

Article

Extending the Physical Functionality of Bioactive Blends of *Astrocaryum* Pulp and Kernel Oils from Guyana

Laziz Bouzidi ¹, Shaveshwar Deonarine ¹, Navindra Soodoo ¹ , R. J. Neil Emery ² , Sanela Martic ³ and Suresh S. Narine ^{1,*}

¹ Centre for Biomaterials Research, Departments of Physics & Astronomy and Chemistry, Trent University, 1600 West Bank Drive, Peterborough, ON K9L 0G2, Canada; lazizbouzidi@trentu.ca (L.B.); shaveshwardeonarine@trentu.ca (S.D.); navindrasoodoo@trentu.ca (N.S.)

² Department of Biology, Trent University, 1600 West Bank Drive, Peterborough, ON K9L 0G2, Canada; nemery@trentu.ca

³ Department of Forensic Science, Trent University, 1600 West Bank Drive, Peterborough, ON K9L 0G2, Canada; sanelamartic@trentu.ca

* Correspondence: sureshnarine@trentu.ca; Tel.: +1-705-748-1011; Fax: +1-705-750-2786

Abstract: Natural lipids with nutritional or therapeutic benefits that also provide desired texture, melting and organoleptic appeal (mouthfeel, skin feel) are difficult to procure for the food and cosmetics industries. Natural *Astrocaryum* pulp oil (AVP) and kernel fat (AVK) from Guyana were blended without further modification to study the potential of extending the physical functionality of the blends beyond that of crude AVK and AVP. An evaluation of non-lipid components by ESI-MS indicated twenty-four (24) bioactive molecules, mainly carotenoids (90%), polyphenols (9%) and sterols (1%) in AVP, indicating important health and therapeutic benefits. Only trace-to-negligible amounts of these compounds were detected in AVK. The thermal transition phase behavior, solid fat content (SFC), microstructure and textural properties of five AVP/AVL blends were used to construct phase diagrams of the AVK/AVP binary system. Binary phase diagrams constructed from the cooling and heating DSC thermograms of the mixtures and description of the liquidus line indicated a mixing behavior close to ideal with a tendency for order, with no phase separation. Melting onsets, solid fat content and measurements of solid-like texture all predictively increased with increasing AVK content. The descriptive decay parameters obtained for SFC, crystal size, hardness, firmness and spreadability were similar and predictive and indicate the way the binary system structure approaches that of a liquid or a functional solid. The bioactive content of the blends was accurately calculated; the work provides a blueprint for the blending of AVP and AVK to deliver targeted bioactive content, stability, spreadability, texture, melting profile, organoleptic appeal and solid content. SFCs at 20 °C ranged from 9.1% to 39.1%, melting onset from −17.5 °C to 27.8 °C, hardness from 0.1 N to 3.5 N and spreadability from 3.3 N·s to 147.1 N·s; indicating a useful dynamic range of physical properties suitable for bioactive oils to bioactive butters.

Keywords: *Astrocaryum*; Guyana; cosmetics; blending; thermal behavior; textural analysis; bioactive; solid fat content



Citation: Bouzidi, L.; Deonarine, S.; Soodoo, N.; Emery, R.J.N.; Martic, S.; Narine, S.S. Extending the Physical Functionality of Bioactive Blends of *Astrocaryum* Pulp and Kernel Oils from Guyana. *Cosmetics* **2024**, *11*, 107. <https://doi.org/10.3390/cosmetics11040107>

Academic Editor: Vasil Georgiev

Received: 20 May 2024

Revised: 11 June 2024

Accepted: 18 June 2024

Published: 26 June 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The demand for natural, bioactive and environmentally friendly products is rapidly growing, driven by rising public interest in sustainability, concerns regarding adverse health effects of synthetic materials, and environmental damages caused by the production of conventional chemically produced materials [1]. Alternatives to traditional means of production including green and ecological approaches and the use of naturally sourced materials are correspondingly being increasingly explored. The pharmaceutical, cosmetic and food sectors, in particular, are actively seeking alternatives to chemically synthesized

ingredients, particularly lipid-based materials. Natural lipids, including those from so-called exotic sources, are pursued as healthier alternatives. The goal is to tailor physical functionality in products while retaining bioactive and green characteristics. The cosmetic industry is actively researching the replacement of potentially harmful conventional cosmetics with products based on natural materials [2]. The food sector is also investing significant resources to achieve healthier and more functional products

Lipids extracted from oleaginous exotic plants, such as the oils and fats from tropical fruits and seeds, potentially offer attributes such as enhanced nutrition and active therapeutic benefits [3], but must be researched to ensure that they can also provide the physical functionality required in cosmetic and food products. Tropical oleaginous species are gaining increasing industrial and research interest particularly because of their high lipid content and the substantial and beneficial bioactive components of their fruits [3]. *Astrocaryum vulgare* (AV, awara in Guyana and tucumã do Amazonas in Brazil) is a species of the *Arecaceae* family native to the Amazonian region and Guiana shield that deserves special attention [4]. The AV fruit's fibrous mesocarp (pulp) contains carbohydrates (7–20%), fibers (11–30%) and lipids (25–50%) and relatively small amounts of proteins (3–10%) and minerals (2–3%) [5–7]. Their lipids possess distinctive bioactive and nutritional properties that can potentially enhance cosmetic, food and pharmaceutical products [8–10].

AV pulp (AVP) has a yield of 34 *w/w*% oil and AV kernel (AVK) has a yield of 27 *w/w*% fat, on a dry basis [11]. AVP produces an oil with a high concentration of unsaturated fatty acids (65–75%) [12], and AVK produces fats of high lauric acid content (45–50%) [13]. AVK lipid is a fat consisting of medium-chain triacylglycerols (TAGs), mainly *propane-1,2,3-triyl tridodecanoate* (LLL) (30.1%), *3-(tetradecanoyloxy)propane-1,2-diyl didodecanoate* (LLM) (26.10%), *3-(decanoyloxy)propane-1,2-diyl didodecanoate* (LLC₁₀) (12.0%), *3-(octanoyloxy)propane-1,2-diyl didodecanoate* (LLC₈) (10.5%) and *3-(dodecanoyloxy)propane-1,2-diyl ditetradecanoate* (MML) (10.0%) and AVP lipid is an oil composed of long-chain TAGs, mainly *2-(palmitoyloxy)propane-1,3-diyl dioleate* (POO) (43.0%), *propane-1,2,3-triyl trioleate* (OOO) (27.9%), *2-(oleoyloxy)propane-1,3-diyl dipalmitate* (POP) (17.3%), *3-(oleoyloxy)propane-1,2-diyl distearate* (SOO) (9.1%) and *propane-1,2,3-triyl tristearate* (SSO) (1.3%) [11].

AVP lipid extract contains high levels of bioactive compounds, particularly carotenoids (122.2–163.7 mg/100 g), sterols, phenolic compounds and α -tocopherol (5.3 mg/100 g) [14,15]. These compounds reportedly impart significant beneficial bioactivity. The bioactive components found in AVP have been demonstrated to impart antimicrobial, antifungal [16], anti-inflammatory [14], antiproliferative [17], cytoprotective [18], skin-protective [8] and antioxidant activity [15,19,20]. Non-lipid bioactive compounds have not been reported in AVK lipid extractions.

AVK lipid extract contains medium-chain fatty acids, making it especially suitable for delivering unique nutrition, flavor and texture in various foods [8,10]. Its moisturizing and emollient capacity can be exploited to produce functional cosmetic products such as lotions and creams [21–23], and it can potentially be safely incorporated in drug formulations and pharmaceutical delivery systems [24,25].

AVK lipid extract can be considered a butter. It has melting and SFC profiles closely resembling those of cocoa butter (CB), the staple lipid ingredient in many food, cosmetics and pharmaceutical formulations. The unique chemical composition [26] of CB results in the development of a crystal structure and microstructure in its solid phase that delivers a preferred physical functionality related to stability, spreadability, texture and mouthfeel [27–29].

AVK lipid extract has a melting point close to CB but higher than the other most-used commercial CB alternatives such as coconut oil (CO), palm kernel oil (PKO) and shea butter (SB) [11,30,31]. CO, PKO and SB are first fractionated, and the higher-melting fractions are used to make CB alternatives (called CB equivalents or CBEs) [32]. AVK fat's sharp melting profile suggests that it would be suitable as a CB replacement in confectionery materials, without the need to first fractionate.

Astrocaryum vulgare's biochemical functions place health-beneficial bioactive compounds in the pericarp but not in the kernel. This would seem to provide a biological design to attract animals that feed on the nutritious and bioactive pulp and distribute the kernel with its hard impenetrable protective "shell" so that the plant proliferates. However, AVP lipid extract is a liquid oil, even at 0 °C. Therefore, there is an opportunity to utilize AVK butter blended with AVP liquid to potentially create a bioactive butter with tailored physical properties in the solid state at useful temperatures. This could potentially lead to a range of natural materials for the food, cosmetic and pharmaceutical industries that impart both desired physical functionality and bioactive content.

Compared to other means of modification such as fractionation, enzymatic or chemical interesterification and hydrogenation, direct blending of fats and oils is the most cost-effective, least destructive and environmentally friendly approach [33]. Direct blending is a straightforward process that involves mechanically mixing fats and oils in a molten state [3]. The incorporation of selected unsaturated TAGs into systems with a high content of saturated TAGs can yield fats with a softer texture, lower melting points and improved plasticity [34]. Similar lauric-rich fats such as palm kernel oil and coconut oil are commonly blended with common unsaturated vegetable oils to make cocoa butter substitutes (CBSs) [35]. Despite completely different TAG compositions, the blends can be directed to exhibit melting points and polymorphism similar to CB such as those formulated by Biswas et al. [36] and Hashem et al. [37] with palm kernel oils and various highly unsaturated vegetable oils such as olive oil and palm oil.

The blends of AVK and AVP lipid extracts studied were formulated with the aim to mimic important fats such as cocoa butter (CB) and shea butter (SB) in terms of physical and functional properties and for suitability as ingredients in food, cosmetics and pharmaceutical applications. Five mixtures were studied ($x_{AVP} = 0.2, 0.4, 0.5$ and 1.0). The bioactive components of the blends were assessed using the relative content determined from the molar concentration of each mixture, and from information derived from electrospray ionization–mass spectrometry (ESI-MS) analysis of the AVP lipid extracts.

The thermal transition behavior, solid fat content (SFC) versus temperature from 5 °C to above the melting point (40 °C) and microstructure of the blends were used to describe the phase behavior of the AVK/AVP binary system. The thermal transition behavior of the mixtures was determined by differential scanning calorimetry (DSC). The liquidus line was established using the offset of melting from the heating thermograms and modeled using the Hildebrand theory and the Bragg–William (BW) approximation [38,39]. The SFC versus temperature curve of the blends was determined by wide-line pulsed nuclear magnetic resonance (p-NMR) measurements and the kinetics of crystallization modeled with the Gompertz model [31,40]. Textural attributes including hardness, firmness, spreadability and adhesiveness were determined using a texture analyzer. The microstructure of the blends was determined using polarized light microscopy (PLM) and related to the thermal transition behavior, SFC and texture. The structure and physical properties of blends were utilized to assess their equivalence with established industrial fats and how closely they mimic physical properties and functions.

2. Materials and Methods

2.1. Materials

2.1.1. Sample Collection, Processing and Handling

Sample AV fruits were handpicked in May 2023 from forests of Guyana; Administrative Regions 1 and 2. Collection, processing and handling of the fruits as well as oil extraction from AVP and AVK were described in detail in our previous publication [11]. In brief, the pulps were separated from the seeds. The kernels were obtained by splitting the seeds with a knife and hammer. Both fresh pulps and kernels were sun-dried under ambient conditions, pulverized to small particles (~10 µm), then stored in sealed Ziploc® bags at room temperature (25 °C). The oils were extracted using mechanical pressing. AVP oil (AVP) was extracted without heating the expeller and AVK fat (AVK) was extracted after

it was preheated to 50 °C for 15 min. The temperature during extraction did not exceed 50 °C for AVP and was between 50 and 80 °C for AVK. It is therefore expected that no loss or alteration of the lipid occurred in both extracts, but some non-lipid components may have been lost in AVK. The oils were immediately stored in glass jars and maintained at 4 °C until the time of analysis.

2.1.2. Preparation of the Blends

Five mixtures of 50 g each were prepared at AVK/AVP molar ratios (x) of 1.0, 0.8, 0.6, 0.5 and 0.4 from melted AVK and AVP (Table 1) according to the average molecular mass of AVK (687.29 g/mol) and AVP (867.99 g/mole) determined from the fatty acid profile of the lipids. The mixtures were blended in conical flasks using a magnetic stirrer (1000 revolutions/min) at a constant temperature of 40 °C for one hour.

Table 1. Molar ratios and masses of AVK fat-AVP oil mixtures.

Mixture	x_{AVP}	Molar Ratio	Mass AVK (g)	Mass AVP (g)	Average Molecular Mass (g)
AVK	0.0 _{AVP}	1.0:0	50	0	687.27
AVK _{0.8} AVP _{0.2}	0.2 _{AVP}	0.8:0.2	38	12	723.41
AVK _{0.6} AVP _{0.4}	0.4 _{AVP}	0.6:0.4	26	24	759.56
AVK _{0.5} AVP _{0.5}	0.5 _{AVP}	0.5:0.5	22	28	777.63
AVK _{0.4} AVP _{0.6}	0.6 _{AVP}	0.4:0.6	18	32	795.70
AVP	1.0 _{AVP}	0:1.0	0	50	867.99

2.2. Methods

2.2.1. Electrospray Ionization–Mass Spectrometry (ESI-MS)

Electrospray ionization–mass spectrometry (ESI-MS) was performed on a Thermo QExactive Orbitrap mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) in the positive ion mode. Samples were injected using a syringe infusion pump (Harvard Apparatus, Holliston, MA, USA) and analyzed using an instrument resolution of 17,500. ESI source temperature was 320 °C and scan rate 12.5 scan/s. Methanol (HPLC grade; VWR, Mississauga, ON, Canada) was used as the source of hydrogen ions, and chloroform (HPLC grade; VWR, Mississauga ON, Canada) was used to dissolve the lipid analyte. Samples (1 ppm wt./v) were dissolved in a 70:30 (v/v) chloroform/methanol solution. The MS data were processed using the Qual Browser tool of Thermo Xcalibur software version 3.1 (Thermo Scientific, San Jose, CA, USA). NIST, Lipid Maps®, MetaboQuest and XCMS online databases were used to identify the molecular ions.

2.2.2. Total Phenolic Content (UV-Vis Spectrophotometry)

Total phenolic content (TPC) was determined using Folin–Ciocalteu’s method [41,42]. An amount of 10 µg of sample oil was dissolved in 1 mL deionized water. The solution (1.0 mL) was then mixed with 2 mL of 20% sodium carbonate (Na₂CO₃) (MilliporeSigma Canada Ltd., Oakville, ON, Canada) in deionized water and 0.5 mL 1 N Folin–Ciocalteu’s phenol reagent (MilliporeSigma Canada Ltd., Oakville, ON, Canada). After incubation at room temperature (20 ± 1 °C) for 1 h, the absorbance at 725 nm against a reagent blank was measured using a UV-Vis spectrophotometer (Cary 60, Agilent Technologies, Santa Clara, CA, USA). The measurements were performed in triplicate. Calibration was performed using gallic acid (HPLC grade; VWR, Mississauga ON, Canada).

2.2.3. Estimation of Total Carotenoid Content (UV-Vis Spectrophotometry)

Total carotenoid content (TCC) was estimated according to an established method [43,44] using a Cary 60 UV-Vis spectrophotometer (Agilent Technologies, Santa Clara, CA, USA). The measurements were performed on samples of 0.5 g dissolved in 50 mL of hexane. The

instrument was operated in scanning mode between 200 nm and 800 nm. The baseline was determined using hexane (HPLC grade; VWR, Mississauga ON, Canada). TCC (mg/L) was calculated using a published equation [45].

2.2.4. Differential Scanning Calorimetry (DSC)

The thermal transition behavior of the samples was determined using a Q200 DSC equipped with a refrigerated cooling system (TA Instruments, Newcastle, DE, USA) and calibrated with pure indium. Samples (4–6 mg) in hermetic aluminum pans were equilibrated at 60 °C for 5 min to erase thermal history, then cooled at 5 °C/min down to −80 °C where it was held isothermally for 5 min to record the crystallization behavior and then heated back to 60 °C at 10 °C/min to investigate the melting behavior. Thermal Advantage universal analysis software (TA Advantage v5.5.24) was used to analyze the DSC data including peak (T_p), onset (T_{On}) and offset (T_{Off}) temperatures and enthalpies (ΔH) of crystallization and melting. Non-resolved peaks were located using first and second derivatives of the heat flow versus temperature curve.

2.2.5. Solid Fat Content (SFC)

SFC was measured on a Minispec mq 20 pulsed NMR spectrometer (Bruker Ltd., Milton, ON, Canada) equipped with a combined high- and low-temperature probe and a BVT3000 temperature controller (Bruker Ltd.). Liquid nitrogen was used for tempering. The fully melted sample was pipetted into the bottom of an NMR tube, filling its bottom to 1 cm ($\sim 0.57 \pm 0.05$ mL), stored at different temperatures (5, 10, 15, 18, 20, 25, 30 and 40 ± 1 °C), and then measured. Bruker's Minispec V2.58 Rev12 and Minispec plus V1.1 Rev05 software were used to collect the SFC data. Uncertainties attached are calculated standard deviations of at least three runs.

2.2.6. Texture Analysis

The textural properties of the samples were evaluated at room temperature using a texture analyzer (TA-TX HD, Texture Technologies Corp, Trenton, NJ, USA). A 90° conical spreadability cone (Model HDP/SR, Stable Micro Systems, Ltd., Godalming, UK) and matching conical sample holder were used to measure firmness, work of shear (spreadability), stickiness and work of adhesion (adhesiveness). Samples were measured after 12 h at room temperature in the compression mode at a test speed of 2.0 mm/s. The force (N) necessary to deform a column sample of 17 mm height was used as a firmness value.

Hardness was measured with a 5 mm diameter ball probe (Model P/5S, Stable Micro Systems, Ltd.). Samples were prepared in 100 mL plastic cups, achieving a uniform height of 20 mm. Hardness was determined as the force (N) required to achieve a penetration depth of 10 mm.

2.2.7. Polarized Light Microscopy (PLM)

A Leica DM2500P polarized light microscope (Leica Microsystems, Wetzlar, Germany) fitted with a digital camera (Leica DFC420C) was used for microstructure studies. A Linkam LS 350 temperature-controlled stage (Linkam Scientific Instruments, Tadworth, Surrey, UK) fitted to the PLM was used to thermally condition the samples. A small droplet of the sample was carefully pressed between a preheated glass slide and coverslip, ensuring a uniform thin layer. The sample was equilibrated at 60 °C for 10 min to erase crystal memory, then cooled down to −65 °C at 1 °C/min. PLM images (50×) were taken at 1 min intervals.

2.3. Statistical Analysis

Pearson Product Moment Correlation was used to measure the linear correlation between variables. Differences between groups were checked using analysis of variance (ANOVA) at a significance level of $p = 0.05$. The coefficient of determination (R^2), Chi-square (χ^2) and residual sum of squares (RSS) were used to evaluate the performance of the models. The Durbin–Watson (DW) statistic was used to test for autocorrelation in the

residuals. Standard error and standard deviation were used to assess the physical relevance of the models’ parameters. The statistical analysis was performed using the Sigmaplot module of Sigmaplot 12.5 software. Built-in and user-defined equations in the nonlinear regression wizard of Sigmaplot 12.5 software were used to fit the data.

3. Results and Discussion

3.1. Non-Lipid Bioactive Composition

The total carotenoid content (TCC) was estimated using Equation (1) [45].

$$TCC(\text{mg/L}) = \frac{A_{446} \times V \times 10^4}{2592 \times m}$$
 (1)

where A_{446} = absorbance at 446 nm, 2592 = extinction coefficient for carotenoids, V = volume of hexane (mL) and m = mass of sample (g). This equation, although specific to beta carotene, is more suitably expressed as the total carotenoid content as it also accounts for other carotenoid compounds being absorbed at the same wavelength as beta carotene [46].

Determination of total phenolic content (TPC) was determined using the linear calibration curve obtained with gallic acid in the 0.5 to 10 mg/L range (Equation (2); $R^2 = 0.995$).

$$Abs_{745} = 0.126GAE - 0.0576$$
 (2)

where Abs_{745} is the absorbance, 745 nm, and GAE is the gallic acid equivalent in mg/L.

TCC and TPC results are provided in Table 2, together with ESI-MS results.

Twenty-four (24) bioactive compounds, falling into three classes—carotenoids, polyphenols and sterols—were identified in AVP. ESI-MS analysis of AVK indicated less than 0.5% of total bioactive compounds. Spectrophotometry indicated only trace amounts of carotenoids and polyphenols. These findings support a biological design of *Astrocaryum vulgare*’s fruit adapted to optimum plant proliferation where animals are attracted by the nutrition and health-beneficial compounds preferentially stored in the pulp while the seed is protected in a hard impenetrable “shell”. MS and spectrophotometry results for the bioactive components of AVK are provided in Table S1 for the reader’s review.

Table 2. Bioactive compounds identified in *Astrocaryum vulgare* pulp oil (AVP) using ESI-MS in positive mode in combination with UV-Vis spectrophotometry for quantification of total carotenoids (TCC) and polyphenols (TPC).

Compounds	Chemical Formula	Theoretical <i>m/z</i>	Experimental <i>m/z</i>	Adduct	Relative Intensity (%)	Concentration (mg/L)	Literature Values (mg/L)	Refs
Carotenoids								
All-trans-β-Carotene All-trans-α-carotene 13-cis-β-carotene 15-cis-β-carotene	C ₄₀ H ₅₆	536.4382	536.4379	[M]	84.32	1928.65	1296 ± 157.4	[14]
All-trans-lutein Zeinoxanthin Cis-lutein	C ₄₀ H ₅₆ O ₂	568.4280	568.5626	[M]	4.17	95.38	0.79 * 1.02 * 0.04 *	[47]
All-trans-β-cryptoxanthin All-trans-α-cryptoxanthin Zeaxanthin	C ₄₀ H ₅₆ O	552.4331	552.4586	[M]	1.31	29.60	1.64 * 1.30 * 0.16 *	[47]
Estimated Total Carotenoid Content (mg/L)						2054.0 ± 91.0	778–2081	[14,41,48]
Polyphenols								
Chlorogenic acid	C ₁₆ H ₁₈ O ₉	354.0951	354.2691	[M + Na] ⁺	1.84	0.22	8.30 ± 0.2 *	[15]
Caffeic acid	C ₉ H ₈ O ₄	180.0422	203.0990	[M + Na] ⁺	3.19	0.38	0.07 ± 0.02 *	
Rutin (quercetin glucoside)	C ₂₇ H ₃₀ O ₁₆	610.1534	633.5074	[M + Na] ⁺	2.55	0.30	7.34 ± 0.1 *	

Table 2. Cont.

Compounds	Chemical Formula	Theoretical m/z	Experimental m/z	Adduct	Relative Intensity (%)	Concentration (mg/L)	Literature Values (mg/L)	Refs
Catechin	C ₁₅ H ₁₄ O ₆	290.0790	313.2376	[M + Na] ⁺	0.82	0.10	27.08 ± 0.04 *	[15]
Myricetin	C ₂₁ H ₂₀ O ₁₂	318.0376	341.1901	[M + Na] ⁺	0.41	0.05	2.01 ± 0.05 *	
Kaempferol	C ₁₅ H ₁₀ O ₆	286.0477	309.0997	[M + Na] ⁺	0.33	0.04	<0.07	
Total Phenolic Content (mg/L)						1.1 ± 0.1	117.42 ± 1.67 *	
Phytosterols								
β-Sitosterol	C ₂₉ H ₅₀ O	414.3862	437.2012	[M + Na] ⁺	0.28	-		
Cycloartenol Cycloeucalenol	C ₃₀ H ₅₀ O	426.3862	449.3476	[M + Na] ⁺	0.55	-		
Arundoin 24-methylenecycloartanol	C ₃₁ H ₅₂ O	440.4018	463.0541	[M + Na] ⁺	0.31	-		

*—Values reported for AVP pulp extract but not for AVP pulp oil.

3.1.1. Carotenoids

Spectrophotometry measurements of AVP oil revealed a high level of carotenoids (2053.67 ± 90.67 mg/L). TCC values reported in the literature for AVP are generally lower by 27 to 1276 mg/L [14,41]. TCC is attributable to several factors including maturation stage, climate, ecology, harvesting method, handling, storage and processing of the fruits as well as extraction temperature [49]. In the present case, AVP oil was extracted using cold pressing at mild temperatures (30–40 °C). The TCC of 686.89 mg/L reported for *Mauritia flexuosa* oil (known as ite in Guyana and buriti in Brazil) [50] and 603.39 mg/L reported for *Elais oleifera* (palm) oil [51] are a third of those measured in AVP in this study.

ESI-MS indicated that carotenes constitute 94% (1928.65 mg/L) of the TCC. This significant presence of carotenes gives the fruit and oil their characteristic orange-red color. The remaining 6% of carotenoids were identified as xanthophylls. Representative chemical structures of carotenoid compounds identified in AVP oil are shown in Figure 1.

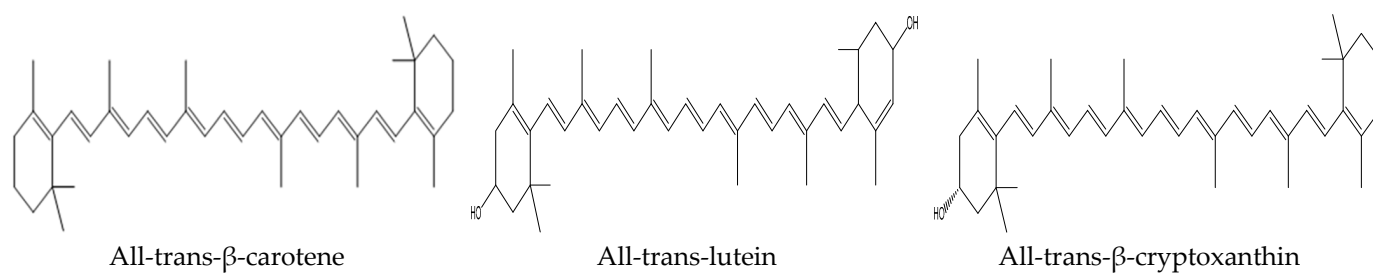


Figure 1. Chemical structures of representative carotenoid compounds identified in AVP oil.

The high level of β-carotene found in AVP makes it an important source of pro-vitamin A. In addition, AVP can potentially be used as a natural coloring agent in foods (e.g., cakes, crackers, candy) that can replace synthetic yellow-orange dyes such as tartrazine and sunset yellow, which have posed health and safety concerns for consumers [52]. Topical application of carotenoid-containing products offers protection against damage to the skin from sunlight, which reduces erythema (redness of the skin caused by inflammation). β-Carotene is known for its ability to protect against sunburns, making it a common ingredient in sunscreen formulations [53,54]. β-Carotene also helps protect the skin against oxidative damage, which manifests as wrinkles, by acting as a scavenger of singlet oxygen. The antioxidant properties of β-carotene also enhance the rate of skin regeneration, slowing the photoaging process [55].

Xanthophylls are a class of carotenoids that are oxygenated (e.g., lutein and cryptoxanthin, see Figure 1), which also offer skin benefits. They are known for their ability to

increase skin hydration, particularly lutein, which penetrates intercellular lipids, reducing roughness of the skin.

3.1.2. Polyphenols

Six polyphenols were identified in AVP oil in small concentrations (TPC = 1.08 ± 0.1 mg/L). This is much lower than the TPC of AVP pulp extract (117.42 ± 1.67) reported in the literature [15], probably because most polyphenols are polar compounds and do not dissolve in non-polar lipids. The TPC of AVP is significantly lower compared to other plant oils of the Amazonian region such as *Caryocar brasiliense* (229.1 mg/L), *Attalea speciosa* (288.0 mg/L) and *Mauritia flexuosa* (309.9 mg/L) [56]. The amounts of polyphenols identified for AVP are lower than the minimum inhibitory concentration (MIC) against common microbes (e.g., *Escherichia coli* and *Staphylococcus aureus*), which ranges from 20 mg/L to 1024 mg/L [57–59]. This suggests that the antimicrobial activity of AVP against *E. coli*, *S. aureus*, *E. faecalis* and other microbes, reported by Rossato et al. [16], may be related to its β -carotene or the fatty acids present. β -Carotene has been shown to be effective against strains of *E. coli*, *S. aureus* at 100 mg/L [60]. Fatty acids, such as oleic acid, which makes up 65% of the fatty acid composition of AVP [12], can act as anionic surfactants that alter bacterial cell walls, which affects their ability to function at low pH levels [61].

3.1.3. Phytosterols

Phytosterols, compounds that closely resemble cholesterol in both structure and function, are found naturally. β -Sitosterol, cycloartenol, cycloeucalenol and arundoin 24-methylenecycloartanol were putatively identified in AVP oil by MS (Table 2). The same compounds were identified in AVP oil by Bony et al. [14] by gas chromatography, with a total content of phytosterols of 1497.2 ± 90.1 mg/L.

Phytosterols are often used as substitutes for lipids high in cholesterol to enhance cardiovascular health [62]. The antimicrobial [63] and anti-inflammatory activities [64] of phytosterols have been confirmed for AVP in in vivo studies [14]. Given its phytosterol content, AVP can potentially function as an edible oil that offers not only a distinct flavor but also health benefits from its anti-inflammatory properties.

3.2. Thermal Transition Behavior and Phase Diagram

The DSC cooling ($5\text{ }^{\circ}\text{C}/\text{min}$) and heating ($10\text{ }^{\circ}\text{C}/\text{min}$) thermograms of the AVK/AVP mixtures are displayed in Figure 2a,b, respectively. The corresponding thermal parameters and phase diagrams are presented in Figure 3a for the cooling cycle (T_{Con} and T_{C1-3}) and Figure 3b for the heating cycle (T_{Moff} and T_{M1-3}). The enthalpies of the individual endotherms represented in Figure 4 are used to estimate the relative content of the phases involved.

The DSC thermograms in Figure 2a,b indicate mainly one crystal phase for AVK (exotherm $T_{C1} \sim 15 \pm 1\text{ }^{\circ}\text{C}$ and endotherm $T_{M1} = 30\text{ }^{\circ}\text{C}$) and a minor phase at a very low temperature ($T_{C3} \sim -40\text{ }^{\circ}\text{C}$ and $T_{M3} = -19\text{ }^{\circ}\text{C}$). Phase 1 accounts for $\sim 96\%$ of the total crystallization enthalpy (85 kJ/mol) and is related to the saturated medium-chain TAGs of the lipid. A slight shoulder (T_1^s at $\sim 10\text{ }^{\circ}\text{C}$ in Figure 2a and $\sim 25\text{ }^{\circ}\text{C}$ in Figure 2b) can be noted at the low-temperature side of T_1 , which indicates a different small group of TAGs that melt at lower temperatures, namely OOO and POO found in AVK at 0.4% and 0.3%, respectively [11].

The AVP cooling thermogram shows a prolonged leading exotherm (T_1 in Figure 2a) over a relatively large window of temperature ($\sim 25\text{ }^{\circ}\text{C}$) followed by two crystallization events. The height of T_1 remained small but almost constant as it was cooled down to $-30\text{ }^{\circ}\text{C}$, suggesting continuous nucleation and growth processes and the slow formation of small and probably disordered lamellar structures. According to its relative enthalpy, half of the material participated in this transformation. The lower-temperature exotherms were related to rapidly forming crystals from the nucleation of the low-melting groups of AVP TAGs, including those comprising mostly polyunsaturated fatty acids (PUFAs) such as

linolenic acid. The phases observed during cooling were confirmed by successive melting events starting with a melt–recrystallization at ~ -30 °C (Figure 2b).

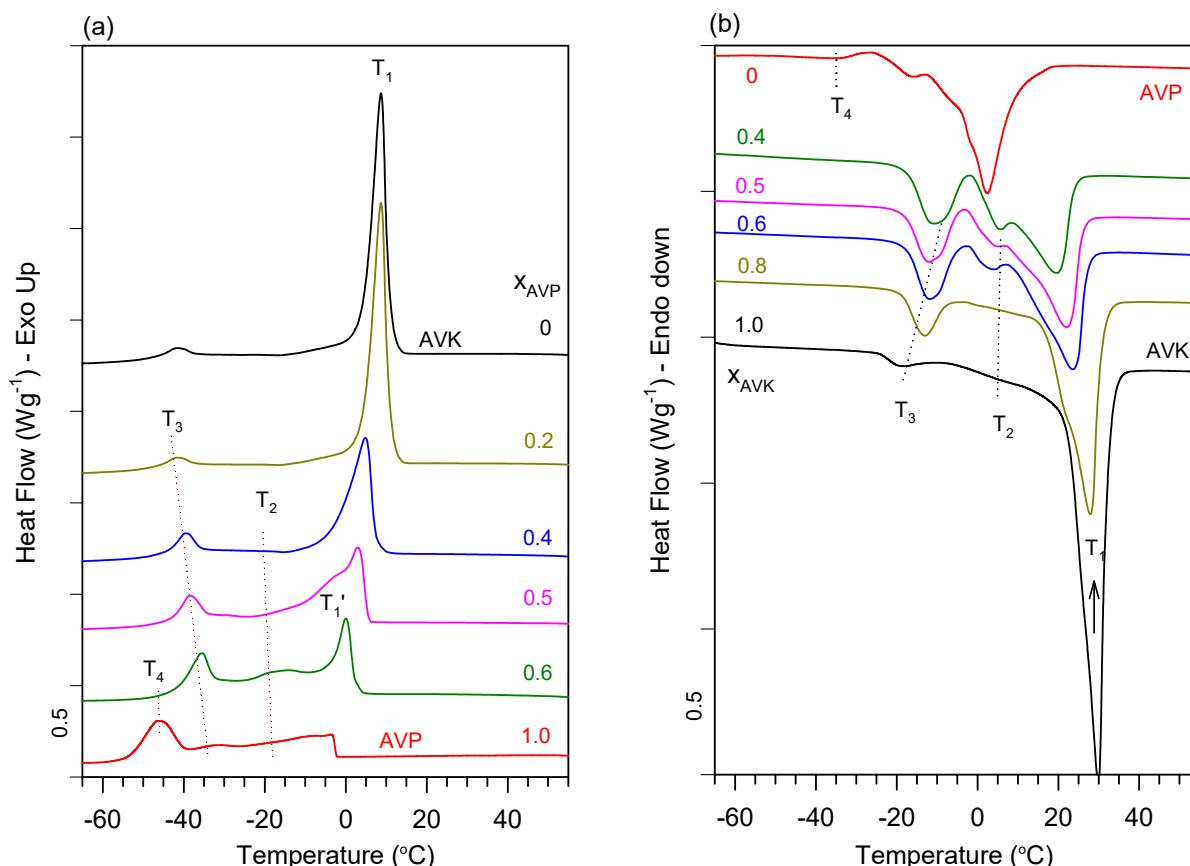


Figure 2. (a) DSC cooling (5 °C/min) and (b) heating (10 °C/min) thermograms of AVK/AVP mixtures.

As AVP was added, the total enthalpy of crystallization and melting both decreased linearly (Figure 3, $R^2 > 0.893$ and S.E.E < 6) at a rate of -31 ± 3 kJ/mol/mol. This indicates that the lattice energy of the fat steadily decreases at a constant rate as the unsaturated TAGs of AVP are mixed with the saturated TAGs of AVK.

With the increase in AVP concentration, the intensity of the leading peak (T_{C1} and T_{M1}), distinguishing the AVK solid, decreases, and its temperature shifts in a monotectic manner to low temperatures (★ in Figure 3a,b). T_{C1} and T_{M1} can be safely assigned to the crystallization and melting, respectively, of a phase made predominantly, if not exclusively, of AVK TAGs. The shoulder peak T_1^s becomes increasingly resolved and shifts to a lower temperature and appears to merge with the T_1 of AVP at concentrations higher than 0.50_{AVPO} . This suggests that AVK TAGs are increasingly taking part in the formation of the early AVP-AVK lamellae phase, which grows in an AVP-based crystal structure. The disappearance of the AVP lowest-temperature event (T_4 in crystallization in Figure 2a and melting and following recrystallization at -35 °C in Figure 2b) from the mixtures' transformation path ($x_{AVK} < 0.40$) and significant increase in the T_3 phase stability indicate that molecular organization improves even at very low temperatures and confirms a direct participation of AVK TAGs in the development of AVP-AVK crystals. The temperature of crystallization of T_3 (Figure 3b), and associated crystallization and melting enthalpies (Figure S1), increased linearly at a rate of 28 ± 3 kJ/mol/mol, indicating a gradual improvement in stability of the lowest-melting-temperature phase owing to the participation of AVK TAGs in its formation. The similar changes observed in T_2 also indicated a direct participation of AVK TAGs with AVP TAGs in the formation of the medium-temperature phase.

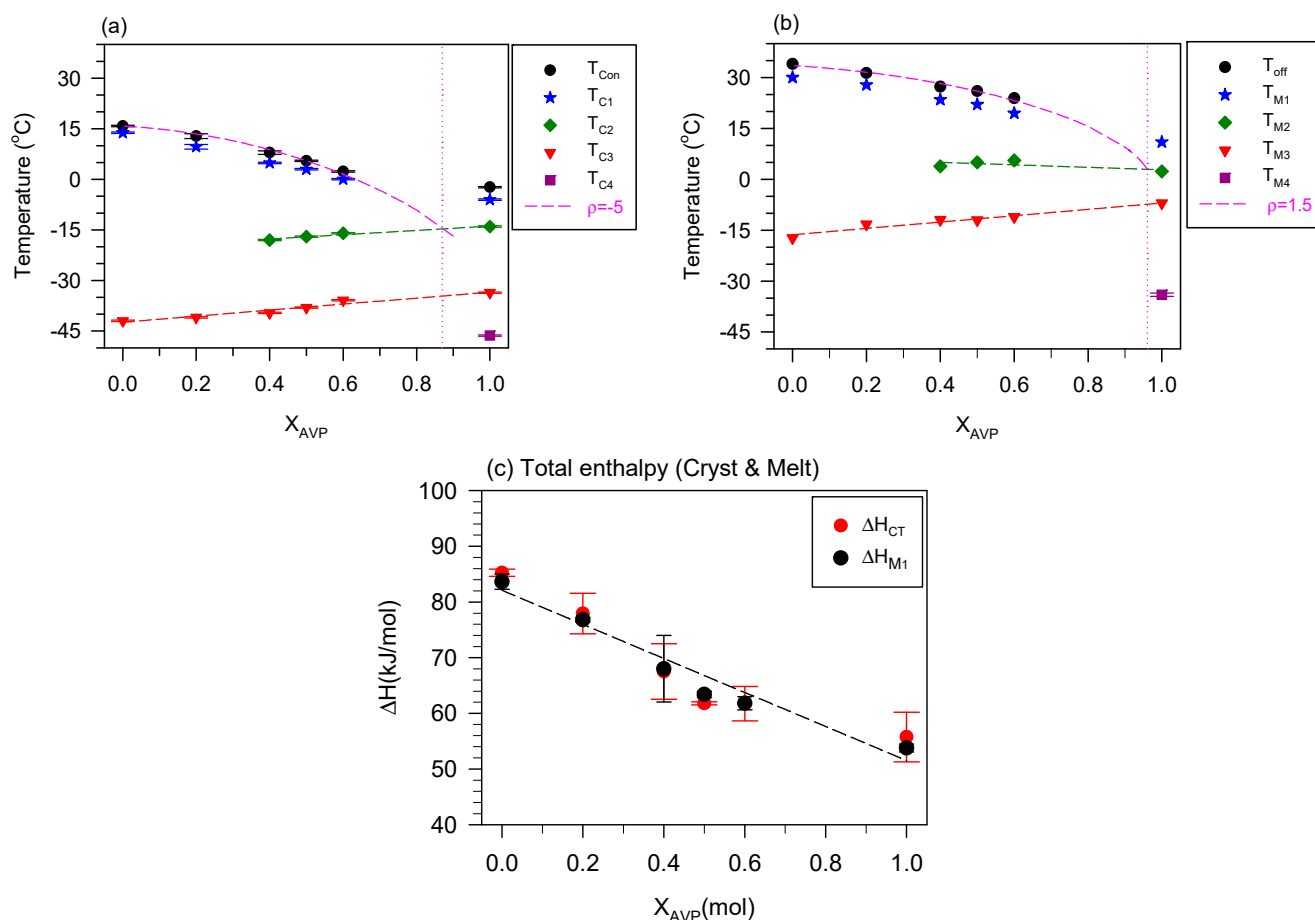


Figure 3. Thermal transition parameters and phase diagram $T(x_{AVP})$ obtained from DSC (a) cooling and (b) heating. Vertical dotted line is presumptive eutectic composition. Symbols in (a,b): ●: onset temperature of crystallization (T_{Con}) or offset temperature of melting (T_{Moff}). ★, v, θ and v: crystallization and melting peak temperatures (T_{C1} , T_{C2} , T_{C3} , T_{C4}) and (T_{M1} , T_{M2} , T_{M3} , T_{M4}), respectively. Lines passing through T_{Con} and T_{Moff} are simulations of the cooling and heating liquidus lines of the AVK/AVP binary system using the BW approximation (Equation (4), $\chi^2 = 1.13$ and 0.19, respectively). Dashed lines passing through T_{C2} , T_{C3} , T_{M2} and T_{M3} data are fit to straight lines ($R^2 > 0.996$). (c) Total enthalpy of crystallization and melting versus x_{AVP} . Dashed line passing through the enthalpy data are fit to a straight line ($R^2 > 0.893$, standard error of estimates < 6).

As AVP was added, T_{M1} decreased in an apparent monotectic manner but its FWHM remained constant at an estimated ~ 6 °C. This suggests that the crystals associated with T_{M1} , probably in the β' form, the main form shown by XRD for AVK (>90% reported in [65]), are essentially AVK TAGs. This AVK crystal phase seems to be relatively resilient to the influence of AVP components and remains well organized at the concentration levels considered here. The crystal nature of this phase and the phase associated with the shoulder peak were not determined for the mixtures, as such a task would involve investigation efforts involving XRD measurements, out of the scope of this work. However, if phase behavior studies of binary mixtures of pure lipid molecules such as those conducted by our research group on binary TAG systems [66,67], propanediol esters [68] and binary TAG/methyl esters systems [38,39,69] are of any indication, the most likely transformation path and phase content would be the common α to β' to β crystal forms. Note that more than one sub-form, particularly of β' , may be present and that the β form may need a specific thermal treatment to be revealed.

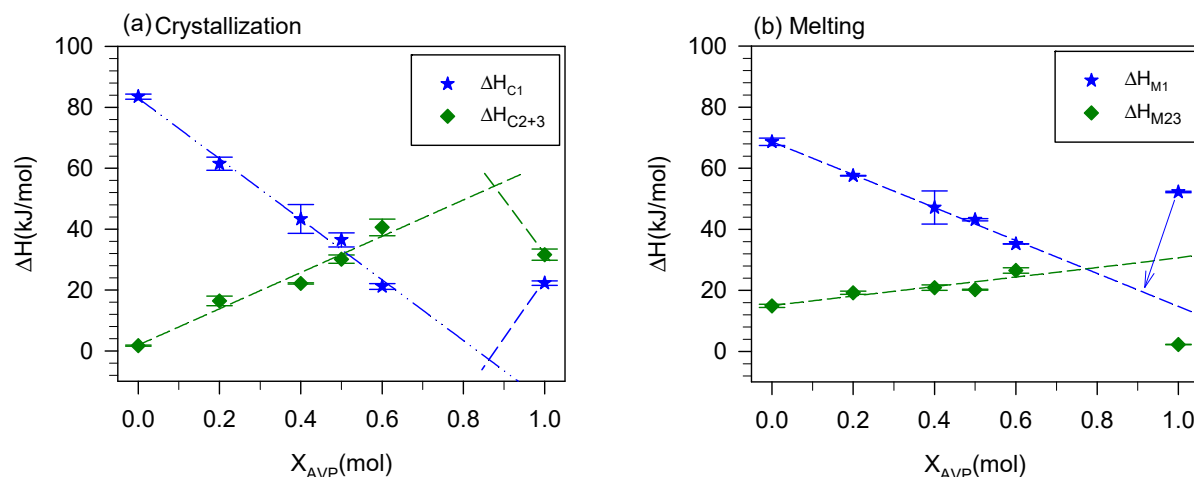


Figure 4. (a,b) Enthalpy of crystallization/melting of the leading peak ($\Delta H_{C/M1}$, ★) and combined trailing peaks ($\Delta H_{C/M2+3}$, v). Dashed lines passing through the enthalpy data are fit to straight lines ($R^2 = 0.816$ – 0.995 , S.E.E of 2–6). Solid drop arrow is a tentative location of the eutectic point using Tamman's diagram.

The AVK/AVP binary system can be related to the results obtained with pure TAGs in many aspects because of the composition homogeneity of each of these lipids and stark difference between the two ensembles [65]. Under these considerations, the binary system can be thought of on average as one made of two distinct “average TAG” molecules: a medium-chain lauric and myristic-acids TAG with a molecular mass of 687.27 g/mol on average for AVK (AVK primarily consisting of medium-chain saturated TAGs, such as LLL, LLM and MMM), and a long-chain oleic and palmitic-acids TAG with a molecular mass of 867.99 g/mol for AVP (predominantly consisting of long-chain unsaturated TAGs, including POO, PPO and OOO). This interpretation is corroborated by recent work on the mixing phase behavior of trilaurin and monounsaturated triacylglycerols based on palmitic and oleic fatty acids [70]. The phase diagrams of LLL/POP and LLL/PPO binary systems not only parallel the AVK/AVP binary system in terms of mixing behavior, they also show eutectic points at the very close level (X_{PPO} and $X_{POP} = \sim 0.8$). The small discrepancy in eutectic composition between these model systems and the AVK/AVP binary system ($x_{AVP} = \sim 0.85$) is attributable to the variety of medium-chain TAGs present in AVP. It is likely that the di-unsaturated TAGs and those comprising linoleic and linolenic fatty acids of AVK are responsible for pushing the eutectic point to higher oil concentrations and lower temperatures.

3.3. Thermodynamic Analysis of the Liquidus Line

Phase diagrams were constructed from both heating and cooling thermograms of the mixtures (cooling and heating phase diagrams in Figure 3a,b, respectively). Unlike DSC heating data, the phase diagram drawn from DSC cooling data does not represent the equilibrium state because of kinetic effects related to mass and energy transfer limitations. Cooling phase diagrams are, however, important as they can be directly contrasted with the pseudo-equilibrium phase diagrams from the DSC heating data. This allows us to gain insight into variations concerning concentrations of kinetic, mass and energy transfer effects. The cooling and heating liquidus lines of the AVP/AVK binary system were generated from the onset temperature of crystallization for the cooling data and offset temperature of melting (T_{Con} and T_{Moff} (●) in Figure 3a,b, respectively), as is typically done in the study of binary lipid mixtures [66–68,71–74]. T_{Moff} is particularly suitable for studying pseudo-equilibrium properties because it is determined by the most stable crystals. T_M (T_C) of the other peaks are used to represent the transition lines after correction for the transition widths of the pure components [75].

Two solidification lines constructed from T_2 and T_3 of the cooling and heating thermograms (v and θ lines in Figure 3a,b) were very well described by slightly sloped straight lines ($R^2 > 0.951$). Line slopes are higher in the cooling phase diagram, which is attributable to greater kinetic effects during cooling. These lines are associated with the formation of α and maybe low-stability β' phases.

The liquidus line was calculated using the Hildebrand equation [76] coupled with the Bragg–William (BW) approximation for the non-ideality of mixing [77,78]. The result is included as dashed lines passing through the liquidus data Figure 3a,b for the cooling and heating phase diagrams, respectively. This model is commonly used to investigate the miscibility of lipid mixtures [39,66–68,79–82]. The deviation from an ideal behavior is described by a non-ideality of the mixing parameter, ρ (J/mol), defined as the difference in energy between mixed pairs (AB) and like pairs (AA and BB):

$$\rho = z \left(u_{AB} - \frac{u_{AA} + u_{BB}}{2} \right) \quad (3)$$

where z is the first coordination number, u_{AB} , u_{AA} and u_{BB} , the interaction energies for AB, AA and BB pairs, respectively. $\rho = 0$ indicates an ideal mixing, and a negative ρ reflects a tendency for order, whereas a positive ρ reflects a tendency of like molecules to cluster, which beyond some critical value leads to phase separation [74,76]

The branches of a liquidus line comprising a eutectic are described by the following equation [82,83]:

$$\ln X_{A(B)} + \frac{\rho(1 - X_{A(B)})^2}{RT} = -\frac{\Delta H_{A(B)}}{R} \left(\frac{1}{T} - \frac{1}{T_{A(B)}} \right) \quad (4)$$

where R is the gas constant. X_A represents the mole fraction of A , ΔH_A and T_A are the molar heat of fusion and the melting point of component A . X_B , ΔH_B and T_B are those corresponding to component B . A or B are considered depending on whether the liquids segment composition is smaller or larger than the eutectic composition X_E .

Considering a monotectic phase diagram, the parameters of AVK (T_A and ΔH_A) were used to simulate the liquidus line. The standard method of least squares approach was used to obtain ρ and calculate the liquidus lines. The results for the cooling and heating liquids lines are shown in Table 3. The calculated p -values are comparable to published values for binary lipid systems [67,84].

Table 3. Parameters of the Bragg–William approximation (Equation (4)) used to simulate the liquidus line and corresponding values of the non-ideality of the mixing parameter, ρ . ΔH_A : enthalpy of melting and T_A : melting temperature.

Liquidus	Region	T_A (C)	T_A (K)	ΔH_A (kJ/mol)	ρ (kJ/mol)	χ^2
Cooling	$0 \leq X_A \leq 0.95_{AVPO}$	14.0	287.2 ± 0.5	76 ± 2	−5	1.13
Heating	$0 \leq X_A \leq 0.90_{AVPO}$	33.5	306.7 ± 0.5	83 ± 3	−1.5	0.19

The calculated liquidus lines perfectly matched the experimental data of AVK and the mixtures but did not pass through the AVP melting point, indicating a eutectic at a high AVP concentration. The T_2 solidification line is, therefore, a eutectic line, whose intersection with the calculated liquidus line indicates a presumptive eutectic point. The T_2 line of the cooling phase diagram intersected with the liquidus line at 0.85_{AVPO} and that of the heating phase diagram at 0.95_{AVP} (vertical dotted lines in Figure 3a,b). The eutectic of the AVK/AVP binary system is likely close to $\sim 0.95_{AVP}$, the point determined from the heating phase diagram, because quasi-equilibrium conditions are achieved during heating but not cooling.

Analyses of the enthalpy of crystallization and melting of the leading peak (T_1) as well as that of the combined trailing peaks T_2 and T_3 ($\Delta H_{C/M1}$, ★ and $\Delta H_{C/M2+3}$, v in Figure 4a,b) suggest a Tamman's triangle shape. Tamman's diagram is an important outcome from the theory of phase diagrams [85,86] and is a characteristic of the eutectic effect and shows linear dependence of molar enthalpy on either side of the eutectic point [87]. The data of Figure 4a,b indicates a point, x_{AVP} , higher than the mixture with the maximum concentration studied here, i.e., 0.6_{AVP} , confirming the results from the cooling and heating phase diagrams of Figure 3a,b.

The presence of eutectic points close to one pure component is common in binary systems comprising pure components with significant differences in structure and melting temperature [88]. Given the high AVP content of the eutectic point, the AVK/AVP binary system may be considered monotectic for all intents and purposes.

The BW approach yielded small negative values for ρ for the simulation of both the cooling and heating liquidus lines (Table 3). The values of ρ obtained for the cooling and heating liquidus lines are rather small (-5 kJ/mol and -1.5 kJ/mol, respectively) and indicate a mixing behavior close to ideal with a tendency for order and exclude the tendency of like molecules to cluster and phase separation [82]. The result indicates that the formation of mixed pairs in the liquid state is not excluded. This result supports the conclusions from the analysis of the individual melting peaks in relation to their associated groups of TAGs. This gives credence to the conclusion that AVK molecules participate with AVP TAGs to increase the stability of the phase that AVP makes at low temperatures (T_{M2} and T_{M3} phases).

3.4. Solid Fat Content

$SFC(T)$ profiles of the AVK/AVP mixtures are reported in Figure 5a. Typical SFC values of CB from the literature [32,89,90] are included in Figure 5b for comparison purposes. When considered from high temperatures (the melt) to low temperatures (solidification), the $SFC(T)$ data of each mixture followed a growth trajectory that was very well described by the three-parameters Gompertz function (Equation (5)).

$$SFC(T) = SFC_0 \exp\left(-\exp\left(-\frac{T - T_0}{b}\right)\right) \quad (5)$$

where SFC_0 is the maximum fraction of solid fat, which specifies the SFC magnitude, T_0 is the inflection point, which in the case of a growing $SFC(T)$ from zero (melt) to a maximum value (SFC_0) quantifies the induction temperature, and b is the maximum specific growth rate, which can be derived by calculating the first derivative at the inflection point.

The fit of the Gompertz function to the SFC versus temperature data of the mixtures above 5°C yielded curves with excellent goodness of fit ($R^2 > 0.998$, standard error of estimates < 0.94). The SFC measured at 5°C is above the calculated maximum because of the unsaturated TAGs present, which start a new mechanism of crystallization that is described by a step segment. The presence of the segment that would represent this mechanism is obvious from the step increases in SFC for all the mixtures. It has not been measured because it is irrelevant to the present study. The model provided values of the parameters, which are significantly different for each material. The Gompertz SFC magnitude decreased with x_{AVP} following a straight line toward a theoretical value of zero for pure AVP (Figure 5c, $R^2 = 0.989$). The large slope obtained for the decrease ($-56 \pm 3\%/mol$) indicates a steep, gradual and continuous drop in overall SFC with increasing AVP. The parameter linked to the induction temperature of the mixtures (T_{0-SFC} ; Figure 5d) also decreased with increasing AVP in an apparent monotectic manner. The rate of change of T_{0-SFC} with AVP departs significantly from that of the DSC liquidus line. The rates of change of $T_0(x_{AVP})$ and $T_{Moff}(x_{AVP})$ data estimated by linear regression ($R^2 = 0.989$) were -7.6 ± 1.0 and $-16.9 \pm 0.7^\circ\text{C}/mol$. This difference is because $T_{Moff}(x_{AVP})$ was obtained from samples crystallized at a fixed rate ($5^\circ\text{C}/min$), whereas the SFC was measured in samples quickly brought to temperature and left to crystallize isothermally.

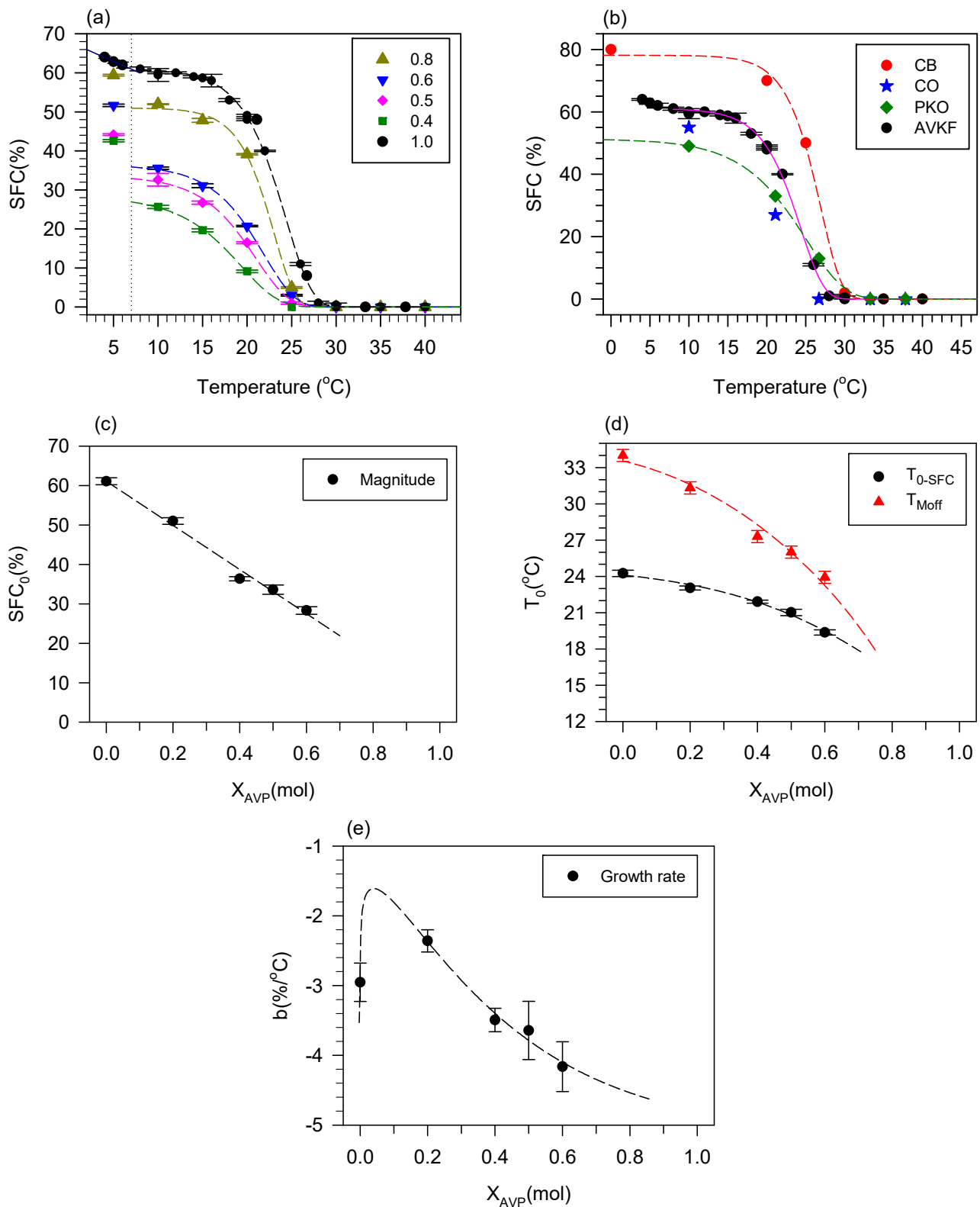


Figure 5. (a) $SFC(T)$ profiles of AVK and AVK/AVP mixtures. Dashed lines are fits of the Gompertz function (Equation (5), $R^2 > 0.998$) to the data. (b) SFC versus temperature of AVK (this work), cocoa butter (CB) [30], coconut oil (CO) [30], palm kernel oil (PKO) [30] and shea butter (SB) [91]. (c–e) Variation with AVP molar ratio x_{AVP} of the Gompertz fit parameters: (c) SFC magnitude (SFC_0), (d) induction temperature (T_0) and (e) maximum SFC specific growth rate, b . Dashed line in (c) is a fit to a straight line ($R^2 = 0.989$) and dashed line in (e) is a fit to a Weibull function ($R^2 = 0.992$).

The specific growth rate of the mixtures started with a value for pure AVK lower than that of the 0.2_{AVP} mixture, then decreased in an exponential manner as the AVP concentration was increased, indicating the occurrence of a maximum between pure AVK and 0.20_{AVP} (Figure 5e). The fit of the $b(x_{AVP})$ data, excluding AVK, indicated that b of the mixtures with $x_{AVP} < 0.3$ is higher than that of AVK. The shape of the $b(x_{AVP})$ curve is reminiscent of a Weibull function with a prolonged tail. The fit of $b(x_{AVP})$ data to the Weibull function was excellent (dashed line in Figure 5e, $R^2 = 0.992$, standard error of estimates = 0.13) and yielded a maximum value at 0.04_{AVP} ($b = -1.6$). This suggests that AVP components have an accelerating effect on the SFC growth of the AVK/AVP mixtures that is exponentially overcome, bringing it to AVK levels at $x_{AVP} \sim 0.3$. This is interesting as it shows that the crystallization of mixtures with $x_{AVP} < 0.3$ is faster than that of pure AVK.

As shown in Figure 5b, AVK has an SFC lower than that of CB and higher than that of the other most-used commercial fat alternatives such as coconut oil (CO) [30], palm kernel oil (PKO) [30] and shea butter (SB) [91].

The SFC values of AVK are overall higher than those of CO, PKO and SB at all temperatures above the melting point. Furthermore, its SFC is sharper in the melting range (20–30 °C). CO, PKO and SB are, in fact, too soft to make CB alternatives (called CB equivalents or CBEs) without being fractionized first [32]. AVK's sharp melting profile, high SFC in the hardness region (SFC > 70% for $T < 25$ °C) and intensive melting in the 27 to 30 °C range, which would bring about a cooling sensation in the mouth and flavor release, suggest that it would serve as an excellent confectionery fat. The zero SFC value at temperatures above 30 °C indicates the absence of a fat fraction, which may cause a waxy taste.

AVK is a lauric fat which, although probably not compatible with CB, would be a good CB substitute (CBS). Small corrections to the SFC profile of AVK may extend its compatibility with CB. The blending of AVK with the pulp oil of the same fruit achieved a range of materials with predictable SFC profiles. Overall, the SFC profiles of the mixtures and the Gompertz analysis indicate SFC phase diagrams with smooth boundaries at all temperatures starting just above the melt. The variation in the Gompertz modeling parameters is consistent with the monotectic nature of the liquidus line of the AVK/AVP binary system. These data indicate that it is possible to formulate AVK/AVP fats and, hence, lipid products that would have physical properties in a continuous spectrum of melting, hardness and plasticity. These fats would be suitable for varied applications ranging from hard coatings to soft fillings for foods, fillers, binders, lubricants, solubilizers, emulsifiers and emollients in a variety of cosmetics and pharmaceuticals delivery systems including tablets, capsules, suppositories, emulsions, ointments, creams and lotions. Furthermore, the AVK/AVP mixtures incorporate therapeutic attributes that are often absent in the conventional fats traditionally employed in these industries.

3.4.1. Implications for Food and Cosmetics Applications

Implications of the Mixtures' Melting Point in Foods and Cosmetics

Fats that have melting points (M_p) below 35 °C are highly valued as both cosmetic and confectionery fats because they melt at body temperature. This property allows them to provide a distinctive melting sensation either in the mouth or on the skin. Common examples of such fats include cocoa butter (CB) ($M_p = 23$ –33 °C) [30,92], coconut oil (CO) ($M_p = 23$ –29 °C) [30,92] and palm kernel oil (PKO) ($M_p = 27$ –29 °C) [93]. The M_p of AVK and mixtures containing ≥ 0.5 mole fraction of AVP (T_{M1} in Figure 2b) are within M_p ranges of CB, CO and PKO, underscoring their potential for similar applications in the food and cosmetic industries.

Fat/oil phase separation is a notable issue in cosmetic products, and is a phenomenon that often appears as "sweating" characterized by the formation of droplets, in items such as balms and lipsticks, impacting their quality and appearance [94]. The mixing behavior as described by the phase diagram and BW model suggests that AVK/AVP mixtures are

not likely to be affected by phase separation and may be considered for use in balms and lipsticks to mitigate issues associated with sweating.

Implications of the Mixtures' SFC in Cosmetics

The SFC significantly affects various qualities of cosmetic products, such as their visual attractiveness, temperature stability, ease of spreading and the sensation they leave on the skin. Low SFC levels prevent cosmetic fats from attaining the required flexibility, leading to an oily film on the skin. Conversely, overly high SFC levels may cause a product to impart a waxy texture. An ideally balanced SFC level, therefore, is key to improving a cosmetic's ease of application and its ability to moisturize the skin effectively, without any unwanted residue [95]. Ideally, fats for cosmetic purposes should have a moderate SFC (30–50%) at room temperature (20 °C), but transition rapidly to an SFC of 0% at body temperature (35 ± 2 °C). This ensures that the product is soft and spreads easily on the skin, but melts quickly on the skin, leaving a cooling sensation [95]. Common examples of cosmetics fats include raw cocoa butter, raw shea butter, mango butter and coconut oil, whose SFCs at 20 °C are 78% [96], 37% [91], 40% [97] and 27%, respectively [30].

The SFC of raw cocoa butter (CB) at 20 °C is higher by more than 28% than that of AVK and AVK/AVP mixtures. Because of this high SFC, raw CB is hard and brittle at room temperature, making it challenging to spread on the skin, and it leaves a waxy feel on the skin. CB is often mixed with other oils, such as mineral oil, to decrease its SFC, to be more suitable for cosmetic use. Notably, pure AVK, which has a lower SFC overall, would require less manipulation to achieve an SFC level suitable for cosmetic formulations.

The mixture containing a 0.2 mole fraction of AVP has an SFC at 20 °C (39%) comparable to shea butter (SB) [91] and mango butter (MB) [97], suggesting that it may be a viable substitute in creams and balms. The substitution would also offer therapeutic properties associated with the bioactive compounds present in AVP. The SFC profile of all AVK/AVP mixtures indicates rapid complete melting above 30 °C, a desirable characteristic in cosmetic fats as it would translate to the melting of the product in contact with the skin without leaving a waxy sensation.

The mixtures containing 0.4 and 0.5 mole fractions of AVP presented lower SFC values at 20 °C (20.7% and 16.7%, respectively) compared to SB, MB and CO and may be more suitable for cosmetic applications where fats with greater fluidity are desired, such as in the formulation of lotions and sunscreens. The mixture with 60% of AVP has an SFC of 9.1% at 20 °C, a relatively low level that may lead to oily residues when applied to the skin. Mixtures with such high AVP concentrations may not be suitable for use as cosmetic fats.

Implications of the Mixtures' SFC in Foods

The SFC plays an important role in the texture of various food products like chocolate, shortenings, margarines and butter [98]. The SFC's value at specific temperatures significantly influences the texture and mouthfeel of these products. For instance, margarine intended for use directly after refrigeration has an SFC of no more than 32% at 10 °C, and below 10% at room temperature (20–22 °C) to ensure optimal spreadability. Additionally, to avoid a waxy sensation in the mouth, the SFC of margarine must be under 3.5% at body temperature (35–37 °C) [99]. Figure 6 compares the SFC of the AVK/AVP mixtures to the recommended SFC of margarine at 10 °C, 20 °C and 35 °C.

The mixtures containing ≥ 0.5 mole fraction of AVP present SFC values at 10 °C, 20 °C and 35 °C that are considered too high for ideal textures in margarine. AVP_{0.6} presents an SFC profile at 10 °C, 20 °C and 35 °C that meets the recommended SFC profile of good-quality margarines. The trends observed in SFC suggest that even higher concentrations can be used as substitutes for margarines and spreads, particularly those containing hydrogenated and partially hydrogenated fats and restricted in North America and Europe due to health concerns [100].

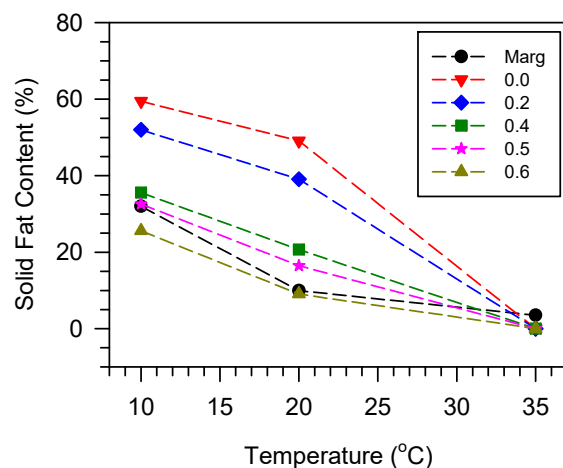


Figure 6. SFC of AVK/AVP mixtures ($x_{AVP} = 0.0\text{--}0.6$) compared to the recommended SFC for margarine (●, Marg).

Fats are also widely used in the food industry as filler shortenings in cookies or wafers. A good filler fat is formulated to provide structural support to the fragile (brittle) cookies or wafers, but also to have a steep melting profile, indicated by a rapid transition from a high SFC at room temperature to an SFC of approximately 0% at around 40 °C [31]. The SFC(*T*) curve of the 80% AVK and 20% AVP blend (Figure 5a) presents a relatively high SFC at 20 °C ($39.1 \pm 0.2\%$) and a steep decrease to 0% at 30 °C, indicating a very short plastic range and potential suitability as a filler.

The SFC profile of the AVK/AVP mixtures suggests that they are not optimal for use as shortenings in bakery products. Their SFC at 40 °C, which is 0%, would not achieve optimal baking results and proper development of dough structure, which require maintaining an SFC of at least 20% at 25 °C and no less than 5% at 40 °C [101].

3.5. Microstructure

Figure 7a shows PLM images of AVK and its mixtures captured while the sample was cooled from the melt at 1 °C/min. Figure 7b–e show the results of the analysis of the PLM including the induction temperature and evolution of the crystal size. The microstructure observed by PLM in AVKF and 0.8_{AVKF} began with the formation of small spots, which expanded radially to form spherulites typical of lauric-rich fats [102]. For the mixtures with higher AVP contents (0.4, 0.5 and 0.6), a significant change in the type of microstructure was observed. In these mixtures, small rods were first formed, then organized in spherical clusters.

The changes in microstructure between the mixtures can be related to crystal growth rate as depicted by the Gompertz parameter $b(x_{AVPO})$ (Equation (6)) $b(x_{AVPO})$ indicated that at low molar concentrations, AVP acts as a catalyst for crystallization up to a critical concentration ($\sim 0.3_{AVP}$), at which time it starts to slow. This suggests that below a concentration threshold, the TAGs with long unsaturated fatty acid chains (e.g., OOO and POO) of AVPO act as a low-viscosity medium in which heat transfer and molecular movement of AVK components are improved compared to AVK in such a way that individual molecular organization and isotropic growth is facilitated. The rod-shaped microstructures observed at a higher-than-threshold concentration ($x_{AVP} > 0.3$) indicate that the AVP TAGs participate more actively in the formation of the early crystals, favoring a single active surface of growth. The clustering of the rods in increasingly smaller spheritic-like entities suggests a persisting but decreasing effect of AVK components on the overall microstructure development with a tendency to favor radial growth.

The phase behavior of trilaurin (LLL) and triolein (OOO) binary systems studied by Paluri et al. [103] mimics in many aspects the present AVK/AVP binary system. Although it differs in some aspects relating to thermal transformation, it shows striking similarities

in terms of microstructure development. Particularly, the LLL/OOO mixture exhibited crystal morphologies like those observed in AVK/AVP mixtures. For instance, and similarly to their AVK/AVP counterparts, the 0.80_{LLL}/0.20_{OOO} mixture developed spherulitic-type crystals, and the 0.60_{LLL}/0.20_{OOO} mixture formed clusters of thin rods [103]. This is not surprising because of the close TAG composition of AVK and AVP to LLL and OOO. AVK is a lauric fat, comprising mostly lauric and myristic fatty acids, and AVP comprise long unsaturated fatty acid chains, mostly oleic acid. The dual effect of the long unsaturated fatty acid TAG on the development of the crystals of medium fatty acid TAGs is probably more prevalent, and its mechanisms warrant further investigations.

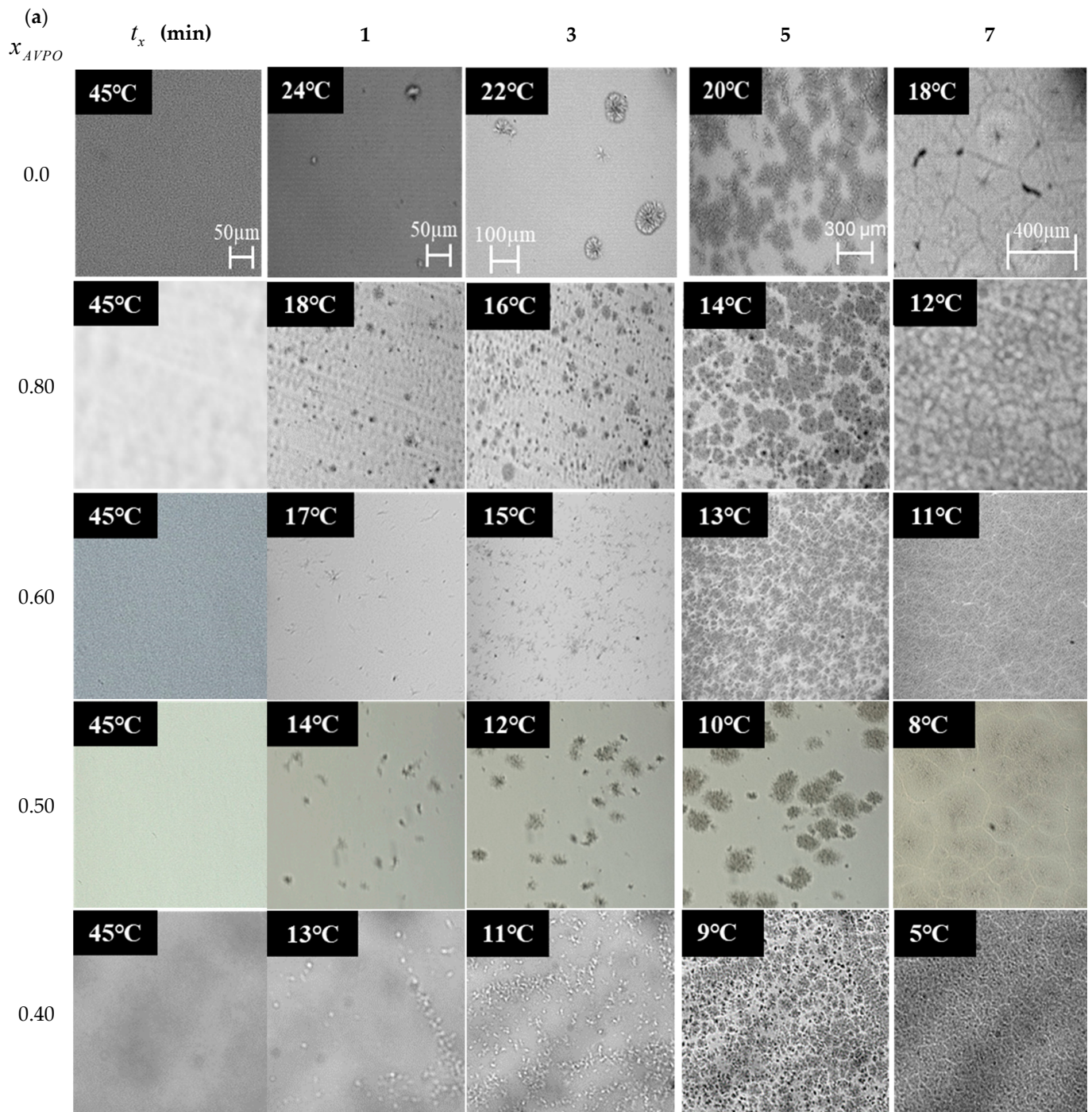


Figure 7. Cont.

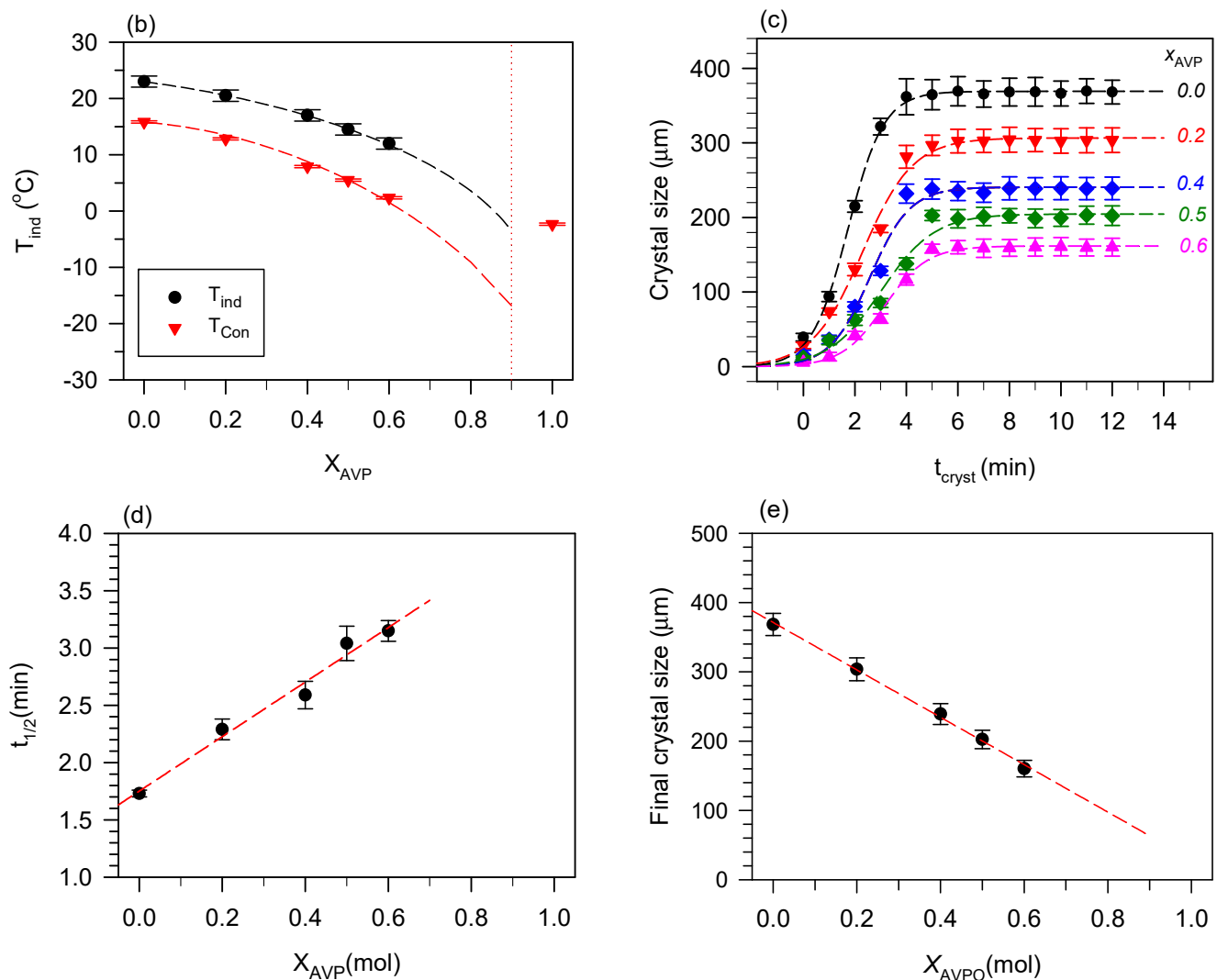


Figure 7. (a) PLM images ($\times 50$ magnification) of AVK/AVP mixture taken during cooling ($1\text{ }^{\circ}\text{C}/\text{min}$) from the melt. t_x is the time (± 0.5 min) after induction temperature is reached. (b) Induction temperature versus AVP molar fraction (x_{AVP}) as determined by PLM ($1\text{ }^{\circ}\text{C}/\text{min}$) compared to onset temperature of crystallization from DSC ($5\text{ }^{\circ}\text{C}/\text{min}$). Dashed lines are simulation of the liquidus line using the Bragg–William approximation (Equation (4), $\chi^2 = 0.45$) and ρ is the calculated BW parameter. (c) Evolution of microstructure size with crystallization time as a function of mole fraction of AVP. Crystallization time is measured after induction time ($t_x = t - t_{ind}$). Dashed lines are simulation of the data with a 3-parameters sigmoid (Equation (6)) (d) $t_{1/2}$ at half maximum ϕ values from (c). (e) Final crystal size versus x_{AVP} . Dashed lines in (d,e) are fit to straight lines ($R^2 > 0.991$).

Figure 7b shows that as the AVP concentration was increased, the PLM induction temperature (T_{ind}) decreased in a monotectic manner, like the liquidus lines T_{C1} and T_{M1} . The T_{ind} versus AVP mole fraction curve lays with the same curvature between the T_{C1} and T_{M1} liquidus lines and is also very well described by the BW approximation with a non-ideality of the mixing parameter, ρ , of -2 kJ/mol. This value is between those obtained for the simulation of the cooling and heating liquidus lines (-5 and -1.5 kJ/mol, respectively). The mixing behavior indicated by microscopy is above that of the DSC cooling experiments because of differences in sample mass and shape as well as cooling rate ($1\text{ }^{\circ}\text{C}/\text{min}$ instead of $5\text{ }^{\circ}\text{C}/\text{min}$) and is significantly close to the quasi-equilibrium state indicated by the DSC heating experiments.

The evolution of crystal size with crystallization time (Figure 7c) follows an S-shape reminiscent of sigmoid functions, which were developed to model general growth under probabilistic assumptions [66]. A three-parameters sigmoid function (Equation (6)) described very well the crystal size versus crystallization time as measured after induction time ($t_x = t - t_{ind}$).

$$\phi(t_x) = \frac{\phi_0}{1 + e^{-\left(\frac{t_x - t_{1/2}}{b}\right)}} \quad (6)$$

The return value (ϕ axis) is in the range of 0 at $t_x = 0$ to the maximum ϕ_0 at the end of crystallization. $t_{1/2}$ is the inflexion point of the curve and defines the half-maximum y value. The slope of the curve is characterized by $1/b$ at its midpoint, and this represents the steepness of the curve. Parameter b was not significantly different for the mixtures (0.86 ± 0.14), indicating a similar homogeneous crystal development. The half-maximum ϕ values were achieved at increasingly longer times. Figure 7d shows that $t_{1/2}$ linearly increased with x_{AVP} ($R^2 = 0.995$) at a rate of 2.4 ± 0.2 min/mol. The final microstructure size versus AVP concentration decreased linearly (Figure 7e, $R^2 = 0.997$) at a rate of $3.42 \mu\text{m}/\%\text{mol}$. The size, shape and distribution of crystals are critical for achieving the desired consistency and consumer acceptance [104]. Products with smaller crystals tend to be firmer, whereas those containing crystals ranging from 30 to 200 μm often exhibit a sandy mouthfeel [105]. The crystals of AVKF/AVPO mixtures as crystallized here (cooling from the melt at $1^\circ\text{C}/\text{min}$) did not present the sandy textures suggested by their size (between 160 μm to 370 μm). This is probably because these microstructures are made of small rod-shaped crystallites, which may be the origin of the smooth feel in the mouth.

3.6. Instrumental Textural Analysis

The principle of the test procedure was to measure the curves that appear during compression with a fixed force (shear) and when the male cone is retracted (adhesive curve) (Figure 8). The textural parameters of the samples were obtained from the shear and adhesive curves. Their peak heights indicate firmness and stickiness, respectively, and peak areas indicate the work of shear, which indicates spreadability, and the work of adhesion, which indicates adhesiveness, respectively.

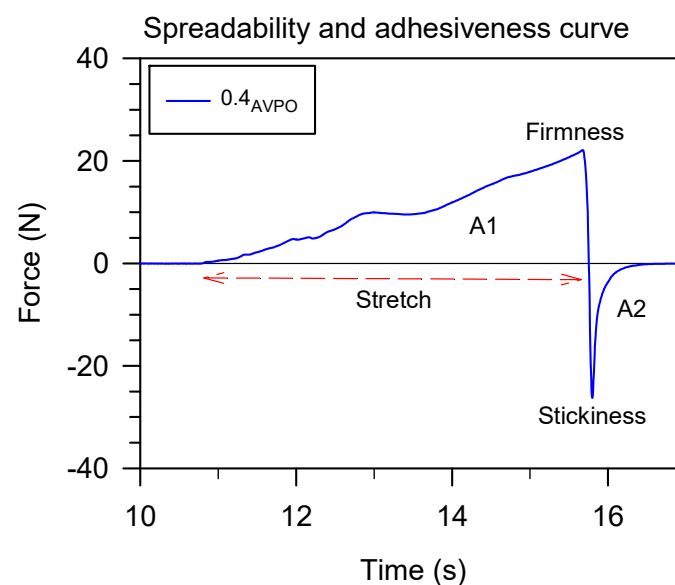


Figure 8. Shear and adhesive curves obtained during fixed force compression and drawing back of the cone spreadability rig for the 0.4_{AVP} mixture. Peak height during compression and drawing back: firmness and stickiness, respectively. Peak area A1 and A2: work of shear and adhesion, respectively.

Measurements of each sample were repeated three times, and the average value and the coefficient of variation were calculated. The stretch values of the curves were not significantly different, indicating similar adhesion to the cone, which justifies quantitative comparison between samples. The results obtained for the AVK/AVP mixtures are presented in Figure 9 for (a) firmness, (b) spreadability, (c) stickiness (adhesion force) and (d) adhesiveness (work of adhesion). The hardness results obtained with the 5 mm diameter ball probe are plotted in Figure 9a to allow for easy visual comparison with the firmness results.

Pearson Product Moment Correlation results (correlation coefficients R^2 and p -values) between spreadability, hardness, firmness, stickiness, work of adhesion, SFC and melting point are presented in Table 4.

Table 4. Pearson Product Moment Correlation results (correlation coefficients R and p -values) between crystal size, spreadability, hardness, firmness, stickiness, work of adhesion, SFC and melting point.

	Spreadability		Hardness		Firmness		Stickiness		Work of Adhesion		SFC		Melting Point		Crystal Point	
	R	$p <$	R	$p <$	R	$p <$	R	$p <$	R	$p <$	R	$p <$	R	$p <$	R	$p <$
Crystal size	0.864	0.06	0.890	0.04	0.879	0.05	0.462	0.43	0.703	0.19	0.991	0.001	0.997	0.0001	0.996	0.0002
Spreadability			0.9998	0.0001	0.999	0.00002	0.815	0.09	0.270	0.66	0.884	0.05	0.854	0.06	0.820	0.09
Hardness					0.999	7×10^{-5}	0.779	0.12	0.326	0.59	0.910	0.03	0.883	0.05	0.850	0.07
Firmness							0.793	0.11	0.304	0.62	0.900	0.04	0.871	0.05	0.838	0.08
Stickiness									0.304	0.62	0.465	0.43	0.427	0.47	0.384	0.52
Work of adhesion											0.688	0.20	0.728	0.16	0.762	0.13
SFC													0.996	0.0003	0.986	0.002

Hardness, firmness and spreadability determined by the cone geometry decrease in a similar exponential fashion toward zero (Figure 9a,b, $R^2 > 0.938$). The decay parameters obtained for hardness, firmness and spreadability are all close (steepness $b = 6.4 \pm 0.2$, 6.9 ± 0.4 and 6.0 ± 0.8 , respectively), indicating that the higher the AVP concentration, the more the mixture's structure approaches that of a liquid.

Stickiness versus x_{AVP} data from the cone spreadability rig (Figure 9d) are very well described by a three-parameters sigmoid function (Equation (6), $R^2 = 0.999$) and standard error of estimate (1.2). The calculated inflexion point of the curve is 0.37_{AVPO} , and the slope at the midpoint is 11 N/mol. The fundamental mechanisms that cause stickiness depend on the nature of the forces involved, adhesive, possibly in combination with cohesive, forces, as well as factors such as viscosity and viscoelasticity [106]. Differences in particle shape and size, liquid channels and external factors like temperature and moisture also contribute to stickiness. The growth model under probabilistic assumptions is a generalized characterization of the way in which an extent to which these forces and parameters contribute to the changes in stickiness with the increase in the oil concentration.

The work of adhesion versus AVP concentration showed a peak-like curve (Figure 9d) reminiscent of the maximum specific growth rate determined for the SFC (Figure 5e). Although the fit with a Weibull function yielded inconclusive parameters, the presumptive location of its peak and critical concentration (value at which the same adhesiveness is recorded) clearly matched. It is, therefore, safe to assume that the main factors affecting stickiness in the AVK/AVP binary system are those related to crystal growth and the resulting microstructure.

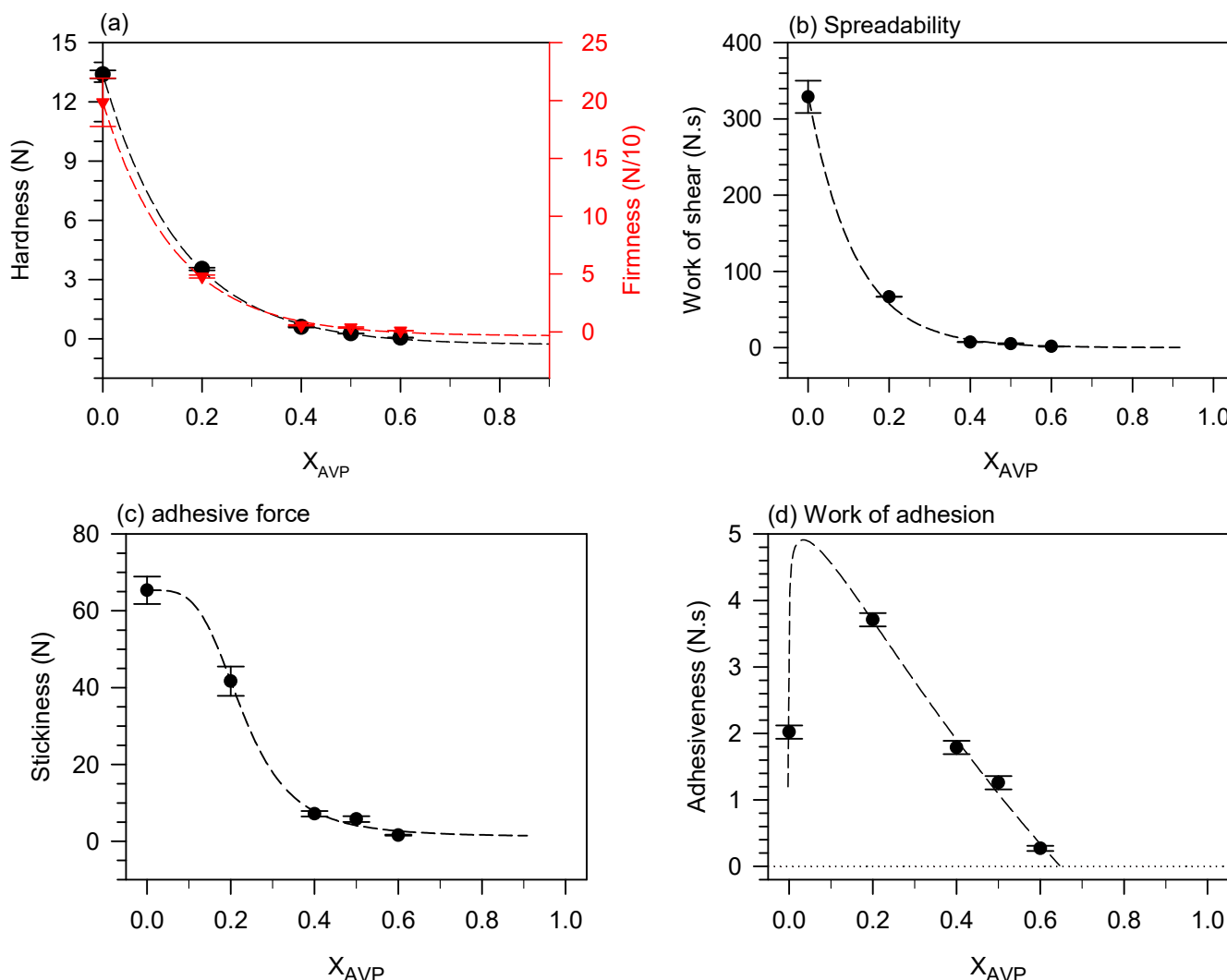


Figure 9. Instrumental textural properties of AVP/AVK blends—(a) hardness (●) and firmness (▼), (b) spreadability (work of shear). Dashed lines in (a,b) are fits to an exponential decay function, $R^2 > 0.996$. (c) Stickiness (●). Dashed line is a fit of a 3-parameters sigmoid function to the data (Equation (6), $R^2 = 0.999$ and standard error of estimates = 1.2), and (d) adhesiveness (work of adhesion) of AVK/AVP mixtures (●). Dashed line is a guide for the eye.

Correlation between the Textural Parameters and SFC, Melting Point and Crystal Size

Pearson Product Moment Correlation results indicated a higher correlation coefficient and lower p -value between firmness and spreadability than between firmness and hardness (Table 4). The relationships between firmness and spreadability and hardness, shown in Figure 10a, indicate that the discrepancy is mainly from the mixtures with high AVK amounts (AVK and 0.2_{AVP}). The comparison of all the mixtures indicated no correlation, for example between firmness and stickiness or spreadability. However, a closer look at the correlation graphs (see, for example, the case of firmness and stickiness in Figure 10b) indicates two strong linear correlations that can be delimited at $\sim 0.3_{AVP}$, one for the AVK-rich side and another for the AVP-rich side of the binary system. This, again, can be related to the stark differences in the crystal and SFC rates of growth discussed above. These data suggest that the properties related to the crystal growth of the present fat/oil mixtures are related to textural properties in two separate ways depending on the shape, size and probably the polymorphism of the phases present. The textural properties of fat are, in fact, the result of the three-dimensional network of fat crystals associated with a continuous oil phase [31,107–109]. The strength of crystal networks depends not only

on the amount of solids present (% SFC) but also on the polymorphic behavior and the crystal sizes formed [110]. In the case of the AVK/AVP binary system, these two ways are dictated by the effects of the unsaturated long-chain TAGs of the oil on the crystallization of the medium-chain TAGs of the fat. The critical concentration at which the crystallization mechanisms change was shown to be 0.3_{AVP} .

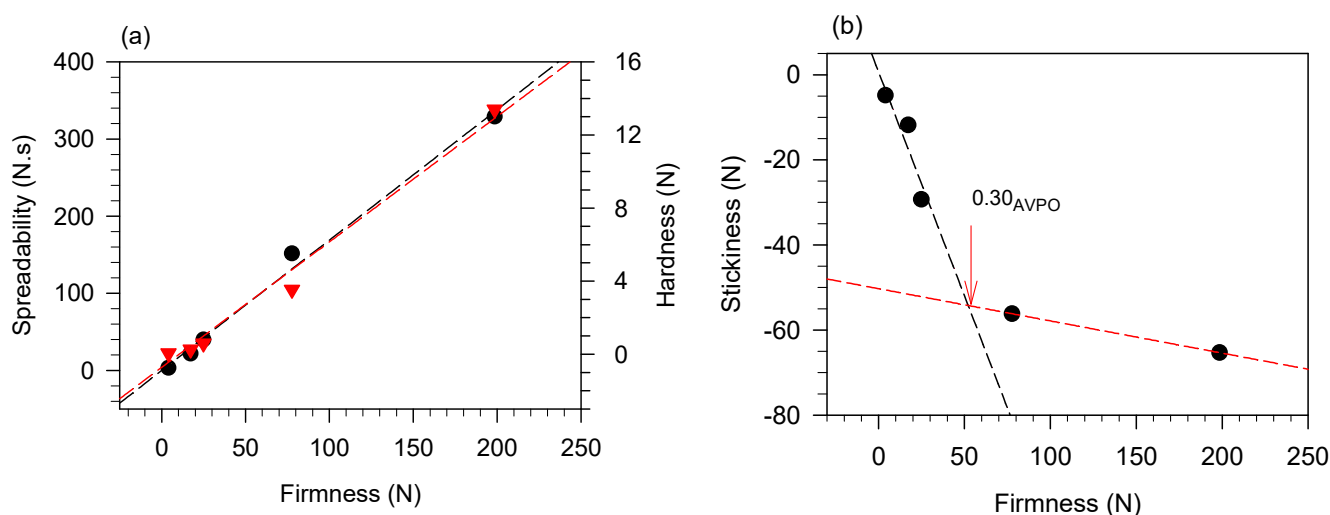


Figure 10. Relationship between (a) firmness and spreadability (●) firmness and hardness (▼), and (b) firmness and stickiness. Dashed lines in (a,b) are fits of the data to straight lines ($R^2 = 0.998$).

Stickiness and the work of adhesion did not correlate in any meaningful way with most of the other textural parameters ($r < 0.5$ and $p > 0.4$) for SFC, while melting and crystallization points were better at ~ 0.7 , with $p > 0.2$ indicating a weak correlation, if any at all (Table 4). Considering the shapes of the relationships and S.E.E, a conclusion was drawn that for all the relationships listed in Table 4, the values of the Pearson correlation $r < 0.9$ do not indicate correlated parameters. The correlations in these cases are weak at best.

The analysis of the relationships between the parameters indicates that the SFC is strongly correlated with the melting and crystallization points ($r > 0.986$, $p < 0.002$), which is confirmed by an S.E.E of 0.4. It is also strongly correlated with crystal size ($r = 0.991$, $p < 0.001$ and standard error of estimate of 0.4). The correlation analysis depicts a picture in which, apart from the above few exceptions, the role of the crystallization parameters in the relationships between the structural properties, as determined with the TA-TX machine, are complex and need further investigations to be clarified. One approach is to consider single or group mixtures with similar crystallization processes, as suggested by Figure 10b.

Viscosity and viscoelastic properties that affect textural properties through interfacial bonds and energy dissipation at a molecular level, in a manner not yet clarified [106,111,112], may be considered as factors for an interpretation of the textural results.

4. Conclusions

The studied mixtures possess a large range of physicochemical and textural properties including good spreadability, ductility and plasticity. AVK/AVP mixtures can be developed for direct consumption or used as fat mimetics in both hard and soft confectionary applications depending on the fat/oil ratio. The mixtures demonstrated good mixing compatibility, as evidenced by their phase diagrams, and effectively mimicked the melting characteristics and SFC profiles of commonly used fats like cocoa butter, coconut oil and palm kernel oil. Importantly, this study has revealed the possibility of formulating functional fats for industrial uses from AVK and AVP—a simple, environmentally friendly and relatively cost-effective solution.

AVK/AVP mixtures can be innovatively used in formulations in multiple industries, catering to the growing consumer demand for products that not only deliver desired

functionality, but also offer health benefits. These developments could also promote sustainability in production processes by reducing dependence on traditional fats that have greater environmental impacts.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/cosmetics11040107/s1>, Figure S1: Associated crystallization and melting enthalpies of T3 vs XAVP; Table S1: Non-lipid bioactive compounds in AVK detected by ESI-MS.

Author Contributions: Conceptualization, L.B., S.D., N.S. and S.S.N.; Methodology, L.B., S.D., N.S. and S.S.N.; Software, L.B., S.D., N.S. and S.S.N.; Validation, L.B., S.D., N.S., R.J.N.E., S.M. and S.S.N.; Formal analysis, L.B., S.D., N.S. and S.S.N.; Investigation, L.B., S.D., N.S. and S.S.N.; Resources, S.S.N.; Data curation, L.B., S.D., N.S. and S.S.N.; Writing—original draft, L.B., S.D., N.S. and S.S.N.; Writing—review & editing, L.B., S.D., N.S., R.J.N.E., S.M. and S.S.N.; Visualization, L.B., S.D., N.S. and S.S.N.; Supervision, L.B., R.J.N.E., S.M. and S.S.N.; Project administration, S.S.N.; Funding acquisition, S.S.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research received funding indirectly from CGX Energy Inc. and Frontera Energy Corporation. The funders were not involved in the study design, collection, analysis, interpretation of data, the writing of this article or the decision to submit it for publication.

Data Availability Statement: Data is contained within the article and Supplementary Material.

Acknowledgments: The Sustainable Guyana Program, a partnership between Trent University and the University of Guyana funded by CGX Energy Inc. and Frontera Energy Corporation, the Natural Sciences and Engineering Research Council of Canada (NSERC) and Trent University are acknowledged. Collaboration with the communities of Surama in Region 9, Guyana and of Cabora, Kamwatta and Waramuri in Region 1, Guyana is also acknowledged.

Conflicts of Interest: The authors declare no conflict of interest. The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. The funders had no role in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Abbreviations

ESI-MS	Electrospray ionization–mass spectrometry
TAGs	Triacylglycerols
LLC ₈	3-(octanoyloxy)propane-1,2-diyl didodecanoate
LLC ₁₀	3-(decanoyloxy)propane-1,2-diyl didodecanoate
LLL	propane-1,2,3-triyl tridodecanoate
LLM	3-(tetradecanoyloxy)propane-1,2-diyl didodecanoate
MML	3-(dodecanoyloxy)propane-1,2-diyl ditetradecanoate
POP	2-(oleoyloxy)propane-1,3-diyl dipalmitate
PPO	3-(oleoyloxy)propane-1,2-diyl dipalmitate
POO	2-(palmitoyloxy)propane-1,3-diyl dioleate
OOO	propane-1,2,3-triyl trioleate
SOO	3-(oleoyloxy)propane-1,2-diyl distearate
SSO	propane-1,2,3-triyl tristearate
UV-Vis	Ultraviolet–visible
TPC	Total phenolic content
TCC	Total carotenoid content
DSC	Differential scanning calorimetry
FWHM	Full width at half max
T _{On}	Onset temperature
T _{Off}	Offset temperature
SFC	Solid fat content
PLM	Polarized light microscopy

References

1. USDA. *Oilseeds: Worldwide Markets and Trade*; U.S Department of Agriculture: Washington, DC, USA, 2024; p. 39.
2. Dini, I.; Laneri, S. The New Challenge of Green Cosmetics: Natural Food Ingredients for Cosmetic Formulations. *Molecules* **2021**, *26*, 3921. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Santos, M.T.d.; Morgavi, P.; Le Roux, G.A.C. Exploring amazonian fats and oils blends by computational predictions of solid fat content. *OCL* **2018**, *25*, D107. [\[CrossRef\]](#)
4. Kahn, F. The genus *Astrocaryum* (Arecaceae). *Rev. Peru. Biol.* **2008**, *15*, 31–48. [\[CrossRef\]](#)
5. Craveiro Holanda Malveira Maia, G.; da Silva Campos, M.; Barros-Monteiro, J.; Eduardo Lucas Castillo, J.; Soares Faleiros, M.; Souza de Aquino Sales, R.; Moraes Lopes Galeno, D.; Lira, E.; das Chagas do Amaral Souza, F.; Ortiz, C.; et al. Effects of *Astrocaryum aculeatum* Meyer (Tucumã) on Diet-Induced Dyslipidemic Rats. *J. Nutr. Metab.* **2014**, *2014*, 202367. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Silva, M.B.; Perez, V.H.; Pereira, N.R.; Silveira, T.d.C.; da Silva, N.R.F.; de Andrade, C.M.; Sampaio, R.M. Drying kinetic of tucum fruits (*Astrocaryum aculeatum* Meyer): Physicochemical and functional properties characterization. *J. Food Sci. Technol.* **2018**, *55*, 1656–1666. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Menezes, E.G.O.; Barbosa, J.R.; Pires, F.C.S.; Ferreira, M.C.R.; de Souza e Silva, A.P.; Siqueira, L.M.M.; de Carvalho Junior, R.N. Development of a new scale-up equation to obtain Tucumã-of-Pará (*Astrocaryum vulgare* Mart.) oil rich in carotenoids using supercritical CO₂ as solvent. *J. Supercrit. Fluids* **2022**, *181*, 105481. [\[CrossRef\]](#)
8. Teixeira, G.L.; Ibañez, E.; Block, J.M. Emerging Lipids from Arecaceae Palm Fruits in Brazil. *Molecules* **2022**, *27*, 4188. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Falcao, A.d.O.; Speranza, P.; Ueta, T.; Martins, M. Antioxidant potential and modulatory effects of restructured lipids from the Amazonian palms on liver cells. *Food Technol. Biotechnol.* **2017**, *55*, 553–561.
10. Bezerra, C.V.; Rodrigues, A.; de Oliveira, P.D.; da Silva, D.A.; da Silva, L.H.M. Technological properties of amazonian oils and fats and their applications in the food industry. *Food Chem.* **2017**, *221*, 1466–1473. [\[CrossRef\]](#) [\[PubMed\]](#)
11. Deonarine, S.; Soodoo, N.; Bouzidi, L.; Narine, S.S. Oil Extraction and Natural Drying Kinetics of the Pulp and Seeds of Commercially Important Oleaginous Fruit from the Rainforests of Guyana. *Processes* **2023**, *11*, 3292. [\[CrossRef\]](#)
12. Rodrigues, A.M.d.C.; Darnet, S.; Silva, L.H.M.d. Fatty acid profiles and tocopherol contents of buriti (*Mauritia flexuosa*), patawa (*Oenocarpus bataua*), tucuma (*Astrocaryum vulgare*), mari (*Poraqueiba paraensis*) and inaja (*Maximiliana maripa*) fruits. *J. Braz. Chem. Soc.* **2010**, *21*, 2000–2004. [\[CrossRef\]](#)
13. Bora, P.S.; Narain, N.; Rocha, R.V.M.; De Oliveira Monteiro, A.C.; De Azevedo Moreira, R. Characterization of the oil and protein fraction of (*Astrocaryum vulgare* Mart.) fruit pulp and kernel. *Cienc. Y Tecnol. Aliment.* **2001**, *3*, 111–116. [\[CrossRef\]](#)
14. Bony, E.; Boudard, F.; Brat, P.; Dussosoy, E.; Portet, K.; Poucheret, P.; Giannis, J.; Michel, A. Awara (*Astrocaryum vulgare* M.) pulp oil: Chemical characterization, and anti-inflammatory properties in a mice model of endotoxic shock and a rat model of pulmonary inflammation. *Fitoterapia* **2012**, *83*, 33–43. [\[CrossRef\]](#) [\[PubMed\]](#)
15. da Silva Sousa, H.M.; Leal, G.F.; da Silva Gualberto, L.; de Freitas, B.C.B.; Guarda, P.M.; Borges, S.V.; Morais, R.A.; de Souza Martins, G.A. Exploration of the chemical characteristics and bioactive and antioxidant potential of tucumã (*Astrocaryum vulgare*), peach palm (*Bactris gasipaes*), and bacupari (*Garcinia gardneriana*) native Brazilian fruits. *Biomass Convers. Biorefinery* **2023**, *13*, 1–14. [\[CrossRef\]](#)
16. Rossato, A.; da Silva Silveira, L.; Lopes, L.Q.S.; De Sousa Filho, W.P.; Schaffer, L.F.; Santos, R.C.V.; Sagrillo, M.R. Evaluation in vitro of antimicrobial activity of tucumã oil (*Astrocaryum vulgare*). *Arch. Biosci. Health* **2019**, *1*, 99–112. [\[CrossRef\]](#)
17. Nascimento, K.; Copetti, P.M.; Fernandes, A.; Klein, B.; Fogaça, A.; Zepka, L.Q.; Wagner, R.; Ourique, A.F.; Sagrillo, M.R.; da Silva, J.E.P. Phytochemical analysis and evaluation of the antioxidant and antiproliferative effects of Tucumã oil nanocapsules in breast adenocarcinoma cells (MCF-7). *Nat. Prod. Res.* **2021**, *35*, 2060–2065. [\[CrossRef\]](#)
18. Copetti, P.; Oliveira, P.; Vaucher, R.; Duarte, M.; Krause, L. Tucumã extracts decreases PML/RARA gene expression in NB4/APL cell line. *Arch. Biosci. Health* **2019**, *1*, 77–98. [\[CrossRef\]](#)
19. Guex, C.G.; Cassanago, G.B.; Dornelles, R.C.; Casoti, R.; Engelmann, A.M.; Somacal, S.; Maciel, R.M.; Duarte, T.; Borges, W.d.S.; Andrade, C.M.d.; et al. Tucumã (*Astrocaryum aculeatum*) extract: Phytochemical characterization, acute and subacute oral toxicity studies in Wistar rats. *Drug Chem. Toxicol.* **2022**, *45*, 810–821. [\[CrossRef\]](#) [\[PubMed\]](#)
20. Bonadiman, B.; Chaves, C.; Assmann, C.E.; Weis, G.C.C.; Alves, A.O.; Gindri, A.L.; Chaves, C.; da Cruz, I.B.M.; Zamoner, A.; Bagatini, M.D. Tucumã (*Astrocaryum aculeatum*) Prevents Oxidative and DNA Damage to Retinal Pigment Epithelium Cells. *J. Med. Food* **2021**, *24*, 1050–1057. [\[CrossRef\]](#) [\[PubMed\]](#)
21. Burlando, B.; Cornara, L. Revisiting Amazonian Plants for Skin Care and Disease. *Cosmetics* **2017**, *4*, 25. [\[CrossRef\]](#)
22. Mosquera Narvaez, L.E.; Ferreira, L.M.; Sanches, S.; Alesa Gyles, D.; Silva-Júnior, J.O.; Ribeiro Costa, R.M. A Review of Potential Use of Amazonian Oils in the Synthesis of Organogels for Cosmetic Application. *Molecules* **2022**, *27*, 2733. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Ibiapina, A.; Gualberto, L.d.S.; Dias, B.B.; Freitas, B.C.B.; Martins, G.A.d.S.; Melo Filho, A.A. Essential and fixed oils from Amazonian fruits: Proprieties and applications. *Crit. Rev. Food Sci. Nutr.* **2022**, *62*, 8842–8854. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Cardona Jaramillo, J.E.; Carrillo Bautista, M.P.; Alvarez Solano, O.A.; Achenie, L.E.K.; González Barrios, A.F. Impact of the Mode of Extraction on the Lipidomic Profile of Oils Obtained from Selected Amazonian Fruits. *Biomolecules* **2019**, *9*, 329. [\[CrossRef\]](#) [\[PubMed\]](#)

25. Rabasco Álvarez, A.M.; González Rodríguez, M.L. Lipids in pharmaceutical and cosmetic preparations. *Grasas Y Aceites* **2000**, *51*, 74–96. [\[CrossRef\]](#)
26. Shukla, V. Confectionery Lipids. *Bailey's Ind. Oil Fat Prod.* **2005**, *4*, 159–173. [\[CrossRef\]](#)
27. Lipp, M.; Simoneau, C.; Ulberth, F.; Anklam, E.; Crews, C.; Brereton, P.; de Greyt, W.; Schwack, W.; Wiedmaier, C. Composition of Genuine Cocoa Butter and Cocoa Butter Equivalents. *J. Food Compos. Anal.* **2001**, *14*, 399–408. [\[CrossRef\]](#)
28. Shukla, V.; Kragballe, K. Exotic butters as cosmetic lipids. *Inform* **1998**, *9*, 512–516.
29. Watanabe, S.; Yoshikawa, S.; Sato, K. Formation and properties of dark chocolate prepared using fat mixtures of cocoa butter and symmetric/asymmetric stearic-oleic mixed-acid triacylglycerols: Impact of molecular compound crystals. *Food Chem.* **2021**, *339*, 127808. [\[CrossRef\]](#) [\[PubMed\]](#)
30. Weiss, T.J. *Food Oils and Their Uses*; AVI Publishing Company: Westport, CT, USA, 1983.
31. Ghotra, B.S.; Dyal, S.D.; Narine, S.S. Lipid shortenings: A review. *Food Res. Int.* **2002**, *35*, 1015–1048. [\[CrossRef\]](#)
32. Torbica, A.; Jovanovic, O.; Pajin, B. The advantages of solid fat content determination in cocoa butter and cocoa butter equivalents by the Karlshamns method. *Eur. Food Res. Technol.* **2006**, *222*, 385–391. [\[CrossRef\]](#)
33. Nor Hayati, I.; Che Man, Y.B.; Tan, C.P.; Nor Aini, I. Physicochemical characteristics of soybean oil, palm kernel olein, and their binary blends. *Int. J. Food Sci. Technol.* **2009**, *44*, 152–161. [\[CrossRef\]](#)
34. Hashempour-Baltork, F.; Torbati, M.; Azadmard-Damirchi, S.; Savage, G.P. Vegetable oil blending: A review of physicochemical, nutritional and health effects. *Trends Food Sci. Technol.* **2016**, *57*, 52–58. [\[CrossRef\]](#)
35. Zhang, Z.; Song, J.; Lee, W.J.; Xie, X.; Wang, Y. Characterization of enzymatically interesterified palm oil-based fats and its potential application as cocoa butter substitute. *Food Chem.* **2020**, *318*, 126518. [\[CrossRef\]](#)
36. Biswas, N.; Cheow, Y.L.; Tan, C.P.; Siow, L.F. Blending of Palm Mid-Fraction, Refined Bleached Deodorized Palm Kernel Oil or Palm Stearin for Cocoa Butter Alternative. *J. Am. Oil Chem. Soc.* **2016**, *93*, 1415–1427. [\[CrossRef\]](#)
37. Hashem, A.; Abdul-fadl, M.; Arafat, S.; Aboulhoda, B. Producing cocoa butter substitutes by blending process of some vegetable oils. *J. Biol. Chem. Environ. Sci.* **2018**, *13*, 133–154.
38. Mohanan, A.; Darling, B.; Bouzidi, L.; Narine, S.S. Mitigating crystallization of saturated FAMES (fatty acid methyl esters) in biodiesel. 3. The binary phase behavior of 1,3-di-oleoyl-2-palmitoyl glycerol—Methyl palmitate—A multi-length scale structural elucidation of mechanism responsible for inhibiting FAME crystallization. *Energy* **2015**, *86*, 500–513. [\[CrossRef\]](#)
39. Boodhoo, M.V.; Bouzidi, L.; Narine, S.S. The binary phase behavior of 1,3-dicaproyl-2-stearoyl-*sn*-glycerol and 1,2-dicaproyl-3-stearoyl-*sn*-glycerol. *Chem. Phys. Lipids* **2009**, *157*, 21–39. [\[CrossRef\]](#)
40. Foubert, I.; Dewettinck, K.; Vanrolleghem, P.A. Modelling of the crystallization kinetics of fats. *Trends Food Sci. Technol.* **2003**, *14*, 79–92. [\[CrossRef\]](#)
41. Sagrillo, M.R.; Garcia, L.F.M.; de Souza Filho, O.C.; Duarte, M.M.M.F.; Ribeiro, E.E.; Cadoná, F.C.; da Cruz, I.B.M. Tucumã fruit extracts (*Astrocaryum aculeatum* Meyer) decrease cytotoxic effects of hydrogen peroxide on human lymphocytes. *Food Chem.* **2015**, *173*, 741–748. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Sánchez-Rangel, J.C.; Benavides, J.; Heredia, J.B.; Cisneros-Zevallos, L.; Jacobo-Velázquez, D.A. The Folin–Ciocalteu assay revisited: Improvement of its specificity for total phenolic content determination. *Anal. Methods* **2013**, *5*, 5990–5999. [\[CrossRef\]](#)
43. de Carvalho, L.M.J.; Gomes, P.B.; Godoy, R.L.d.O.; Pacheco, S.; do Monte, P.H.F.; de Carvalho, J.L.V.; Nutti, M.R.; Neves, A.C.L.; Vieira, A.C.R.A.; Ramos, S.R.R. Total carotenoid content, α -carotene and β -carotene, of landrace pumpkins (*Cucurbita moschata* Duch): A preliminary study. *Food Res. Int.* **2012**, *47*, 337–340. [\[CrossRef\]](#)
44. Siqueira, E.M.d.A.; Rosa, F.R.; Fustinoni, A.M.; de Sant'Ana, L.P.; Arruda, S.F. Brazilian Savanna Fruits Contain Higher Bioactive Compounds Content and Higher Antioxidant Activity Relative to the Conventional Red Delicious Apple. *PLoS ONE* **2013**, *8*, e72826. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Rodriguez-Amaya, D.B.; Kimura, M. *HarvestPlus Handbook for Carotenoid Analysis*; International Food Policy Research Institute (IFPRI) Washington: Washington, DC, USA, 2004; Volume 2.
46. Tee, E.S.; Lim, C.-L. The analysis of carotenoids and retinoids: A review. *Food Chem.* **1991**, *41*, 147–193. [\[CrossRef\]](#)
47. de Rosso, V.V.; Mercadante, A.Z. Identification and Quantification of Carotenoids, By HPLC-PDA-MS/MS, from Amazonian Fruits. *J. Agric. Food Chem.* **2007**, *55*, 5062–5072. [\[CrossRef\]](#) [\[PubMed\]](#)
48. Ferreira, M.J.A.; Mota, M.F.S.; Mariano, R.G.B.; Freitas, S.P. Evaluation of liquid-liquid extraction to reducing the acidity index of the tucuma (*Astrocaryum vulgare* Mart.) pulp oil. *Sep. Purif. Technol.* **2021**, *257*, 117894. [\[CrossRef\]](#)
49. Rodriguez-Amaya, D.B. *A Guide to Carotenoid Analysis in Foods*; ILSI Press: Washington, DC, USA, 2001; Volume 71.
50. Freitas, M.L.F.; Chisté, R.C.; Polachini, T.C.; Sardella, L.A.C.Z.; Aranha, C.P.M.; Ribeiro, A.P.B.; Nicoletti, V.R. Quality characteristics and thermal behavior of buriti (*Mauritia flexuosa* L.) oil. *Grasas Y Aceites* **2017**, *68*, e220. [\[CrossRef\]](#)
51. Ferreira, C.D.; da Conceição, E.J.L.; Machado, B.A.S.; Hermes, V.S.; de Oliveira Rios, A.; Druzian, J.I.; Nunes, I.L. Physicochemical Characterization and Oxidative Stability of Microencapsulated Crude Palm Oil by Spray Drying. *Food Bioprocess Technol.* **2016**, *9*, 124–136. [\[CrossRef\]](#)
52. Amchova, P.; Kotolova, H.; Ruda-Kucerova, J. Health safety issues of synthetic food colorants. *Regul. Toxicol. Pharmacol.* **2015**, *73*, 914–922. [\[CrossRef\]](#) [\[PubMed\]](#)
53. Köpcke, W.; Krutmann, J. Protection from sunburn with beta-Carotene—A meta-analysis. *Photochem. Photobiol.* **2008**, *84*, 284–288. [\[CrossRef\]](#) [\[PubMed\]](#)

54. Eicker, J.; Kürten, V.; Wild, S.; Riss, G.; Goralczyk, R.; Krutmann, J.; Berneburg, M. Betacarotene supplementation protects from photoaging-associated mitochondrial DNA mutation. *Photochem. Photobiol. Sci.* **2003**, *2*, 655–659. [[CrossRef](#)] [[PubMed](#)]
55. Morganti, P.; Bruno, C.; Guarneri, F.; Cardillo, A.; Del Ciotto, P.; Valenzano, F. Role of topical and nutritional supplement to modify the oxidative stress. *Int. J. Cosmet. Sci.* **2002**, *24*, 331–339. [[CrossRef](#)] [[PubMed](#)]
56. Ferreira, B.S.; De Almeida, C.G.; Faza, L.P.; De Almeida, A.; Diniz, C.G.; Silva, V.L.d.; Grazul, R.M.; Le Hyaric, M. Comparative Properties of Amazonian Oils Obtained by Different Extraction Methods. *Molecules* **2011**, *16*, 5875–5885. [[CrossRef](#)] [[PubMed](#)]
57. Chai, B.; Jiang, W.; Hu, M.; Wu, Y.; Si, H. In vitro synergistic interactions of Protocatechuic acid and Chlorogenic acid in combination with antibiotics against animal pathogens. *Synergy* **2019**, *9*, 100055. [[CrossRef](#)]
58. Kępa, M.; Mikłasińska-Majdanik, M.; Wojtyczka, R.D.; Idzik, D.; Korzeniowski, K.; Smoleń-Dzirba, J.; Wąsik, T.J. Antimicrobial Potential of Caffeic Acid against *Staphylococcus aureus* Clinical Strains. *Biomed. Res. Int.* **2018**, *2018*, 7413504. [[CrossRef](#)] [[PubMed](#)]
59. Mikłasińska-Majdanik, M.; Kępa, M.; Wąsik, T.J.; Zapletal-Pudęłko, K.; Klim, M.; Wojtyczka, R.D. The Direction of the Antibacterial Effect of Rutin Hydrate and Amikacin. *Antibiotics* **2023**, *12*, 1469. [[CrossRef](#)] [[PubMed](#)]
60. Abdulhadi, S.Y.; Gergees, R.N.; Hasan, G.Q. Molecular identification, antioxidant efficacy of phenolic compounds, and antimicrobial activity of beta-carotene isolated from fruiting bodies of *Suillus* sp. *Karbala Int. J. Mod. Sci.* **2020**, *6*, 4. [[CrossRef](#)]
61. Duarte, S.; Rosalen, P.L.; Hayacibara, M.F.; Cury, J.A.; Bowen, W.H.; Marquis, R.E.; Rehder, V.L.; Sartoratto, A.; Ikegaki, M.; Koo, H. The influence of a novel propolis on mutans streptococci biofilms and caries development in rats. *Arch. Oral Biol.* **2006**, *51*, 15–22. [[CrossRef](#)] [[PubMed](#)]
62. Barkas, F.; Bathrellou, E.; Nomikos, T.; Panagiotakos, D.; Liberopoulos, E.; Kontogianni, M.D. Plant Sterols and Plant Stanols in Cholesterol Management and Cardiovascular Prevention. *Nutrients* **2023**, *15*, 2845. [[CrossRef](#)] [[PubMed](#)]
63. Burčová, Z.; Kreps, F.; Greifová, M.; Jablonský, M.; Ház, A.; Schmidt, Š.; Šurina, I. Antibacterial and antifungal activity of phytosterols and methyl dehydroabietate of Norway spruce bark extracts. *J. Biotechnol.* **2018**, *282*, 18–24. [[CrossRef](#)] [[PubMed](#)]
64. Shih, C.-C.; Lin, C.-H.; Lin, W.-L. Effects of *Momordica charantia* on insulin resistance and visceral obesity in mice on high-fat diet. *Diabetes Res. Clin. Pract.* **2008**, *81*, 134–143. [[CrossRef](#)] [[PubMed](#)]
65. Deonarine, S.; Soodoo, N.; Bouzidi, L.; Emery, R.J.N.; Martic, S.; Narine, S.S. Molecular, Crystalline, and Microstructures of Lipids from *Astrocaryum* Species in Guyana and Their Thermal and Flow Behavior. *Thermo* **2024**, *4*, 140–163. [[CrossRef](#)]
66. Boodhoo, M.V.; Kutek, T.; Filip, V.; Narine, S.S. The binary phase behavior of 1,3-dimyristoyl-2-stearoyl-sn-glycerol and 1,2-dimyristoyl-3-stearoyl-sn-glycerol. *Chem. Phys. Lipids* **2008**, *154*, 7–18. [[CrossRef](#)] [[PubMed](#)]
67. Boodhoo, M.V.; Bouzidi, L.; Narine, S.S. The binary phase behavior of 1, 3-dipalmitoyl-2-stearoyl-sn-glycerol and 1, 2-dipalmitoyl-3-stearoyl-sn-glycerol. *Chem. Phys. Lipids* **2009**, *160*, 11–32. [[CrossRef](#)] [[PubMed](#)]
68. Abes, M.; Bouzidi, L.; Narine, S.S. Crystallization and phase behavior of 1,3-propanediol esters II. 1,3-Propanediol distearate/1,3-propanediol dipalmitate (SS/PP) and 1,3-propanediol distearate/1,3-propanediol dimyristate (SS/MM) binary systems. *Chem. Phys. Lipids* **2007**, *150*, 89–108. [[CrossRef](#)] [[PubMed](#)]
69. Baker, M.; Bouzidi, L.; Narine, S.S. Mitigating crystallization of saturated FAMES (fatty acid methyl esters) in biodiesel: 2. The phase behavior of 2-stearoyl diolein–methyl stearate binary system. *Energy* **2015**, *83*, 647–657. [[CrossRef](#)]
70. Macridachis, J.; Bayés-García, L.; Calvet, T. Mixing phase behavior of trilaurin and monounsaturated triacylglycerols based on palmitic and oleic fatty acids. *J. Therm. Anal. Calorim.* **2023**, *148*, 12987–13001. [[CrossRef](#)]
71. Höhne, G.; Hemminger, W.; Flammersheim, H.-J. (Eds.) *Differential Scanning Calorimetry*, 2nd ed.; Springer: Berlin/Heidelberg, Germany, 2003; p. 298.
72. Inoue, T.; Hisatsugu, Y.; Ishikawa, R.; Suzuki, M. Solid–liquid phase behavior of binary fatty acid mixtures: 2. Mixtures of oleic acid with lauric acid, myristic acid, and palmitic acid. *Chem. Phys. Lipids* **2004**, *127*, 161–173. [[CrossRef](#)] [[PubMed](#)]
73. MacNaughtan, W.; Farhat, I.; Himawan, C.; Starov, V.; Stapley, A. A differential scanning calorimetry study of the crystallization kinetics of tristearin–tripalmitin mixtures. *J. Am. Oil Chem. Soc.* **2006**, *83*, 1–9. [[CrossRef](#)]
74. Costa, M.C.; Rolemberg, M.P.; Boros, L.A.D.; Krähenbühl, M.A.; de Oliveira, M.G.; Meirelles, A.J.A. Solid–Liquid Equilibrium of Binary Fatty Acid Mixtures. *J. Chem. Eng. Data* **2006**, *52*, 30–36. [[CrossRef](#)]
75. Inoue, T.; Motoda, I.; Hiramatsu, N.; Suzuki, M.; Sato, K. Phase-behavior of binary mixture of palmitoleic acid (cis-9-hexadecenoic acid) and asclepic acid (cis-11-octadecenoic acid). *Chem. Phys. Lipids* **1993**, *66*, 209–214. [[CrossRef](#)]
76. Hildebrand, J.H. Solubility XII. Regular solutions. *J. Am. Chem. Soc.* **1929**, *51*, 66–80. [[CrossRef](#)]
77. Bragg, W.L.; Williams, E.J. The effect of thermal agitation on atomic arrangement in alloys. *Proc. R. Soc.* **1934**, *145*, 699–730.
78. Moore, W.J. *Physical Chemistry*, 4th ed.; Prentice-Hall: Englewood Cliffs, NJ, USA, 1972; pp. 229–278.
79. Inoue, T.; Hisatsugu, Y.; Yamamoto, R.; Suzuki, M. Solid-liquid phase behavior of binary fatty acid mixtures 1. Oleic acid/stearic acid and oleic acid/behenic acid mixtures. *Chem. Phys. Lipids* **2004**, *127*, 143–152. [[CrossRef](#)] [[PubMed](#)]
80. Abes, M.; Bouzidi, L.; Narine, S.S. Crystallization and phase behavior of fatty acid esters of 1,3 propanediol III: 1,3 propanediol dicaprylate/1,3 propanediol distearate (CC/SS) and 1,3 propanediol dicaprylate/1,3 propanediol dipalmitate (CC/PP) binary systems. *Chem. Phys. Lipids* **2008**, *151*, 110–124. [[CrossRef](#)] [[PubMed](#)]
81. Lee, A.G. Lipid Phase-Transitions and Phase-Diagrams.1. Lipid Phase-Transitions. *Biochim. Biophys. Acta* **1977**, *472*, 237–281. [[CrossRef](#)] [[PubMed](#)]
82. Lee, A.G. Lipid Phase-Transitions and Phase-Diagrams.2. Mixtures Involving Lipids. *Biochim. Biophys. Acta* **1977**, *472*, 285–344. [[CrossRef](#)] [[PubMed](#)]

83. Tenchov, B.G. Non-uniform lipid distribution in membranes. *Prog. Surf. Sci.* **1985**, *20*, 273–340. [[CrossRef](#)]
84. Nibu, Y.; Inoue, T. Miscibility of binary phospholipid mixtures under hydrated and non-hydrated conditions.2. Phosphatidylethanolamines with different acyl-chain lengths. *Chem. Phys. Lipids* **1995**, *76*, 159–169. [[CrossRef](#)]
85. Rycerz, L. Practical remarks concerning phase diagrams determination on the basis of differential scanning calorimetry measurements. *J. Therm. Anal. Calorim.* **2013**, *113*, 231–238. [[CrossRef](#)]
86. Findlay, A. *The Phase Rule and Its Applications*; Longmans, Green and Company: Selinsgrove, PA, USA, 1904; p. 361.
87. Matsuoka, M.; Ozawa, R. Determination of solid-liquid phase equilibria of binary organic systems by differential scanning calorimetry. *J. Cryst. Growth* **1989**, *96*, 596–604. [[CrossRef](#)]
88. Timms, R.E. Phase behaviour of fats and their mixtures. *Prog. Lipid Res.* **1984**, *23*, 1–38. [[CrossRef](#)] [[PubMed](#)]
89. Petersson, B.; Anjou, K.; Sandström, L. Pulsed NMR Method for Solid Fat Content Determination in Tempering Fats, Part I: Cocoa Butters and Equivalents. *Fette Seifen Anstrichm.* **1985**, *87*, 225–230. [[CrossRef](#)]
90. Nillson, J. Measuring solid fat content. *Manuf. Confect.* **1986**, *5*, 88–91.
91. Lovett, P.N. 5—Shea butter: Properties and processing for use in food. In *Specialty Oils and Fats in Food and Nutrition*; Talbot, G., Ed.; Woodhead Publishing: Sawston, UK, 2015; pp. 125–158. [[CrossRef](#)]
92. Ghazani, S.M.; Marangoni, A.G. Molecular Origins of Polymorphism in Cocoa Butter. *Annu. Rev. Food Sci. Technol.* **2021**, *12*, 567–590. [[CrossRef](#)] [[PubMed](#)]
93. Siew, W.L. Crystallisation and melting behaviour of palm kernel oil and related products by differential scanning calorimetry. *Eur. J. Lipid Sci. Technol.* **2001**, *103*, 729–734. [[CrossRef](#)]
94. Matsuda, H.; Yamaguchi, M.; Arima, H. Separation and crystallization of oleaginous constituents in cosmetics: Sweating and blooming. In *Crystallization Processes in Fats and Lipid Systems*; CRC Press: Boca Raton, FL, USA, 2001; pp. 499–518.
95. Pereira, E.; Ferreira, M.C.; Sampaio, K.A.; Grimaldi, R.; Meirelles, A.J.d.A.; Maximo, G.J. Physical properties of Amazonian fats and oils and their blends. *Food Chem.* **2019**, *278*, 208–215. [[CrossRef](#)] [[PubMed](#)]
96. Torbica, A.; Jambrec, D.; Tomić, J.; Pajin, B.; Petrović, J.; Kravić, S.; Lončarević, I. Solid Fat Content, Pre-Crystallization Conditions, and Sensory Quality of Chocolate with Addition of Cocoa Butter Analogues. *Int. J. Food Prop.* **2016**, *19*, 1029–1043. [[CrossRef](#)]
97. Jahurul, M.H.A.; Soon, Y.; Shaarani Sharifudin, M.; Hasmadi, M.; Mansoor, A.H.; Zaidul, I.S.M.; Lee, J.S.; Ali, M.E.; Ghafoor, K.; Zzaman, W.; et al. Bambang (Mangifera pajang) kernel fat: A potential new source of cocoa butter alternative. *Int. J. Food Sci. Technol.* **2018**, *53*, 1689–1697. [[CrossRef](#)]
98. da Silva Lannes, S.C.; Ignácio, R.M. Structuring fat foods. In *Food Industry*; Muzzalupo, I., Ed.; IntechOpen: London, UK, 2013; pp. 65–91. [[CrossRef](#)]
99. Silva, T.J.; Barrera-Arellano, D.; Ribeiro, A.P.B. Margarines: Historical approach, technological aspects, nutritional profile, and global trends. *Food Res. Int.* **2021**, *147*, 110486. [[CrossRef](#)] [[PubMed](#)]
100. Bhandari, S.D.; Delmonte, P.; Honigfort, M.; Yan, W.; Dionisi, F.; Fleith, M.; Iassonova, D.; Bergeson, L.L. Regulatory Changes Affecting the Production and Use of Fats and Oils: Focus on Partially Hydrogenated Oils. *J. Am. Oil Chem. Soc.* **2020**, *97*, 797–815. [[CrossRef](#)]
101. Latip, R.A.; Lee, Y.-Y.; Tang, T.-K.; Phuah, E.-T.; Tan, C.-P.; Lai, O.-M. Physicochemical properties and crystallisation behaviour of bakery shortening produced from stearin fraction of palm-based diacylglycerol blended with various vegetable oils. *Food Chem.* **2013**, *141*, 3938–3946. [[CrossRef](#)] [[PubMed](#)]
102. Hondoh, H.; Ueno, S. Polymorphism of edible fat crystals. *Prog. Cryst. Growth Charact. Mater.* **2016**, *62*, 398–399. [[CrossRef](#)]
103. Paluri, S.; Heldman, D.R.; Maleky, F. Effects of Structural Attributes and Phase Ratio on Moisture Diffusion in Crystallized Lipids. *Cryst. Growth Des.* **2017**, *17*, 4661–4669. [[CrossRef](#)]
104. Chawla, P.; Deman, J.; Smith, A. Crystal morphology of shortenings and margarines. *Food Struct.* **1990**, *9*, 2.
105. Watanabe, T. The impact of grain boundary character distribution on fracture in polycrystals. *Mater. Sci. Eng. A* **1994**, *176*, 39–49. [[CrossRef](#)]
106. Adhikari, B.; Howes, T.; Bhandari, B.R.; Truong, V. Stickiness in Foods: A Review of Mechanisms and Test Methods. *Int. J. Food Prop.* **2001**, *4*, 1–33. [[CrossRef](#)]
107. Macias-Rodriguez, B. Rheology-Based Techniques. In *Advances in Oleogel Development, Characterization, and Nutritional Aspects*; Springer: Berlin/Heidelberg, Germany, 2024; pp. 471–496.
108. Deman, J.; Beers, A. Fat crystal networks: Structure and rheological properties. *J. Texture Stud.* **1987**, *18*, 303–318. [[CrossRef](#)]
109. Glibowski, P.; Zarzycki, P.; Krzepkowska, M. The Rheological and Instrumental Textural Properties of Selected Table Fats. *Int. J. Food Prop.* **2008**, *11*, 678–686. [[CrossRef](#)]
110. DeMan, L.; DeMan, J.; Blackman, B. Polymorphic behavior of some fully hydrogenated oils and their mixtures with liquid oil. *J. Am. Oil Chem. Soc.* **1989**, *66*, 1777–1780. [[CrossRef](#)]

111. Guillemenet, J.; Bistac, S.; Schultz, J. Relationship between polymer viscoelastic properties and adhesive behaviour. *Int. J. Adhes. Adhes.* **2002**, *22*, 1–5. [[CrossRef](#)]
112. Hoppu, P.; Grönroos, A.; Schantz, S.; Juppo, A.M. New processing technique for viscous amorphous materials and characterisation of their stickiness and deformability. *Eur. J. Pharm. Biopharm.* **2009**, *72*, 183–188. [[CrossRef](#)] [[PubMed](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.