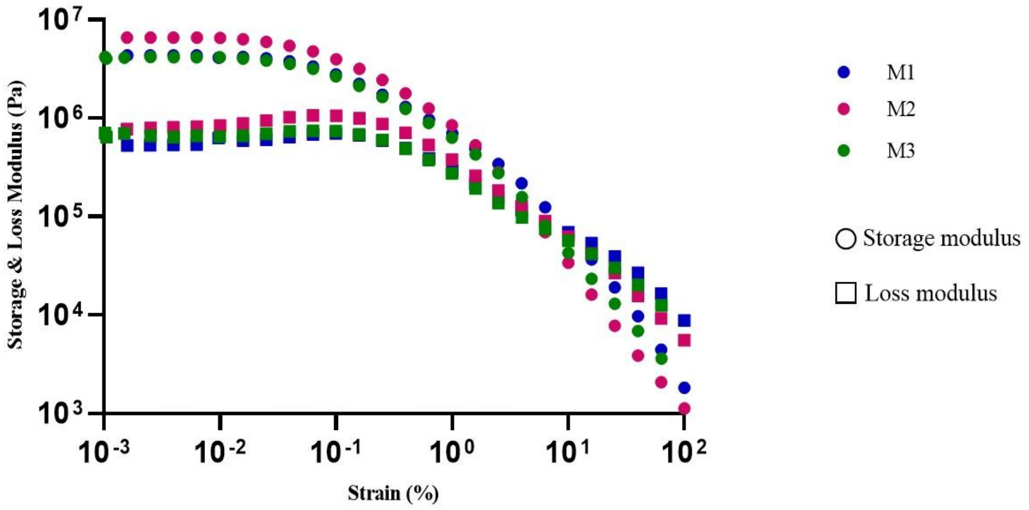


Figure 3. Amplitude sweeps of three margarines (M1, M2, M3) produced with slightly different processing conditions. Measurements were performed at 18°C.

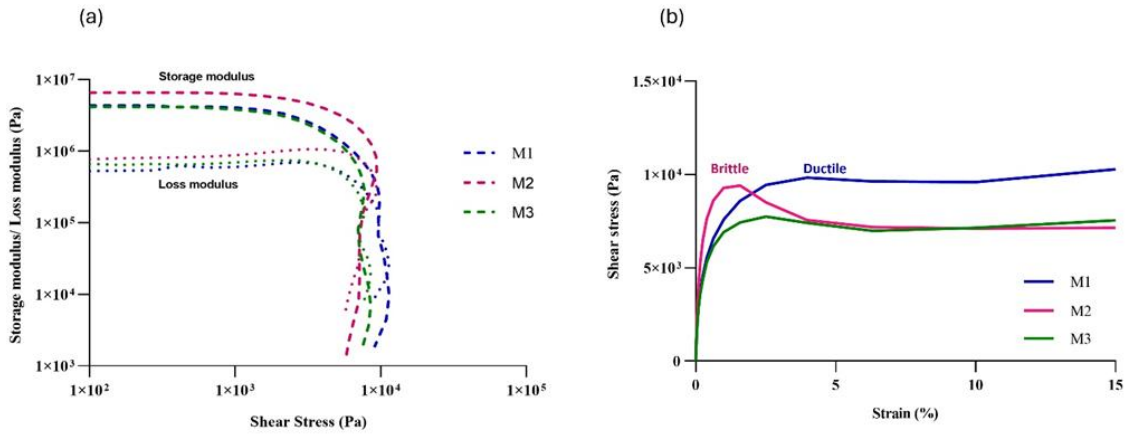


Figure 4. (a) Storage and loss modulus against shear stress, & (b) Shear stress against shear strain – ductile and brittle characteristics of margarines (M1, M2, M3) produced with slightly different processing conditions. Measurements were performed at 18°C.

To understand the nonlinearity at larger strain amplitudes, elastic Lissajous-Bowditch (L-B) stress-strain outputs are plotted (Fig. 5). With amplitude strain levels exceeding 0.10%, the change in shapes, area and shift from y-axis of the elastic L-B plots became prominent. At strain amplitudes surpassing 0.30%, M1 displayed a more elliptical shape compared to M3, while M2 already was getting parallel to the x-axis. At higher amplitude strain (at 1%) M1 shows less deviation from y-axis which indicates less phase lag between stress and strain amplitude, compared to M2 and M3. Additionally, the enclosed area (shape) of the elastic L-B plots at a strain of 10% suggests storing more energy elastically and recovering more upon unloading. Dynamic viscosities at minimum (η'_m) and large (η'_L) strain rates are shown in Fig.6 (a) & (b), respectively. Significant differences among the margarines became apparent as the strain exceeds 0.1%. From the plots, it can be inferred that M1 is relatively more viscous at higher strains than M2 and M3. The onset of viscous moduli drop of M2 was observed to be earlier than that of M1 and M3, indicating potential shear-thinning. M1 shows a higher resistance to shear thinning behavior compared to M2. In this case, the deformation contribution was clear from the viscous components. These findings also align with the findings of (Macias-Rodriguez & Marangoni, 2018a). Pronounced shear thinning behavior can help in lamination, however, very high early shear thinning behavior can also impact the integrity of the layer's formation in the puff-pastry.

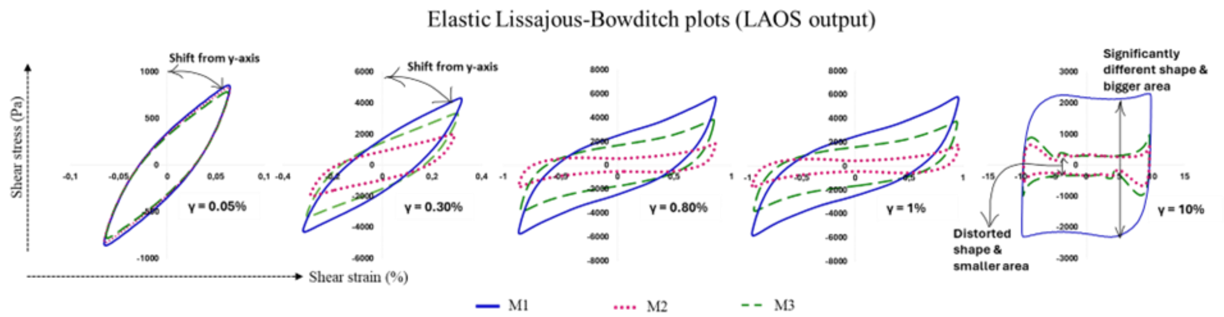


Figure 5. LAOS study at a range of amplitude strain (0.05% to 10%). Output is shown in the form of Lissajous-Bowditch curves. Measurements were performed at 18°C.

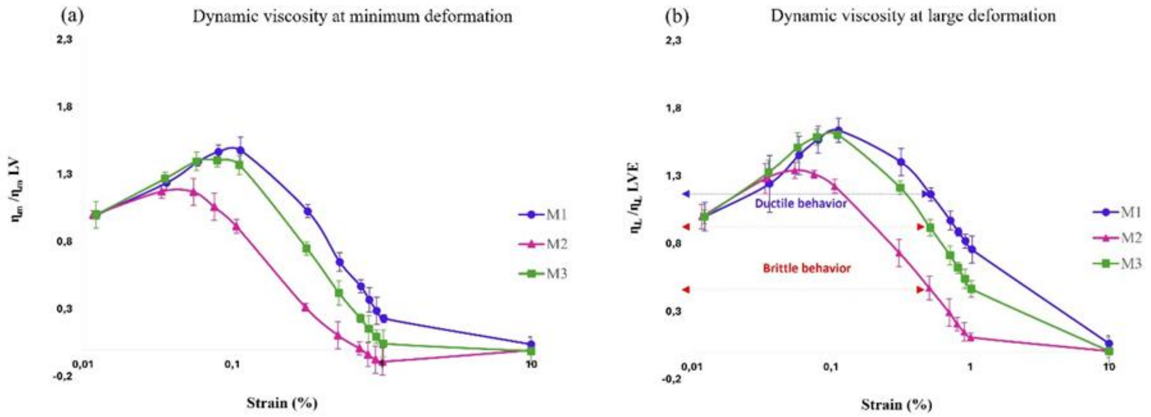


Figure 6. Local dynamic viscosity normalised with the viscosity at linear viscoelastic region (a) at minimum amplitude strain, & (b) at large amplitude strain. Output from the LAOS study for the viscous component. Measurements were performed at 18°C.

4.3. Puff pastry baking performance

The baking performance revealed that puff pastries baked using M1 exhibited an average height of 6.4±0.3cm, puffs made with M3 attained 4.5±0.3cm, and M2 resulted in the least rise of 3±0,1cm. M1 displayed a notably high rise, followed closely by M3, while M2 exhibited the least rise in puff pastry through which the plastic behavior of the used margarines can be confirmed (Fig. 7).

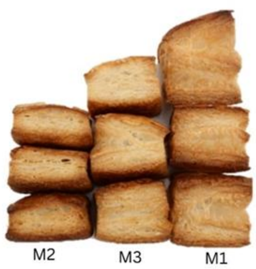


Figure 7. Puff pastry baking performances of margarines (M1, M2, M3) produced with slightly different processing conditions.

Discussion

While hardness, SFC and rheological measurements predicted similar baking performance of the margarines M1 and M2, discrepancies were observed for M3. Specifically, the thumb test suggested M3 had plastic properties like M1, while hardness and SFC values aligned more closely with M2. However, rheological tests (SAOS & LAOS) revealed that M3 exhibited viscoelastic properties more akin to M1 in SAOS and M2 at higher strain amplitude in LAOS. Ultimately its baking performance showed a medium rise range compared to M1 and M2. These findings underscore the limitations of relying solely on subjective or simplified measures and emphasize the crucial role of rheological analysis in providing a comprehensive assessment of margarine functionality, particularly for predicting complex behavior like baking performance.

Case study II

In the second case study, three different maturation temperatures (14°C, 18°C, 22°C) were applied on M1 and M2 margarine, reported in case study I. These two margarines were selected to understand if maturation temperature can improve their viscoelastic properties and if any of the above-utilized methods can differentiate their viscoelastic properties. In the end, puff pastry was baked to confirm the performances of the margarines.

4.4. Sensorial and physical properties assessment (Thumb test, Hardness, SFC)

Thumb test evaluated that M1, when matured at 18°C (hereafter referred to as M1-18) and 22°C (M1-22), exhibited more plasticity compared to when matured at 14°C (M1-14), which was classified as having medium plasticity (Figure 8a). For margarine, M2, very low plastic properties were predicted when matured at 14°C (M2-14) and low plastic characteristics when matured at 18°C (M2-18). However, plasticity improved to medium when matured at 22°C (M2-22). Based on the evaluations, the thumb test predicted M1-22 would behave the best, followed by M1-18 and both were expected to have a baking performance better than M1-14. For M2, the prediction was on similar lines; M2-14 was expected to perform poorly as compared to M2-18 and M2-22 with M2-22 being the best among M2 margarines.

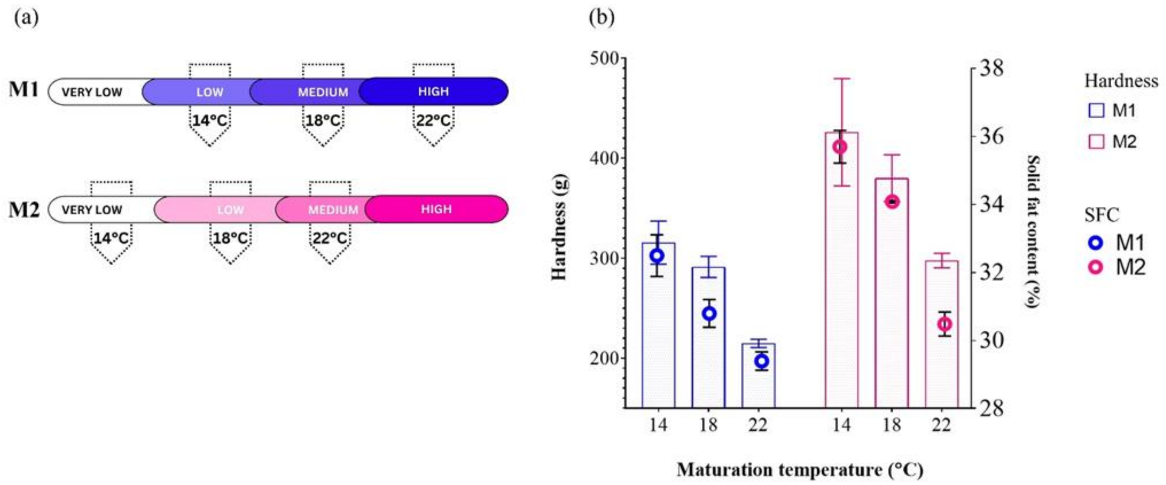


Figure 8. (a) Thumb test, & (b) Hardness and SFC of margarines (M1, M2) after application of three maturation temperatures (14°C, 18°C, 22°C). Measurements were performed at 18°C.

Hardness and solid fat content (SFC) were measured for all margarines (Fig. 8b). It was noted that margarine matured at low temperature showed higher hardness and SFC, while matured at high temperature showed lower hardness and SFC. When margarine matured at 14°C, the product exhibited higher hardness and low plastic properties compared to the product matured at 22°C. The product remained in the medium range of hardness and plastic properties when matured at 18°C. Additionally, hardness was measured after 15 days of production for this case study to understand if any indication of the processing conditions and the maturation effect could be noticed. While measuring hardness, the trendline of the force was noticed behaving irregularly with an increase in the penetration level of the probe for M2; however, M1 showed no irregularity (Fig. 9a). It was observed that for M1, when matured at all three different temperatures, the trendline was smoother compared to M2. However, the force trendline for M2-14 and M2-18 exhibited a rough inclination, potentially indicating a tendency toward a brittle product (Cavillot et al., 2009; Danthine & Deroanne, 2003). On the contrary, M2-22 has shown a smoother line, indicating that the product behaves more ductile with increased temperature. Additionally, the hardness of M1 after 15 days of production remains the same as during month 1 (Fig. 9b) however, the hardness of M2 increased significantly from day 15 to month 1. It can be further inferred that M1 was processed in a manner that led to an initiation of crystallization during the process; however, for M2, insufficient or slow cooling led to post-hardening during its storage. Although these margarines have the same formulation, differences in the cooling and shear rate could potentially have induced different crystal arrangements and led to varied mechanical properties (Miskandar et al., 2005). Additionally, from the standard deviation reported in hardness measurement of M2, M2-14 has the highest standard deviation followed by M2-18 and least deviation for M2-22. The standard deviation of hardness might be indicating the heterogeneous distribution of fat crystals in the margarine.

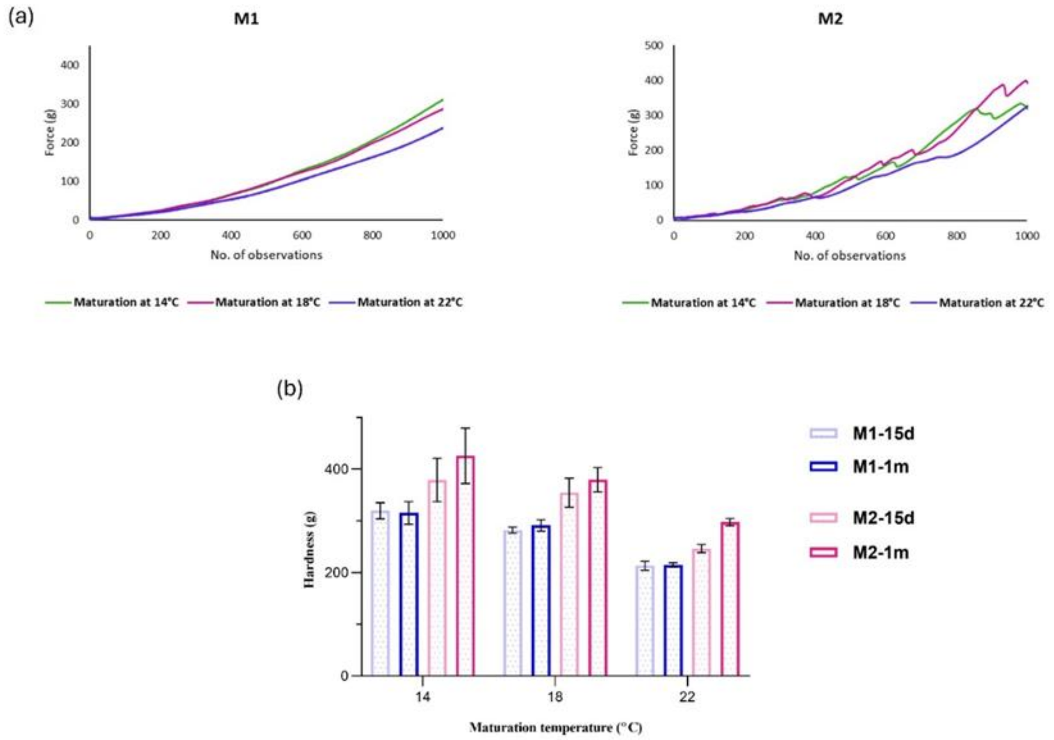


Figure 9. (a) Force trendline observed during hardness measurement after 15 days of production, & (b) Hardness measurements after 15 days (M1-15d & M2-15d) and 1 month (M1-1m & M2-1m) of production. Measurements were performed at 18°C.

Both physical and sensorial assessment predicted similar trends in the baking performances of margarines (M1-22 > M1-18 > M1-14 and M2-22 > M2-18 > M2-14). However, the baking results (Fig. 14(a)) demonstrated otherwise indicating that these assessments lack sufficient insight in the viscoelastic and plastic behaviors of the margarines.

4.5. Rheological tests

Small amplitude oscillatory shear (SAOS) tests were performed to identify the LVR (linear viscoelastic region) of M1 and M2 (Fig. 10). M1-22 exhibited lower storage and loss moduli compared to M1-14 and M1-18. However, the LVR for M1 remains identical. For M2 margarines, maturation temperature showed slightly different results for the LVR. M2-18 showed an early deviation in loss modulus indicating onset of nonlinearity as compared to M2-14 and M2-22.

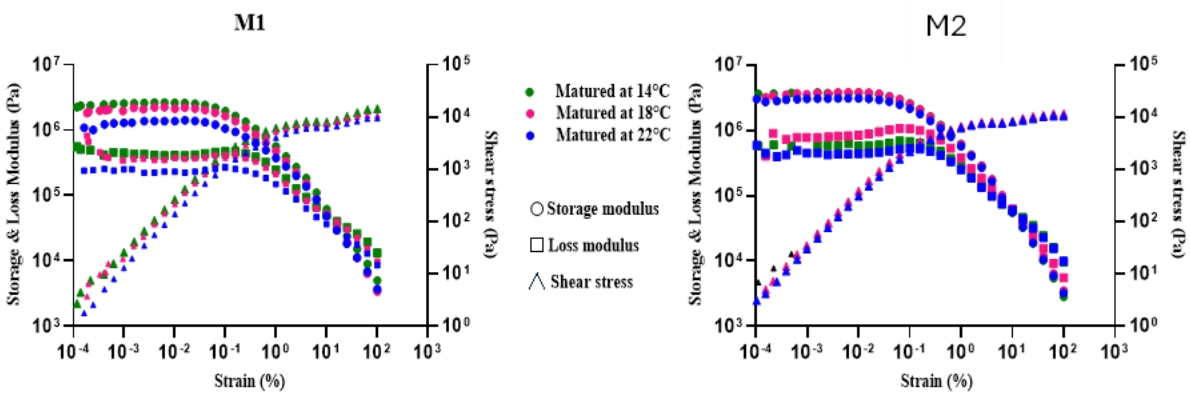


Figure 10. Amplitude sweeps of margarines (M1, M2) after application of three maturation temperatures (14°C, 18°C, 22°C). Measurements were performed at 18°C.

Shear stress versus strain data was plotted for M1 and M2 (Fig. 11). For M1, no steep slope was observed, and all three differently matured margarines showed ductile properties. However, for M2 margarines, the results differed based on their maturation temperatures. M2-18 showed a steeper local slope followed by a drop, as was observed for M2 in case study I, indicating potential brittle behavior (Macias-Rodriguez & Marangoni, 2018b). The amplitude sweep showed certain differences between the differently matured margarines which indicate potential differences in their viscoelastic properties. However, this analysis is not sufficient to predict the baking performance.

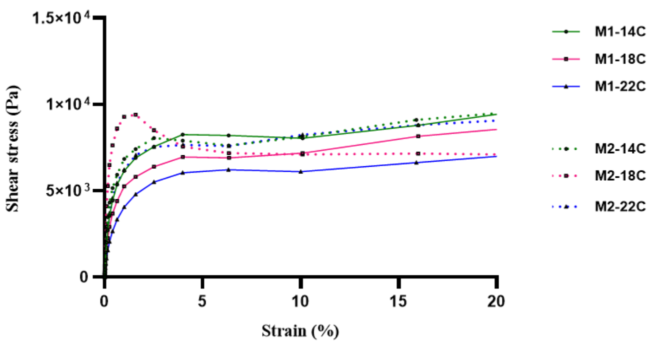


Figure 11. Shear stress against shear strain – ductile and brittle characteristics of margarines (M1, M2) matured at three different maturation temperatures (14°C, 18°C, 22°C). Measurements were performed at 18°C.

According to the large amplitude oscillatory shear (LAOS) output, at lower amplitude strain of 0.50% (Fig. 12a), M1 margarines matured at different temperatures showed overlapping Lissajous-Bowditch (L-B) loops. At 1% strain, a significant change in shape was observed. However, all three differently matured margarines of M1 (14°C, 18°C, 22°C) showed similar L-B loops of overlapping shapes. At large strain amplitude (10%), M1-22 shows a greater area enclosed under the elastic L-B loop than M1-14 and M1-18. Larger enclosed areas in the elastic L-B loops are occurring as the margarine is attaining a constant stress over a range of strain amplitude which generally is seen for a product with high plastic behavior (Donley et al., 2020; Macias-Rodriguez et al., 2018). However, the area under the L-B loops can be attributed more towards energy storage and dissipation than the confirmation of plasticity. Based on the dynamic viscous component response (Fig. 12b), M1-18 was seen to experience a relatively early onset of viscous decay which indicates that it transitions to a more fluid-like state at a much lower amplitude strain compared to M1-14 and M1-22. This also suggests that M1-18 is less likely to maintain its structure at higher amplitude strain. M1-14 & M1-22 indicate a later onset of viscous behavior which could help them hold their elastic properties for a longer time. However, the global elastic and viscous component provides information often derived from linear viscoelastic models and may not be sufficient to characterize the nonlinear rheological response of the material, particularly at higher strain amplitudes. According to the observations (Fig, 12 d, e), the third to first harmonic ratio of elastic (e3/e1) and viscous (v3/v1) components of M1 margarines matured at all three temperatures show a similar trend. The higher harmonics of the elastic component show dominance with increasing amplitude strains. However, the viscous components show comparatively less dominance in the nonlinear region. Additionally, G_L-G_M/ G_L plots were analyzed to characterize the margarines for their nonlinear elastic behavior which indicates a higher value at higher amplitude strain. This can be inferred as a strain stiffening behavior of the product. However, all three margarines seem to exhibit a similar behavior (Fig. 12c). According to these results, it will be reasonable to predict that at higher strain amplitude, all three margarines of M1 will behave similarly in baking. With this, it was interpreted that M1 (14°C, 18°C, 22°C) exhibits pronounced strain stiffening behavior as a large rectangular area in stress-strain Lissajous-Bowditch (L-B) loops and a strong nonlinear elastic component at higher harmonics was observed. However, the area under the elastic L-B plots (stress versus total strain) signifies energy dissipation and cannot directly quantify energy storage, which is essential to understand the elastic behavior. Elastic energy storage can be determined more precisely by calculating the recoverable strain component from the total strain. For this purpose, additional strain recovery tests have been added to confirm the interpretations which is discussed further in this section.

Conversely, M2 (Fig. 13a, b) displayed distinct behavior under different maturation conditions from a strain of 0.30% and above. M2-14 and M2-22 exhibit relatively similar elastic and viscous L-B loop shapes, suggesting similar viscoelastic properties. M2-18 shows a more distorted elastic L-B shape with a reduced area under the loop indicating strong potential nonlinear behavior. Moreover, the viscous L-B (Fig. 13b) shows a smaller loop area for M2-18 with an increase in the amplitude strain. The reduction in area of the viscous L-B loop signifies less energy dissipation, often correlating fluid-like behavior under higher strain. Further, G_L-G_M/ G_L (Fig. 13d) plots were analyzed to understand their nonlinear behavior, which indicates that M2-22 exhibits a stronger nonlinear elastic response, compared to M2-18 and M2-14. Additionally, M2-22 showed a higher strain stiffening character compared to M2-14 and M2-18. M2-18 shows a sudden decay in nonlinear elastic properties at higher strain amplitudes indicating the inability to store energy elastically. These findings also align with the interpretations made from the L-B plots. According to the dynamic viscosity analysis (Fig, 13c), M2-14 and M2-22 show a similar trend, a relatively later decay in viscosity, especially M2-22. Whereas M2-18 shows an early onset which indicates a less solid-like structure at lower amplitude strain. It is possible that M2-18 shows a higher shear thinning property compared to M2-14 and M2-22. The higher harmonics from Fourier transformation of elastic component (e3/e1) show a deviation in the behavior of M2-18 as compared to M2-14 and M2-22 with increasing strain amplitudes (Fig. 13e). For the viscous component (v3/v1) (Fig. 13f) M2-18 shows an onset of early decay at higher strain amplitudes. With this, it would be reasonable to predict that in the nonlinear region M2-18 shows a higher shear thinning behavior compared to M2-14 and M2-22. This can indicate that at higher strain amplitudes, M2-18 is deforming and transitioning to fluid-like earlier and faster than M2-14 and M2-22. Based on the large amplitude oscillatory shear (LAOS) results of M2, it could be predicted that the baking performance of M2-18 will be significantly poorer than M2-14 and M2-22.

Recent studies have described an excellent method to understand the plasticity of the product by coupling recovery rheology with LAOS methodology (Donley et al., 2020; Lee et al., 2019). These studies provide deeper insights to understand further the output of LAOS and the time-dependent factors. In our study, we created a similar strain recovery test complementary with LAOS as described in section 3.4.4. Two distinct margarines M1-18 and M2-18 were chosen for this study (Fig.15). It was observed that both margarines show a decay in recoverable strains with increasing strain amplitudes. However, M2-18 shows a faster decay, and the onset could be spotted post the amplitude strain of 0.80%, as compared to 1.50% for M1-18. M1-18 showed a larger area under the elastic L-B loop and a higher strain recovery at 10 % strain amplitude compared to M2-18. This behavior can be attributed to the margarine's (M1-18) ability to store energy elastically due to the significant presence of solid-like structure. This balance of elastic, viscous and plastic properties of M1-18 ensures a robust ability to evenly spread and at the same time hold its shape and structure within the dough layers during lamination. This indicates the presence of a sufficiently stronger fat crystal network in M1-18 which does not melt or collapse abruptly during lamination and baking. In contrast, for M2-18 the early decay in strain recovery combined with the distorted and smaller area under the L-B loops suggest an early transition to a fluid like behavior. An early fluid like behavior of margarine can indicate collapsing of fat crystal networks which help to hold the structure. This leads to weakening of certain areas of the dough due to layers sticking to each other disrupting uniformity necessary for expansion during baking. Previously, it was indicated in the literature, that lamination margarines generally show a lower strain recovery compared to other margarines (all-purpose or cake) (Macias-Rodriguez et al., 2017). However, when two lamination margarines are compared, it is worth noting that a certain amount of recovery is required to hold the structure during lamination which was seen for M1.

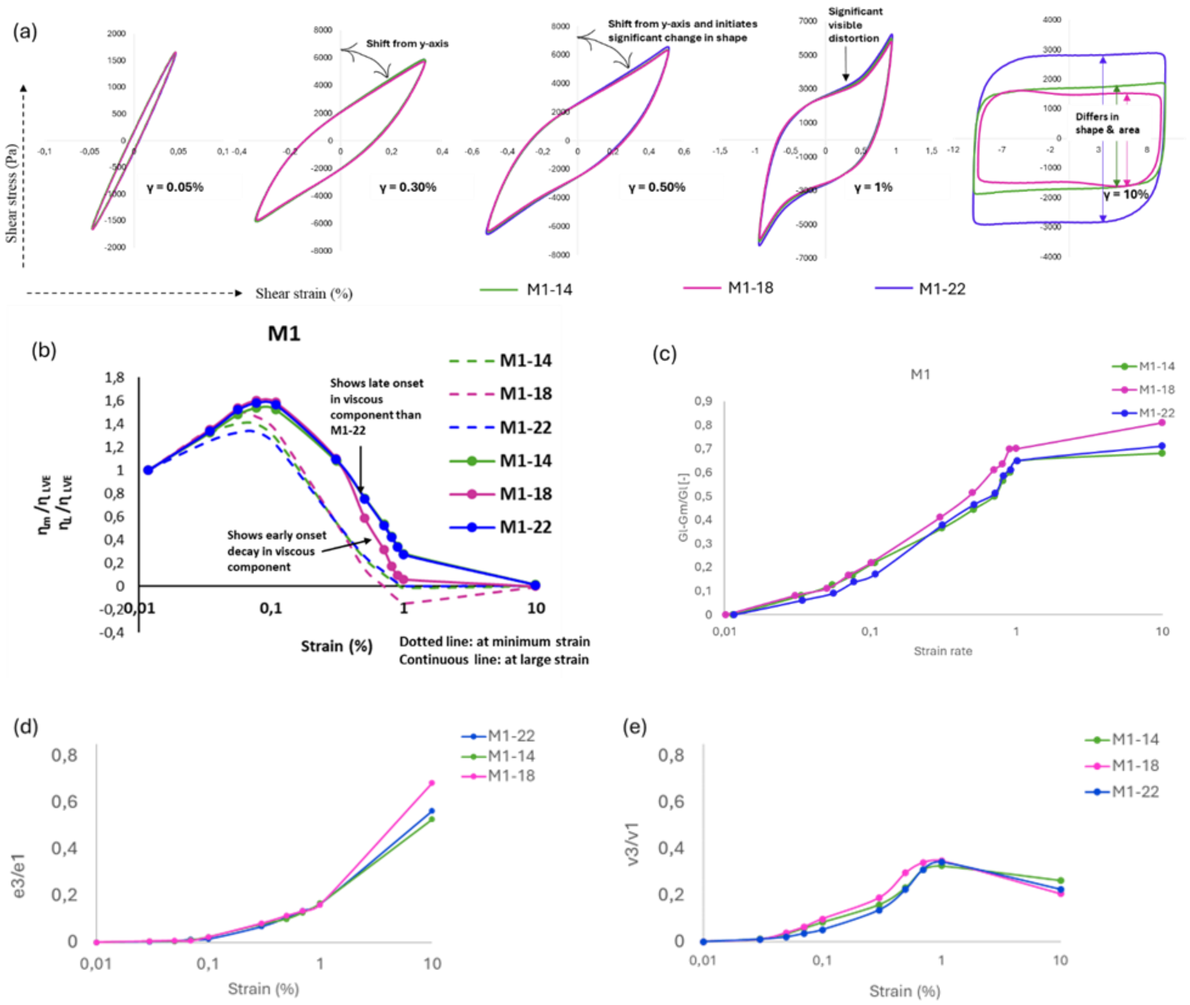
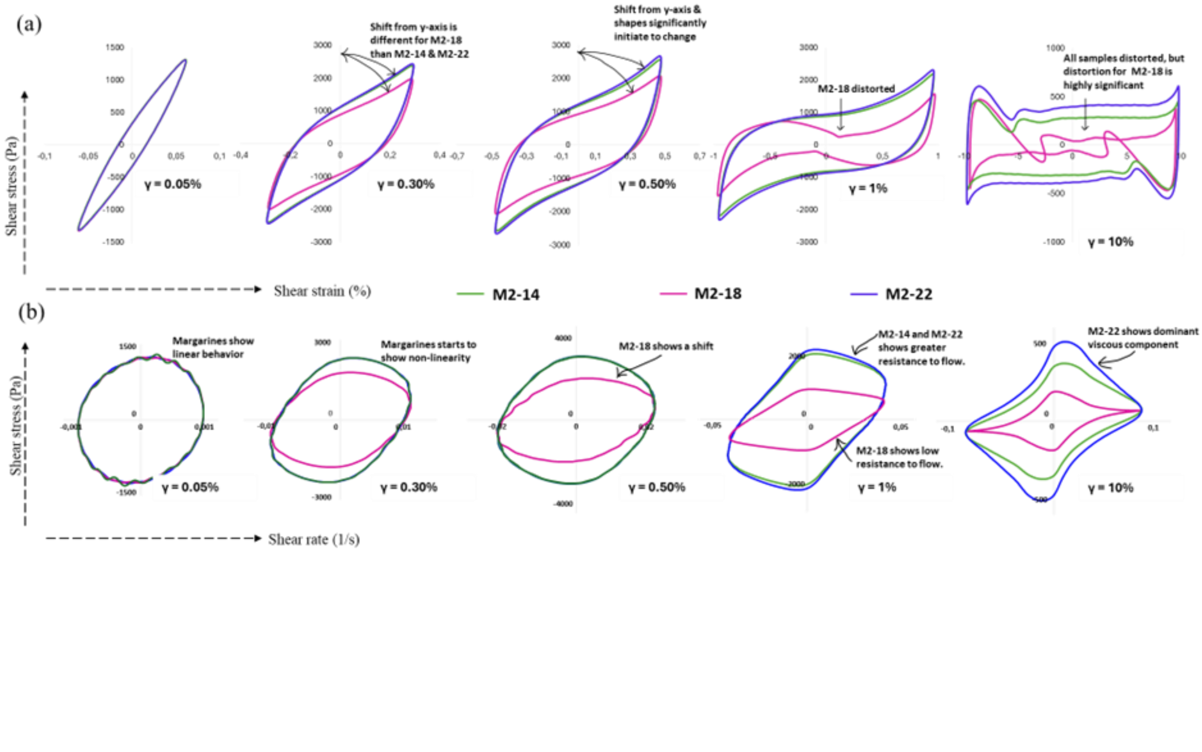


Figure 12. M1: LAOS study at a range of amplitude strain. (a)The elastic output is shown in Lissajous-Bowditch curves, & (b)local dynamic viscosity normalised with the viscosity at the linear viscoelastic region at minimum and large amplitude strain. (c)Normalized difference between local elastic measures: minimum strain (G_M') and large strain modulus (G_L') as a function of amplitude strain input at ω =3.6 rad s^{-1}. (d, e) Third-order harmonics ratio for elastic e3/e1 and viscous υ3/υ1 Chebyshev coefficients as a function of amplitude strain at ω =3.6rads^{-1}. Measurements were performed at 18°C.



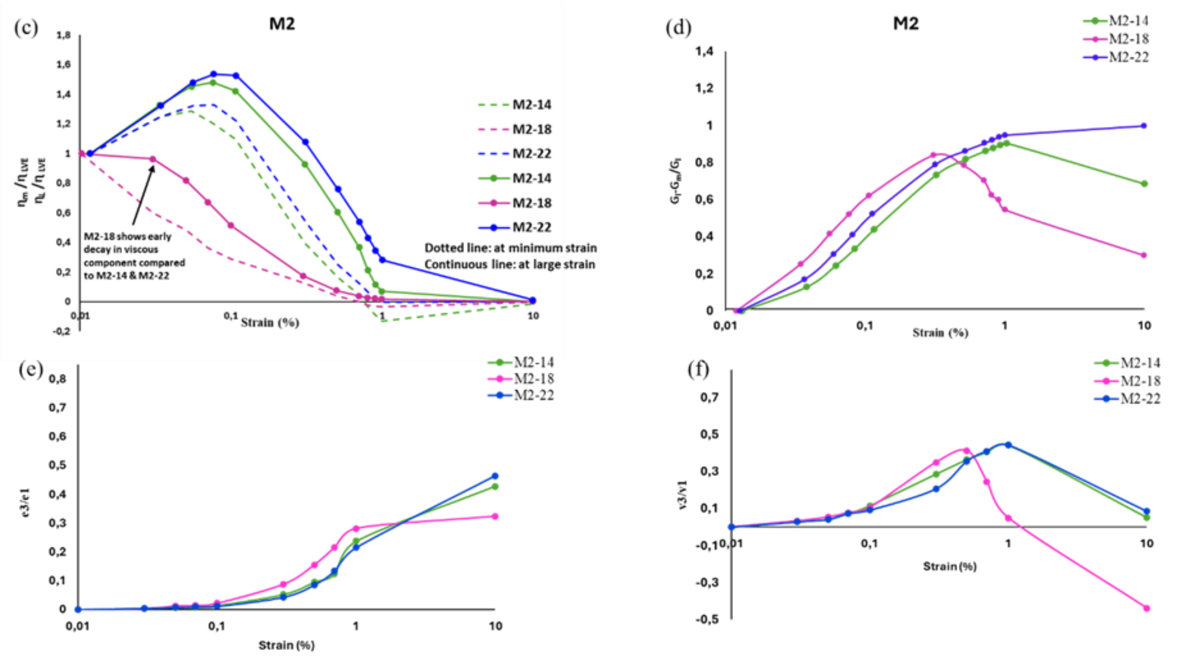


Figure 13. M2: LAOS study at a range of amplitude strain. (a, b) The elastic and viscous output is shown in Lissajous-Bowditch curves, & (c) local dynamic viscosity normalised with the viscosity at the linear viscoelastic region at minimum and large amplitude strain. (d) Normalized difference between local elastic measures: minimum strain (G_M') and large strain modulus (G_L') as a function of amplitude strain input at ω =3.6 rad s^{-1}. (e, f) Third-order harmonics ratio for elastic e3/e1 and viscous υ3/υ1 Chebyshev coefficients as a function of amplitude strain at ω =3.6rads^{-1}. Measurements were performed at 18°C.

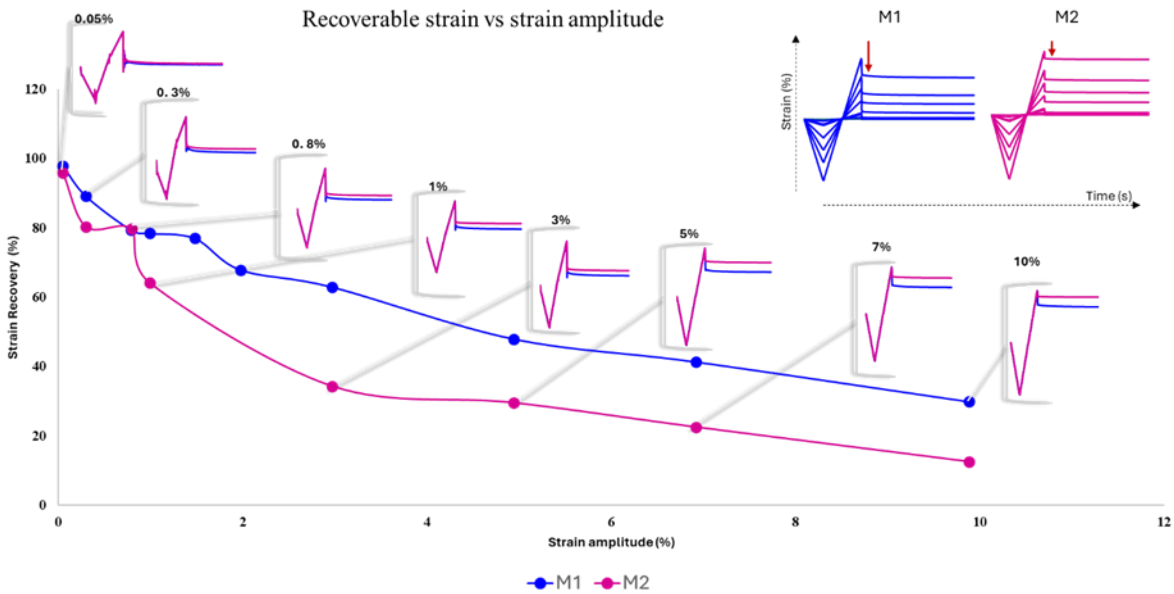


Figure 15. Recoverable strain plotted against their strain amplitude for M1 and M2 (M1-18 and M2-18).

4.6. Puff pastry baking performance

Figure 14a shows the puff pastries obtained after baking. The rise in puff pastry with M1 margarines matured at different temperatures was not significantly different. However, M2 exhibited variations across the different maturation temperatures. Specifically, margarines M2-14 and M2-22 resulted in a desirable increase in puff pastry rise compared to M2-18. Furthermore, volume measurements revealed significant differences between M2-18 and M2-

22. The average volume of puff pastries for each margarine type also differed significantly between M2-14 and M2-18, as well as between M2-18 and M2-22. In addition to the volumes, the heights of the puff were also measured (Fig.14b), where M1-14, 18, and 22 were reported to be 6.3±0.2cm, 6.4±0.4cm, 6.3±0.1cm, respectively. For M2, 5.8±0.2cm, 3.4±0.1cm & 6.2±0.2cm for 14°C, 18°C and 22°C maturation, respectively.

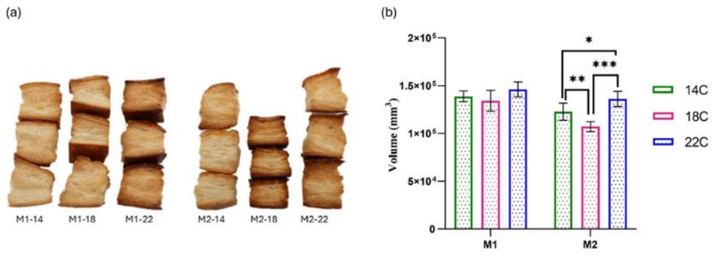


Figure 14. (a) Puff pastry baking performances, & (b) volume of margarines (M1, M2) after application of three maturation temperatures (14°C, 18°C, 22°C). Stars in the figure represent significant differences ($p < 0.05$) between the margarines (M2) subjected to different maturation temperatures.

5. Discussion

When the large amplitude oscillatory shear (LAOS) outputs were compared between the differently matured margarines of M1 and M2 (14, 18, 22), both seemed to undergo a shear thinning behavior ($v3/v1 < 1$) at higher amplitude strain. However, the magnitude of shear thinning behavior is different for M1-14, M1-18, M1-22 compared to M2-14, M2-18, M2-22. Overall, at higher harmonics which explain the nonlinear deformation M1-14, M1-18 and M1-22 show a similar behavior. This indicates that the processing conditions applied to M1 are less sensitive to temperature fluctuation which helps in maintaining similar viscoelastic properties even when matured at different temperatures. This could indicate that this margarine (M1) was produced in a more controlled and with appropriate processing parameters which allowed it to complete its majority of crystallization during the production process.

In contrast, M2-14, M2-18 and M2-22 have shown a high sensitivity to viscous change with increase in amplitude strain. M2-18 were seen to be most sensitive compared to M2-14 and M2-22 as it shows a much drastic change in viscous and elastic nonlinear response at higher amplitude strain. Additionally, M2-18 showed an early onset in strain recovery compared to M1-18. Generally, a balance of strain stiffening and softening behavior is desired for a proper rise of puff pastries. Here, an early strain softening was observed for M2-18 which might not have helped during the lamination, indicating an inappropriate production process leading to a heterogeneous fat crystal network. For M2-14 and M2-22, the shear thinning was not abrupt and much slower and quite like M1. This could be due to the change in temperature during maturation to storage which provided an opportunity of reorganization of fat crystals. M2-18, which is constantly matured and stored at the same temperature, does not undergo a reorganization of crystals. Without a change in temperature, the fat crystals are not subjected to significant thermal stress, which can minimize structural changes too.

Considering the hardness and solid fat content of M2-18 it will be fair to interpret that the product is hard and resistant to laminating in some regions and could be flowing in other regions (shear-thinning), thus, having an overall uneven distribution. This uneven distribution could be caused due to the processing parameters applied during production. The uneven distribution of weak and strong network structure of fat network can also be confirmed when the puff pastry was baked in case study I, M2 showed 3cm of height and in case study II, M2-18 showed 3.4cm of height. The height and volume of the puff pastry were different, however, poor when compared to others. Generally, uniform fat crystal networks as in the case of M1 are expected to create even layers during lamination and allow better steam release during the baking. Due to the uneven distribution of fat network in M2-18, the ability to entrap the steam during baking is inconsistent and overall low. This further leads to poor separation of the layers and results in poor lift and flat pastry.

6. Conclusion

This study investigated rheological methods (especially large amplitude oscillatory shear - LAOS) that can predict the performances of lamination margarines based on their viscoelastic properties. The viscoelastic properties of lamination margarine with slightly different processing conditions could be differentiated using SFC, hardness, and rheology as instrumental measurements and the subjective thumb test. When two differently processed margarines were subjected to three different maturation temperatures, the subjective thumb test, hardness measurements, and SFC indicated differences, however, unable to predict the baking performance which relies on crucial viscoelastic and plastic properties of margarines. In contrast, rheological tests were able to predict the baking performance more accurately and provide deeper insight on the behavior of the margarines during lamination and baking operations.

Based on the obtained results, it could be beneficial for edible fat industry to apply non-linear rheological approach, specifically LAOS coupled with recovery rheology which enable a close prediction of the performances of lamination margarine for puff pastry baking.

The mechanical study demonstrates enhanced precision in predicting and analyzing the viscoelastic properties of similar laminated margarines compared to previous investigations, even when subtle differences exist. Integrating this testing method as a quality control parameter within the industry offers several advantages. Firstly, it facilitates improved control over processing and post-processing conditions. Secondly, it enables proactive identification and mitigation of non-compliance during production by allowing for real-time quality assessment against desired specifications. Finally, by characterizing the viscoelastic and plastic properties of subtly varying laminated margarines, this approach contributes to delivering consistent and high-quality products to consumers.

In this study, the LAOS and complementary strain recovery tests were performed separately however, they can be combined into a single sequence (Donley et al., 2020) to ease integration into industrial quality checks to reduce evaluation time and to better quantify products viscoelasticity and plasticity. Additionally, future studies can focus on quantitative predictive modeling to establish a relationship between the rheological parameters and the final output of the product application (puff pastry baking).

Abbreviations and symbols:

CM: Cake margarine

LAOS: Large amplitude oscillation shear

M1, M2, M3: Margarine samples of the same composition produced using slightly different processing conditions

M1-14, M1-18, M1-22: Margarine (M1) samples of the same composition and processing conditions but matured at different temperatures (at 14°C, 18°C, 22°C)

M2-14, M2-18, M2-22: Margarine (M2) samples of the same composition and processing conditions but matured at different temperatures (at 14°C, 18°C, 22°C)

NMR: Nuclear magnetic resonance

PPM: Puff-pastry margarine

SAOS: Small amplitude oscillation shear

SFC: Solid fat content

Mm: Millimeter

Pa: Pascal

η'_m: Dynamic viscosity at minimum strain

η'_L: Dynamic viscosity at minimum strain

η'_m / η_{LVE}: Dynamic viscosity at minimum strain normalized with the viscosity at the linear visco-elastic region

η'_L / η_{LVE}: Dynamic viscosity at large strain normalized with the viscosity at the linear visco-elastic region

γ: Amplitude strain

ω: Frequency

t: Time

$\dot{\gamma}$: Strain rate

Sin: Sine function

Cos: Cosine function

$\sigma(t; \omega, \gamma_0)$: The signal at time t

γ_0: Strain

e3/e1: Ratio of the third-order harmonics to first order in elastic component

$\upsilon 3/\upsilon 1$: Ratio of the third-order harmonics to first order in viscous component

G_L': Elasticity at large amplitude strain

G_M': Elasticity at minimum amplitude strain

N: force expressed in 'Normal'

7. References

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