UNIVERSITÀ CATTOLICA DEL SACRO CUORE

Sede di Piacenza

Dottorato di ricerca per il Sistema Agro-alimentare

Ph.D. in Agro-Food System

Ciclo XXXVII

S.S.D. AGRI-07/a

Development of high-value-oil-based systems through innovative structuring agents for the nutritional and/or functional enhancement of food matrices

Coordinator:

Dear Prof. Paolo Ajmone Marsan

Candidate:

Marco Panzanini

Matriculation n: 5114941

Academic Year 2023/2024

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Summary

Chapter 1

State of the art

“Biopolymers and their interaction within emulsion-filled-hydrogel for the elderly and dysphagics”

1. INTRODUCTION

1.1 Tree nuts

Nuts have been a part of the human diet since ancient times. Almonds, hazelnuts, pistachios, walnuts, pine nuts, and chestnuts are traditionally cultivated in the Mediterranean region. These nuts are valued for their sensory properties and versatility as ingredients in various culinary preparations. They are also a rich source of essential nutrients, such as vitamins, unsaturated and polyunsaturated fatty acids, and dietary fiber (Brufau et al., 2006).

Currently, almonds and walnuts make up 32% and 19% of global nut production, respectively, followed by cashews (17%), pistachios (15%), and hazelnuts (11%). The remaining 5% is comprised of pecans, macadamia nuts, pine nuts, and Brazil nuts. The United States leads in global production, especially for almonds, pistachios, and walnuts. Turkey follows with 11% of the global output, driven by its substantial hazelnut and pistachio harvests. Europe is the largest consumer of nuts, with almonds being the most consumed variety worldwide (32%), followed by walnuts, pistachios, cashews, and hazelnuts, at 19%, 17%, 16%, and 10% respectively, according to 2020 data (INC, 2021/2022). A standard serving size for nuts is 30 grams per day, which equates to 7-8 walnuts, 15-20 almonds or hazelnuts, or 3 tablespoons of peanuts, pine nuts, or sunflower seeds, as recommended by LARN (Nutrient and Energy Reference Intake Levels for the Italian Population, SINU 2014). According to Altamimi et al. (2020), incorporating nuts into the diet positively affects health by reducing total cholesterol, increasing HDL cholesterol (which plays a protective role against cardiovascular disease), lowering LDL cholesterol (a risk factor for heart conditions), and providing antioxidant and anti-inflammatory effects. These health benefits are attributed to the nutrient profile of nuts, including tocopherols, minerals, unsaturated fatty acids, fiber, and polyphenols.

1.2 Lipids

Chemically, lipids are defined as esters formed by fatty acids and an organic alcohol, such as glycerol, sphingosine, or cholesterol. Fatty acids, the fundamental components of lipids, are categorized as either saturated or unsaturated, depending on the absence or presence of double bonds in their carbon chain. In biological systems, they mainly exist as phospholipids within cell membranes, contributing to membrane fluidity, and as energy reserves stored as triglycerides. Dietary fats contribute about 30% of the total daily energy intake (Tvrzicka et al., 2011). While the human body can synthesize some fatty acids, others, termed "essential fatty acids," must be obtained through diet. These include linoleic acid (LA, 18:2, n-6) and alpha-linolenic acid (ALA, 18:3, n-3), as well as long-chain polyunsaturated fatty acids (PUFAs) like eicosapentaenoic acid (EPA, 20:5, n-3) and

docosahexaenoic acid (DHA, 22:6, n-3) (Patted et al., 2024). Saturated and trans fatty acids are associated with negative health effects (Tvrzicka et al., 2011), leading to the establishment of a Suggested Dietary Target (SDT). This target indicates a nutrient intake level that reduces the risk of chronic diseases and is set below 10% of total energy intake for adults and the elderly.

For total lipids, PUFA, and both n-3 and n-6 PUFAs, the LARN defines a Reference Intake (RI) range (SINU, 2014). This range ensures adequate intake of all essential macro- and micronutrients while mitigating the health risks associated with extreme intake levels. Unsaturated fatty acids should contribute 10-15% (monounsaturated) and 5-10% (polyunsaturated) of daily energy intake for adults and the elderly. Specifically, n-6 and n-3 PUFAs should constitute 4-8% and 0.5-2% of total daily energy, respectively.

Nuts contain between 50% and 70% fats, making them a significant source of monounsaturated (MUFA) and polyunsaturated fatty acids (PUFA), while saturated fatty acids are comparatively less abundant (Astrup et al., 2011). The total lipid content in various types of nuts ranges from 44.4% to 75.8% (Ros & Mataix, 2006). The highest lipid percentages are observed in:

- Macadamia nuts: 76%
- Pecans: 71.8%
- Walnuts: 68.1%
- Hazelnuts: 64%
- Almonds: 55.3%
- Pistachios: 48.9% (CREA, 2019).

MUFA, primarily in the form of oleic acid, dominate in:

- Almonds: 57-64% (Maestri et al., 2015)
- Hazelnuts: 72-82% (Maestri et al., 2020)
- Macadamia nuts: 58% (Ros & Mataix, 2006)
- Pecans: 40.8% (Ros & Mataix, 2006) to 68% (Maestri et al., 2020)

Walnuts have the highest PUFA content, accounting for 75% of their total lipid composition Table 1. Brazil nuts and pine nuts contain similar MUFA proportions. Notably, Brazil nuts and Macadamia nuts also have significant saturated fat content, 15.1% and 12.1%, respectively (Ros & Mataix, 2006). Geographic origin and cultivar significantly influence lipid content, fatty acid profile, and vitamin E levels in nuts, due to varying climatic conditions during cultivation (Gonçalves et al., 2023). For example, the oleic acid content is 72% for Italian Bronte pistachios, 70% for Turkish varieties, and

55% for Iranian varieties. Conversely, Iranian pistachios have a higher linoleic acid proportion (28.9%) compared to Italian (13.3%) and Turkish (15.6%) varieties (Arena et al., 2007). Hazelnuts also demonstrate regional differences in fatty acid composition. Turkish hazelnuts contain 77.81-80.90% oleic acid, whereas Italian hazelnuts show a higher range of 81.92-83.91% (Król & Gantner, 2020).

Table 1. Acidic profile composition of some nuts

	Fat % (w/w)	**MUFA% (w/w) On 100g of fat**		**PUFA% (w/w) On 100g of fat**			**SFA%(w/w) On 100g of fat**				
		C18:1	total	C18:2	C18:3	total	C16:0	C18:0	others	total	Source
Almond	50	50-80		16-34			4-13	2-5			(Maestri et al., 2015)
Almond	52.03 -64.47	65.18-79.66		14.50-25.78			5.28-7.38	1.40-2.43			(Sanahuja et al., 2021)
Brazil nut	64.9 - 67.3	30				40		12		26	(Maestri et al., 2020)
Cashew nut	40-51		57-64			16-21	9.5	9			(Maestri et al., 2020)
Hazelnut	55-65	72-82				5.35-17	4-7	1-3			(Maestri et al., 2020)
Macadamia nut	70-73	34-59				>5			12-40		(Maestri et al., 2020)
Pecan nut	58-66	66.6	68	23.6		25				7	(Maestri et al., 2020)
Pistachio	50-60	55-65		12-30	0.5					12	(Maestri et al., 2020)
Walnut		18.9	19.1	58.5	11.7	70.3	7.5			10.2	(M. Liu et al., 2023)
Black cherry stone	31.89	35.45		42.34	0.13		6.54			11.2	(Kazempour-Samak et al., 2021)
Pine nut	15.71		18.78	60.39	6.94					4.43	(Matthaus & Özcan, 2013)

1.3 Tocopherols: Vitamin E

Tocopherols and tocotrienols are classes of fat-soluble compounds that constitute Vitamin E (Yoshida et al., 2003). They act as biological antioxidants by preventing the oxidation of polyunsaturated lipids. Both classes consist of four types (α, β, γ, δ) and differ in the presence of a saturated or unsaturated side chain: tocopherols have a saturated side chain at position 2 of the aromatic ring, while tocotrienols have an unsaturated side chain with three double bonds at positions 3, 7, and 11. This difference in side chain saturation influences their mobility and ability to penetrate cell membranes. Tocotrienols, due to their unsaturated chain, can more easily insert into the phospholipid membrane

and diffuse more rapidly, potentially making their antioxidant action more efficient (Shahidi & De Camargo, 2016). Biologically, alpha-tocopherol is the most potent and active form of Vitamin E as it contains all eight stereoisomers of Vitamin E, has a pronounced lipophilic nature that allows it to be affine to cell membranes, and presents three methoxy groups that make it more efficient in donating electrons or hydrogen to neutralize free radicals. In membranes, tocopherol counteracts excess free radicals and thus prevents oxidative damage (Szewczyk et al., 2021). It is used for comparative evaluations among the eight different forms of Vitamin E. The EFSA uses the term "alpha-tocopherol equivalent (α-TE)" which corresponds to: 1 Tocopherol Equivalent = 1 mg α - tocopherol = 1.5 IU (international units) = 2 mg β-tocopherol = 3 mg γ-tocotrienol = 10 mg γ-tocopherol (EFSA, 2015) Chemically, tocopherols are oily compounds insoluble in water and soluble in nonpolar solvents, easily degraded by oxygen and UV rays but fairly heat-resistant. If in ester form, they undergo hydrolysis before being absorbed in the small intestine. Absorption varies between 20% and 40% of what is ingested with food and is carried out by enterocytes (epithelial cells). They are then released and incorporated into chylomicrons (lipoproteins that collect triglycerides and cholesterol), enter the lymphatic circulation, and are released into the systemic circulation. They are transported in the bloodstream within lipoproteins (Mohamad, 2023). In the liver, hepatic lipoproteins primarily incorporate natural tocopherol (three chiral atoms in the R configuration) thanks to the specific α-TBP (α-tocopherol binding protein) that binds, transports it to cellular compartments, and allows its inclusion in lipoproteins. Vitamin E is mainly contained in low-density lipoproteins (LDL); in smaller quantities in VLDL and high-density lipoproteins. The vitamin is exchanged between different lipoproteins (Traber, 2013) and transferred to erythrocytes and various tissues through the action of lipase that cleaves triglycerides and allows the release of tocopherol. Its metabolism is slow and is eliminated with faces, in the form of α-tocopherol hydroquinone and α-tocoquinone, and with urine, in the form of tocopheronic acid (Huang et al., 2011).

1.3.1 mechanism of action:

As previously mentioned, Vitamin E plays a role in preventing the oxidation of polyunsaturated fatty acids in the lipid peroxidation process (Sabliov et al., 2009). This is triggered by the action of free radicals that continue the process through a chain reaction. The vitamin can block this phenomenon by donating a hydrogen atom to peroxyl radicals, making them less reactive and stopping peroxidation. In doing so, Vitamin E transforms into an α-tocopheroxyl radical, which is quite stable due to resonance phenomena, and can react with Vitamin C, glutathione, or coenzyme Q10 to reform α-tocopherol. The development of peroxidation can cause profound alterations in cell membranes, which is why the role of Vitamin E is so important in maintaining these structures intact. This role is

also verified by the fact that erythrocytes (red blood cells), which are particularly subjected to oxidative stress, are quite sensitive to Vitamin E deficiency, becoming more prone to hemolysis (Huang et al., 2011; Niki, 2014).

According to CREA tables (CREA, 2019), hazelnuts are among the nuts with the highest Vitamin E content (considering the total tocols). The Vitamin E in almonds instead is mostly composed of γ-tocopherol and to a lesser extent α-tocopherol (Table 2). This means that almonds, despite having the highest total Vitamin E content, exert less antioxidant power compared to hazelnuts.

The antioxidant activity of Vitamin E in foods is often expressed as α-tocopherol equivalents (α-TE), calculated using conversion factors for different vitamers (EFSA, 2015):

- α-tocopherol (mg) × 1.0
- β-tocopherol (mg) × 0.5
- γ-tocopherol (mg) × 0.1
- δ-tocopherol (mg) × 0.03
- α-tocotrienol (mg) × 0.3
- β-tocotrienol (mg) × 0.05

The biological activities of γ-tocotrienol and δ-tocotrienol is negligible due to the low conversion factors. These factors illustrate the greater nutritional contribution of α-tocopherol compared to other vitamers. EFSA used these factors to express total tocopherol and tocotrienol intake as α-tocopherol equivalents, establishing adequate intake (AI) levels. The AI for Vitamin E, as α-TE, is 11 mg/day for women and 13 mg/day for men. For children aged 3 to 10 years, the AI is 9 mg/day for both genders (EFSA, 2015).

Table 2. Vitamin E content and homolog composition in some tree nuts matrices. The values are expressed in ppm (mg/kg of oil).

	α	β	γ	δ	
Bronte pistachio P.O.D.	7.7±1.2	0.4±0.1	191.9± 3.1	4,3±0,9	(D'Evoli et al., 2015)
Bronte pistachio P.O.D.	5.1±0.4	105.4±10.3			(Gentile et al., 2007)
Pistachio (Iran)	n.d.	100-434		n.d.-23	(Kornsteiner et al., 2006)

Hazelnut (Italy)	118-440	10	10	10	(Crews et al., 2005)
Hazelnut (Turkey)	404.0	15.3	83.3	5,3	(Alasalvar et al., 2010a)
Hazelnut (Georgia)	157-421	43-94		n.d.- 3	(Kornsteineret al., 2006)
Apricot kernel	19.6-40	n.d.	315.4-502.3	28,3-58,8	(Stryjecka et al., 2019)
Apricot kernel	19.51±4.46	0.38±0.19	475.11±62.35	12,64 ±3,14	(Turan et al., 2007)
Apricot kernel	n.d.	92±1.27		2.6±0.20	(Pavlović et al., 2018)

1.4 Hazelnut

The hazelnut (*Corylus avellana*) grows in temperate regions of Europe, Asia, and North America (Caruso, 2016). Over 90% of global hazelnut production is designated for industrial use, transforming into products like granules, paste, cream, flour, and oil, or used in foods such as ice cream, biscuits, cakes, chocolate bars, and plant-based beverages (Lodato et al., 2024). Turkey is the largest hazelnut producer, contributing 70% of the global supply, with Italy ranking third. Italy also has the highest per capita hazelnut consumption worldwide, averaging 1.97 kg annually between 2009 and 2013, followed by Austria (1.35 kg) and Switzerland (1.17 kg) (INC, 2021/2022).

Hazelnuts are a valuable source of dietary lipids, particularly monounsaturated (MUFA) and polyunsaturated fatty acids (PUFA). The average lipid content ranges from 62% to 70% of the nut. The predominant fatty acid is oleic acid, comprising 45.7% of total fats, while PUFA makes up 5-17% (Table 1). Saturated fatty acids, mainly palmitic and stearic acids, do not exceed 10% of total lipids. The high unsaturated fat content of hazelnuts, including derivatives like oil, is associated with a reduced risk of cardiovascular diseases (Li & Parry, 2011).

Hazelnuts also contain significant vitamin E amounts (200-650 mg/kg of tocopherols), providing antioxidant protection by inhibiting free radical propagation (Renzo et al., 2014). These qualities make hazelnuts valuable in the food industry. The high lipid content makes them ideal for oil extraction, which is influenced by variety, geography, climate, light exposure, pathogen impact, and field treatments (Schmitzer et al., 2011). Crews et al., (2005) highlight variability in linoleic acid

content among different varieties, while total oil content can range from 57.85% to 68.31% in Turkish hazelnut varieties (Alasalvar et al., 2010; Li & Parry, 2011).

1.4.1 Italy vs Turkey

Different varieties of hazelnuts have varying tocopherol contents, and the origin of the hazelnuts influences their characteristics (Table 3). A comparison of oils obtained from Turkish and Italian hazelnuts reveals a higher presence of α-tocopherol in Turkish hazelnuts (319-492 mg/kg) compared to Italian varieties (118-440 mg/kg). Gamma-tocopherol is also more prevalent in Turkish hazelnuts (up to 130 mg/kg), whereas Italian hazelnuts do not show values exceeding 10 mg/kg (Crews et al., 2005). The same study indicates that, regarding fatty acid composition, Italian varieties have a higher oleic acid content, while Turkish varieties have a higher linoleic acid content. Among the parameters that differ depending on the varieties considered, mineral composition is also notable (Botanicae et al., 2013).

Table 3. Comparison of the main tocopherol content between Italian and Turkish hazelnuts (Crews et al., 2005).

	Italy	**Turkey**
α-tocopherol	118-440 mg/kg	319-492 mg/kg
γ-tocopherol	max 10 mg/kg	max 130 mg/kg
C18:1	80.3/83.4%	75.7%/82.9%
C18:2	6.2/10.6%	8.1/15.4%

1.5 Roasting

Industrial roasting is primarily employed to facilitate the removal of the perisperm, deactivate enzymes, and eliminate microorganisms that can damage the product and alter its sensory properties. This process also enhances technological parameters, such as increased brittleness, which aids in oil extraction (Ogundipe et al., 2024). The studies (Renzo et al., 2014; Maestri et al., 2020) highlighted hazelnuts as a valuable source of nutrients. To maximize nutrient preservation, it is essential to understand how roasting treatments affect the final composition. Crews et al., (2005) and Shahidi et al. (2007) recommend 25 minutes at 165°C, while Lucchetti et al. (2018) and Kirbas & Erkmen, (2004) identify 135°C for 15 minutes as an optimal time-temperature combination to minimize nutrient loss and modification. Generally, higher temperatures and longer roasting times lead to greater water loss. Roasting can also damage membranes and increase protein denaturation, facilitating lipid extraction. Furthermore, the oxidation rate of fatty acids increases with higher unsaturation levels, linking roasting to a decrease in the ratio of unsaturated to saturated fatty acids

(Kirbas & Erkmen, 2004). However, unoptimized roasting poses several disadvantages (Durmaz & Gökmen, 2011):

- Acrylamide formation, a carcinogenic compound produced at high temperatures.
- Changes in the composition; certain fatty acids (especially unsaturated ones, which oxidize at high temperatures) and amino acids degrade during roasting.

Different tocopherols exhibit varying degradation patterns based on matrix type and temperature (Bruscatto et al., 2019). Amaral et al., (2006) suggest that α-tocopherol remains stable at high temperatures in the absence of oxygen, while others (Bruscatto et al., 2019) indicate it is the most susceptible to degradation, possibly due to its antioxidant properties. Delta-tocopherol is noted for its relative stability (Amaral et al., 2006). If roasting conditions are optimized, tocopherol loss may be minimal, or their levels may even increase, potentially due to the breaking of bonds between tocopherols and phospholipids, enhancing extractability (Marzocchi et al., 2017). In summary, roasting reduces oleic acid presence, decreases the ratio of unsaturated to saturated fatty acids, positively impacts the presence of phenolic compounds, and does not significantly affect tocopherol content.

1.6 Oil extraction techniques

There are various extraction techniques, like chemical (using solvents or supercritical CO_2), mechanical (employing different types of presses), or through distillation. Each of these has advantages and disadvantages depending on the treated matrix. The application of pretreatments such as roasting or the use of enzymes (Çakaloğlu et al., 2018) is beneficial for optimizing the extraction process, particularly for mechanical methods, which typically yield less compared to solvent-based methods. The most used in industrial processes is solvent extraction. This method has the advantage of achieving a high oil yield (over 98%), with the disadvantage of using chemical agents that can leave potential toxic residues on the product, cause environmental damage, pose risks to operators, incur high solvent costs, and require subsequent purification operations (including neutralization, bleaching, degumming, and deodorization). Techniques that use mechanical means (such as hydraulic pressing or screw pressing) allow for the best preservation of essential fatty acids, phenols, flavonoids, and tocopherols (Teh & Birch, 2013) (Table 4) in the oils and simultaneously produce cakes (which can be a high-potential byproduct) free of toxic solvents (Celenk et al., 2020). However, they have the limitation of low extraction yield, which also depends on the type of matrix used, the pretreatments performed (peeling and roasting), and the operational parameters employed.

Table 4. Comparison between cold extraction and Soxhlet extraction and the respective tocols content (Al Juhaimi et al., 2018).

	Hazelnut		Pistachio		Apricot kernel	
mg/kg (oil)	**Cold-pressed**	**Soxhlet**	**Cold-pressed**	**Soxhlet**	**Cold-pressed**	**Soxhlet**
α-tocopherol	257.42	209.73	0.07	0.03	167.85	149.84
β- tocopherol	10.67	8.84	17.34	15.71	4.71	4.21
γ- tocopherol	134.76	113.79	21.78	19.42	7.50	6.32
δ- tocopherol	6.71	5.94	0.06	0.04	0.17	0.13

1.6.1 Supercritical Fluid Extraction

Supercritical fluid extraction produces higher quality oils, but their price is very high. This method is still rarely used for obtaining vegetable oils, although it has the great advantage of not leaving residues in the product (and in the cake) and at the same time allows achieving a high extraction yield, close to that obtained from solvent extraction (Jesus et al.,2014).

1.6.2 Distillation

Distillation is mainly applied for obtaining essential oils (Çakaloğlu et al., 2018). In this case, the principle of immiscibility between oils and water is exploited, where steam carries some of the volatile components from the starting matrix. The steam is then condensed, allowing the separation of the oily fraction from the aqueous one.

1.6.3 Mechanical Methods

Mechanical methods are the oldest for oil extraction. Among their main advantages are the absence of chemical solvents, low energy consumption for operations, and reduced risk for operators. On the other hand, they have a lower oil yield, although the higher residual oil content in the cake, from a potential valorisation perspective, could increase the value of this byproduct (Cravotto et al., 2023).

1.6.4 Hydraulic press

Typically, operating a hydraulic press involves placing the seeds or nuts on a sieve and then lowering the piston onto them (**Figure 1**). The seeds equilibrate at the pressing temperature for at least 30 minutes without applying pressure. Subsequently, a low degree of pressure is initially applied, after which its value increases (either instantaneously or linearly) until reaching the final pressure (up to 100 MPa), which is maintained for the working time (Willems et al., 2008).

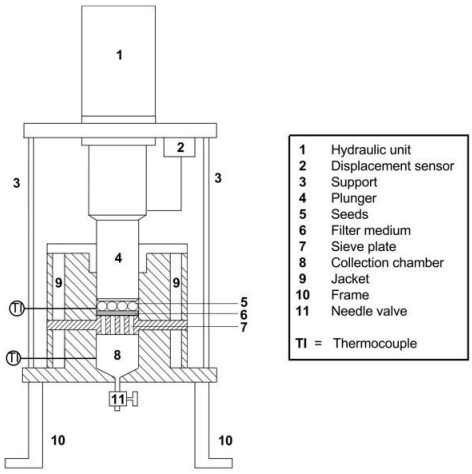

Figure 1. structure of a hydraulic press

(Willems et al., 2008)

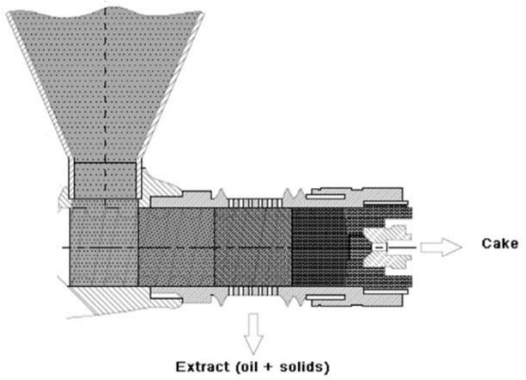

Figure 2. Structure of a Screw Press

(Maestri et al., 2015)

1.6.5 Screw Press

The principle of operation of the screw press involves a helical screw that moves the material, extracting the oil by compression and separating it from the cake (Figure 2). The product is fed through an inlet, and there are also outlets for the waste material and the extracted oil (Maestri et al., 2015). Inside the central body, where the screw is located, spacers are positioned to allow oil drainage as the pressure on the grains increases. Some machines use cold water circulation in the walls to remove the heat generated by the friction of the grains (Cravotto et al., 2023).

1.6.6 Cold Pressing

"Cold pressing" refers to an oil extraction process that maintains the temperature below 30°C during its execution (Celenk et al., 2020). Both methods (hydraulic pressing or screw pressing) are considered cold extraction methods, although screw extraction can reach temperatures of 40/50°C, which can lead to changes in the organoleptic characteristics of the oil. The amount of oil obtained is generally higher in the case of the screw press by up to 4-6% (Celenk et al., 2020). This parameter varies especially with temperature fluctuations, which are greater in screw pressing, where the temperatures reached are higher and less constant during the process. Specifically, a lower rotation speed in the screw press results in higher temperatures due to friction (Table 6), leading to a higher oil extraction yield. Conversely, when the rotation speed is high, the continuous input of new raw material helps cool the system (Rabadán et al., 2017).

1.6.7 Additional Processes

Other processes can be coupled with extraction, such as preliminary roasting, which is done in the case of oil extraction with a hydraulic press and improves the sensory properties of the oil (Table 5). This is not applied in the case of the screw press, as the working temperature reaches values that produce effects similar to those obtained with the roasting process. After obtaining the oil, water, resins, residual proteins, and fibers that would make the product dark and opaque are eventually removed through a clarification process, allowing phase separation between these compounds and the oil, which distributes on the surface layer to be collected. If this step is not sufficient, the oil can be filtered with a press filter or a centrifuge (Cravotto et al., 2023). Clarification may be followed by slight heating to remove residual water and destroy enzymes and bacteria before filtration. An additional brief heating to 100°C is then performed to eliminate the remaining moisture traces (Celenk et al., 2020).

Table 5. Examples of temperature and roasting time combinations applied to various types of nuts.

Source	Type of nut	Temperature (°C)	Time (min)
(Shahidi et al., 2007b)	Hazelnut	165	25
(Kirbas & Erkmen, 2004)	Hazelnut	135	15
(Marzocchi et al., 2017)	Hazelnut	130	50
(Marzocchi et al., 2017)	Hazelnut	160	25

(Crews et al., 2005)	Hazelnut	165	25
(Lucchetti et al., 2018)	Hazelnut	180	20
(Ling et al., 2016)	Pistachio	160	20
(Gentile et al., 2007)	Pistachio	160	40
(Gentile et al., 2007)	Pistachio	160	40
(Maestri et al., 2020)	Pistachio	50–75	/
(Maestri et al., 2020)	Pistachio	100–125	/

Table 6. Examples of extraction processes applied to various types of nuts: raw materials, press type, pressure, working times, temperatures, and oil yield obtained are reported.

Source	Type of nut	Type of press	Pressure	Time (min)	Temperature (°C)	Yield (%)
(Ling et al., 2016)	Pistachio	hydraulic	58 bar	15	/	31,57
(Ling et al., 2016)	Pistachio	hydraulic	58 bar	15	/	33,27
(Rabadán et al., 2017)	Pistachio	hydraulic	58 bar	10	/	25/35
(Ojeda-Amador et al., 2018)	Pistachio	screw	0,5 Hz	/	50	20/25
(Pavlović et al., 2018)	Apricot kernel	screw	20 Hz	/	60	36,78

1.7 Hazelnut oil

The oil content in hazelnuts ranges from 55% to 65% and can be extracted through physical or chemical processes. Chemical methods involve solvents, while physical methods use hydraulic presses or screw presses. The cold extraction method preserves bioactive compounds (such as phenols and tocopherols) and fatty acid composition, and it also produces solvent-free press cakes suitable for further processing to add value to this by-product. The main parameters affecting extraction yield are pressure and processing time. The extracted oil is decanted and filtered before bottling (Maestri et al., 2020). Hazelnut oil is sold as a finished product or used in the confectionery industry. It also has significant potential in the pharmaceutical and cosmetic industries (for example in moisturizing creams) due the presence of valuable bioactive substances like tocopherols, unsaturated and polyunsaturated fatty acids, phenols, carotenoids, and minerals (potassium, calcium, and magnesium). Despite good stability at 4°C (Crews et al., 2005), tocopherols and linolenic acid levels decrease over time, while saturated fatty acids increase. Therefore, cold-pressed hazelnut oil should

be stored in the dark and at low temperatures (Celenk et al., 2020). Hazelnut oil can be obtained from hazelnut seeds through cold mechanical pressing. Its use is comparable to virgin olive oil due to similar physicochemical characteristics, making it ideal for raw seasoning, cooking, and frying. The extraction is highly efficient, achieving 60% yield, and allows the separation of the oily part from the creamier part while maintaining all organoleptic properties. After extraction, the oil is decanted, filtered, and bottled (Maestri et al., 2020).

1.8 Defatted Cake (DFC)

The press cake also called defatted cake or partially defatted cake is a by-product of oil extraction from the matrix, and contains residual oil ranging from 10.7-11.4% (Ojeda-Amador et al., 2019), reaching up to 17.38% for some Turkish varieties (Saricaoglu et al., 2018) but mainly depends on the extraction techniques and extraction parameters. The moisture content for raw hazelnuts is typically 2.7-4.1%, increasing to 5% in the press cake due to the concentration of other matrix components following oil extraction. For roasted hazelnuts, moisture decreases depending on the intensity of the roasting process (time and temperature parameters). In the study by (Marzocchi et al., 2017), hazelnuts roasted for 30 minutes at 160°C showed the greatest water loss, from 4.86% to 0.39%. Regarding the remaining composition of the press cake, it generally contains up to 43.77% proteins, 25.20% carbohydrates, and 4.97% ash (Saricaoglu et al., 2018). Tocopherols, due to their apolar characteristics, separate into the oil phase during extraction, resulting in limited presence in the press cake: α-tocopherol levels are 41-49 mg/kg and γ-tocopherol levels are 1.8 mg/kg (Ojeda-Amador et al., 2019). Phenolic compounds, however, concentrate in the press cake due to their polarity. For example, in hazelnut press cake (Tonda Gentile delle Langhe), phenolic compound levels reach 2262 mg/kg (Ojeda-Amador et al., 2019). These compounds have strong antioxidant capacity, making press cakes potential functional ingredients for food formulations to enhance nutritional characteristics. The press cake is free of toxic solvents as it is mechanically extracted. Following oil extraction, all other matrix components concentrate. The composition per 100g of press cake includes:

- Oil: 10-18g
- Moisture: 5g
- Proteins: 43g
- Carbohydrates: 25g (of which 25g of fiber)
- Ash: 5g

(Saricaoglu et al., 2018)

Tocopherols tend to separate into the oil phase during extraction, thus their quantity in the press cake

is limited. Conversely, phenolic compounds increase in absolute terms due to their polarity. The press cake contains 40 mg/kg of α-tocopherol and 2260 mg/kg of phenolic compounds (Ojeda-Amador et al., 2019). These phenolic compounds have significant antioxidant capacity, making the press cake a potential functional ingredient for food formulations to improve nutritional characteristics.

1.9 Apricot

The apricot (*Prunus armeniaca* L.) is a fruit native to Armenia, belonging to the Rosaceae family. It is commonly cultivated in temperate regions and holds significant economic importance. In recent years, production has increased considerably: in 2020, the global harvest area was 562,475 hectares, with a production of 3.72 million tons (FAO, 2022). Turkey is the largest producer, followed by countries such as Uzbekistan, Iran, Algeria, Italy, Afghanistan, Spain, Greece, Pakistan, and Morocco (Pawar et al., 2023). Apricots are rich in essential nutrients, including sugars, vitamins (A and C, which have antioxidant activity), minerals (potassium, phosphorus, sodium, iron, and calcium), and fiber (CREA, 2019). The fruit is high in water content (86.3 g per 100 g of product), but also contains sugars (9.8 g per 100 g of product), fiber (1.5 g per 100 g), and provides only 42 kcal per 100 g (CREA, 2019). The apricot is a drupe measuring between 3.5 and 6 cm, with a yellow-orange color, red hues, and slightly velvety skin. The fruit contains a single seed called an “armellina” (similar to an almond). It requires 3-6 months to develop and ripen, after which it is hand-picked (between May and July). They are primarily consumed fresh, but since they are fragile and perishable fruits, they are often subjected to treatments that allow for longer preservation. These treatments can include drying, canning in syrup, or freezing and storing in cans. The market also offers derived products such as juice, jam, and jelly. In this thesis, apricots were used in the form of pasteurized puree stored in laminated pouches (Al-Soufi et al., 2022).

1.10 Dietary fiber

Dietary fibers are polysaccharides of plant origin that are unavailable (neither digested nor absorbed by the stomach and small intestine). However, colonic bacterial flora partially digest and ferment them (Barber et al., 2020). The most important physicochemical properties are:

- Water-holding capacity
- High viscosity
- Cation exchange capacity
- Fermentation capacity

Fiber plays a structural role in plant organisms, forming the main structures. Its importance for the human body is found in aspects related to digestion and intestinal well-being, as it slows down the assimilation of nutrients, improves intestinal motility, and reduces the glycemic index of carbohydrates. Additionally, it increases the sense of satiety and reduces the risk of cardiovascular diseases, cancer, and diabetes (Huang et al., 2015).

There are two types of dietary fibers:

- Soluble dietary fibers (in water): These can form a gel with water that distends the gastric walls and stimulates mechanoreceptors responsible for transmitting the sense of satiety to the brain (suitable for weight loss diets); they reduce the intestinal absorption of digestion products, partially depriving the body of them. Examples include pectins, gums, and mucilages.
- Insoluble dietary fibers (in water): These can absorb a large amount of water, increasing the volume and weight of feces, thereby accelerating intestinal motility and shortening the transit time of fecal matter, reducing constipation and the risk of colon cancer, this category includes cellulose.

(Maqbool et al., 2023; Slavin, 2013)

1.11 Citrus Fiber

Citrus fruits, including oranges, lemons, grapefruits, and limes, are among the most widely cultivated and economically significant crops globally, contributing substantially to the agricultural industry. The global demand for citrus fruits has risen steadily, driven by their nutritional value, high vitamin C content, and widespread use in fresh consumption, juice production, and processed foods. However, the processing of these fruits generates a substantial quantity of organic waste, posing a significant environmental challenge (Satari et al., 2016). This waste predominantly comprises inedible peels, seeds, and pulp remnants, which are often challenging to manage due to their high organic load and rapid decomposition rate. The disposal of citrus waste has environmental and economic implications, particularly in regions with intensive citrus processing industries. The large volume of waste not only increases disposal costs but also contributes to pollution due to its high moisture and sugar content, which can attract pests and lead to fermentation if left untreated (Medina-Herrera et al., 2024).

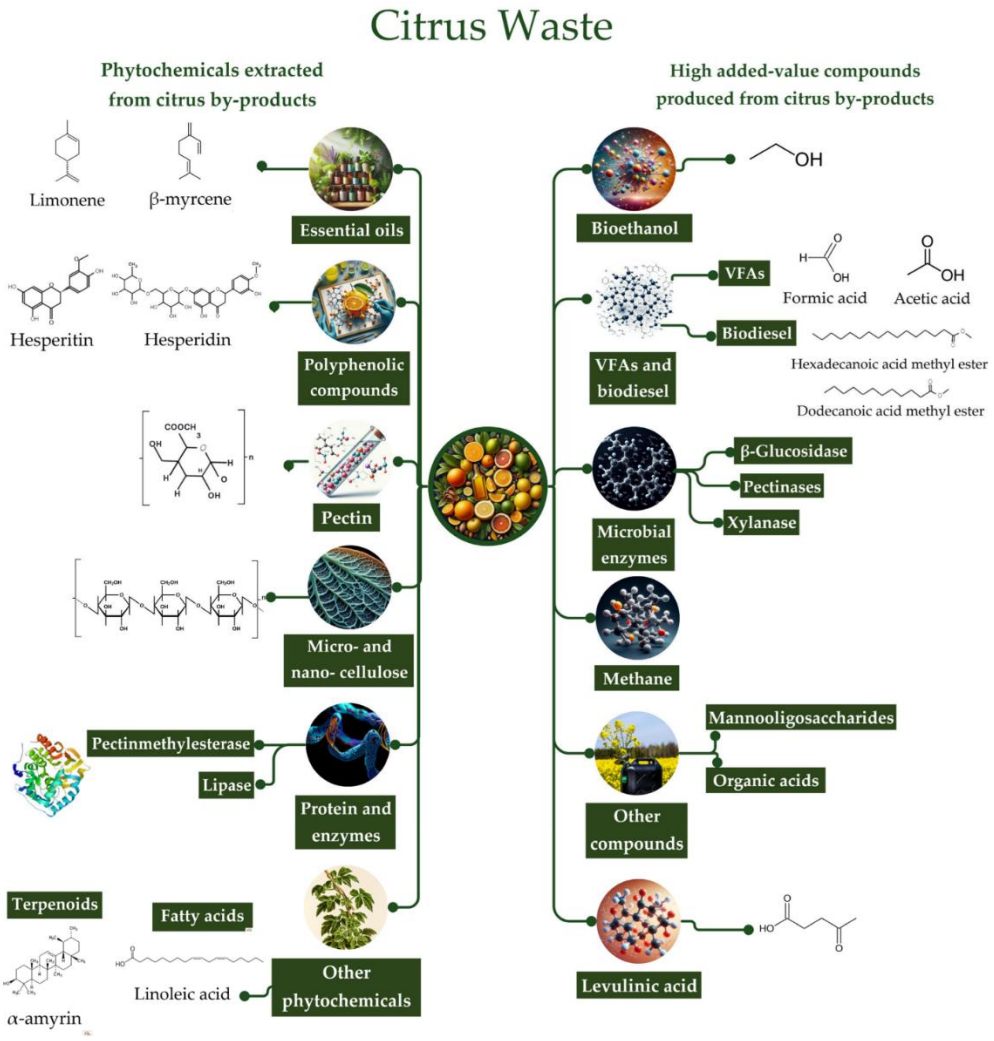

Figure 3. Diagram of compounds derived from the valorisation of citrus by-products (Medina-Herrera et al., 2024).

1.11.1 Bioactive compounds extraction

Emerging environmental trends emphasize on minimizing waste by recovering or producing high-value-added compounds through a cascade biorefinery model. This model involves sequential processing through various unit operations to valorise organic waste, resulting in multiple value-added products, bioproducts, and biofuels (Figure 3) (Espinosa et al., 2022).

To achieve this, both physicochemical and biotechnological approaches are utilized. Physicochemical techniques typically involve solvent extraction methods, including conventional methods like homogenization and Soxhlet extraction, non-conventional methods such as microwave- and ultrasound-assisted extraction, and supercritical fluid extraction. These methods are employed to recover phytochemicals from citrus waste. On the other hand, biotechnological techniques rely on biochemical processes, primarily using enzyme and fermentation technologies to produce bioproducts and biofuels. These techniques can be applied either separately or in sequence, depending on the specific objectives, often within a biorefinery framework (Sharma et al., 2022).

The valorization of citrus waste offers a promising approach for producing a wide range of valuable bioactive compounds, addressing environmental concerns, and supporting sustainable industry practices. Various innovative processes are applied to citrus peel and other by-products to extract molecules with diverse applications in food, energy, pharmaceuticals, and cosmetics. For instance, citrus peel waste can be fermented using microorganisms like Trichoderma species and Escherichia coli to produce mucic acid, which holds significant value in pharmaceutical and chemical manufacturing due to its versatile chemical properties (Jeong et al., 2021).

Essential oils, particularly D-limonene, are another highly sought-after product derived from citrus waste. Microwave Hydrodiffusion and Gravit and steam distillation efficiently extract these oils from orange peel. The resulting essential oils are widely used in fragrances, cleaning agents, and food additives, leveraging their natural aroma and preservative qualities (Boukroufa et al., 2015; John et al., 2017). In addition to essential oils, ultrasound-assisted and enzyme-assisted processing methods enable the extraction of polyphenols and flavonoids from *Citrus sinensis* cv. *Malta* peel. These bioactive compounds are potent antioxidants and are highly valued in the health and wellness sectors for their anti-inflammatory and cell-protective properties (Kaur et al., 2023).

Citrus waste also serves as a renewable resource for bioethanol production. Through enzymatic hydrolysis and fermentation, citrus peel waste can be converted into bioethanol, providing a sustainable alternative to fossil fuels and contributing to the reduction of greenhouse gas emissions (John et al., 2017). Technologies like pulsed electric field processing applied to pomelo peels facilitate the extraction of naringin, a flavonoid compound with known health benefits, including antioxidant and anti-inflammatory effects. This compound is popular in dietary supplements and functional foods (Kaur et al., 2023). The application of microwave-assisted processing succeeded in phenolic compounds extraction from citrus and grape marc, another by-product with strong antioxidant properties. These compounds are integral in promoting health and are frequently incorporated into nutraceuticals and dietary products (Sharma et al., 2022). This variety of methods underscores the economic potential of citrus waste valorization demonstrating the environmental advantages of converting agricultural by-products into valuable, high-demand compounds.

1.11.2 Food application

However, the extraction of bioactive compounds is just one of the many potential uses of such a valuable byproduct. It is also possible to extract dietary fiber from the peels. This fiber plays a significant role in our food system. With technological applications that have been known for some time and are still being discovered, we will explore it in detail in the following chapters. Due to the numerous health benefits of citrus fiber, researchers and the food and pharmaceutical industries are

increasingly interested in extraction and modification. Current research is investigating the relationship between the structural characteristics of citrus fiber and its biological activity. Additionally, recognizing the positive effects of plant-insoluble dietary fibers (IDF) on human health, food processing research is now focusing on developing methods to increase the yield and improve the functional properties of soluble dietary fibers. Recent interest has emerged in repurposing citrus residues for various food applications. Citrus peels, which constitute the majority of the waste, are rich in dietary fiber often containing up to 50% more fiber than the edible fruit itself (Rafiq et al., 2018). The main substances that compose citrus fiber are insoluble fiber, consisting of cellulose and hemicellulose, which makes up 60% of the contained fiber, while the remaining part is represented by the soluble fraction (Zhang et al., 2023). Regarding extraction from orange peel, it has the advantage of being an inexpensive and easily obtainable byproduct (Fan et al., 2022). The extraction process has an environmental impact that can be reduced by using innovative processes such as "subcritical water." Using this technique, cellulose, hemicellulose, and pectin can be effectively extracted by applying a hydrothermal treatment within an extractor, with a temperature range of 160 to 320°C. This method is advantageous for obtaining these substances without having negative environmental impacts (Maqbool et al., 2023). Another technique that can be used for extraction from the peel is the PEF (Pulsed Electric Field) technique. A study conducted by Fan and collaborators (Fan et al., 2022) demonstrated that fiber can be obtained while also increasing the extraction yield. By applying short high-voltage electric pulses to the plant product, the process is based on the theory that when a living cell is placed in an electric field, once a critical value is reached, electroporation occurs in the weaker areas of the membrane, allowing the release of cytoplasmic liquid and cellular content (Martínez et al., 2018). Extraction can also be performed from pomace, which is the residue obtained from pressing (Maqbool et al., 2023). The pomace is first subjected to distillation to remove essential oils. This results in fiber composed of an insoluble fraction and a soluble fraction. The soluble part, mainly consisting of pectins, is removed, leaving only the insoluble part at the end of the process. Therefore, citrus fiber derives from a valorization process (Fan et al., 2022) and can be exploited thanks to its nutritional and technological properties, which will be detailed in the following paragraphs. Fibers have the peculiar characteristic of not being metabolized by digestive enzymes, serving as carbon sources for the intestinal microflora. Therefore, pectins and hemicelluloses can be fermented by bifidobacteria, exerting a prebiotic action. Regarding their use in food product formulation, they are generally used to improve rheology and structural properties (Rahman et al., 2023).

1.11.3 Citrus fiber constituents

1.11.3.1 Pectin

Pectin (Figure 4) is a compound extracted from fruit, from the protopectin contained within it. It is a heteropolysaccharide composed of d-galacturonic acid units linked by α-1,4-glycosidic bonds with a series of branches represented by methoxyl groups. It is found in the cell wall and intercellular layer of citrus fruits and has gelling and thickening properties. It is used as an additive in food and medicine because it regulates permeability between membranes (Yi et al., 2024)

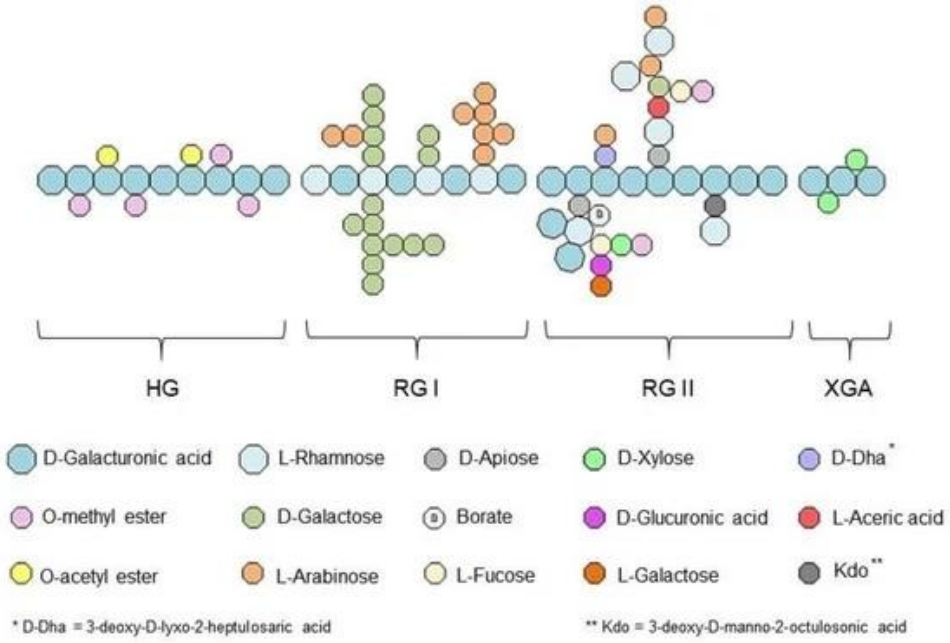

Figure 4. Pectin chemical structure (Freitas et al., 2021)

1.11.3.2 Cellulose

Cellulose (Figure 5), the main component of insoluble fiber in citrus fruits, is an unbranched polymer comprising glucose units held together by β-(1-4) glycosidic bonds. It contributes to forming part of the fruit's cell wall: together with hemicellulose, it participates in forming an interstitial structure that allows increased water (WBC) and oil (OBC) adsorption and retention (Deng et al., 2024).

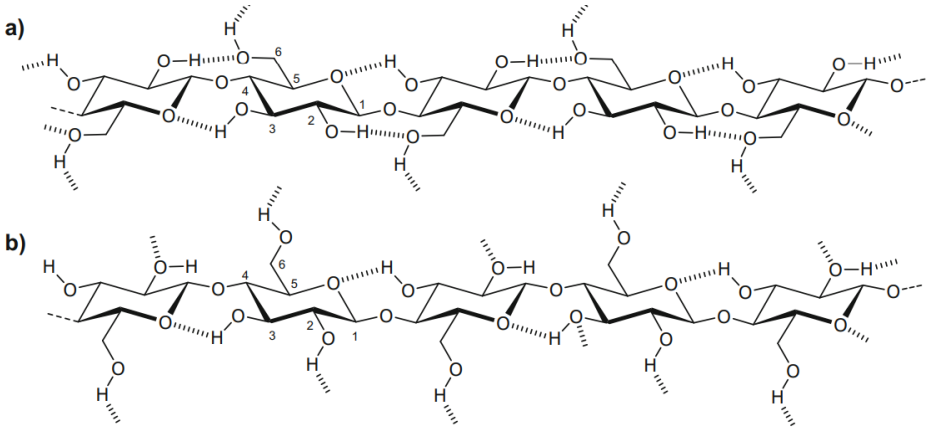

Figure 5. Cellulose chemical structure (Tashiro & Kobayashi, 1991)

1.11.3.3 Hemicellulose

Hemicellulose (Figure 6) is a polysaccharide associated with cellulose, from which it can be extracted. It has a branched structure composed of five-carbon sugars (arabinose and xylose) and six-carbon sugars (glucose, mannose, and galactose). It is easily hydratable and used as a binder and stabilizer in foods. They are non-cellulose polysaccharides found in the cell walls of both vegetative and storage tissues of annual and perennial plants and constitute a vast renewable resource of biopolymers. They exist in a wide range of structural forms, categorized into four main groups: xylans, mannans, mixed linkage β-glucans, and xyloglucans. Along with cellulose, it contributes to forming the cell wall and increases water absorption and retention capacity (WBC) (Pauly et al., 2013).

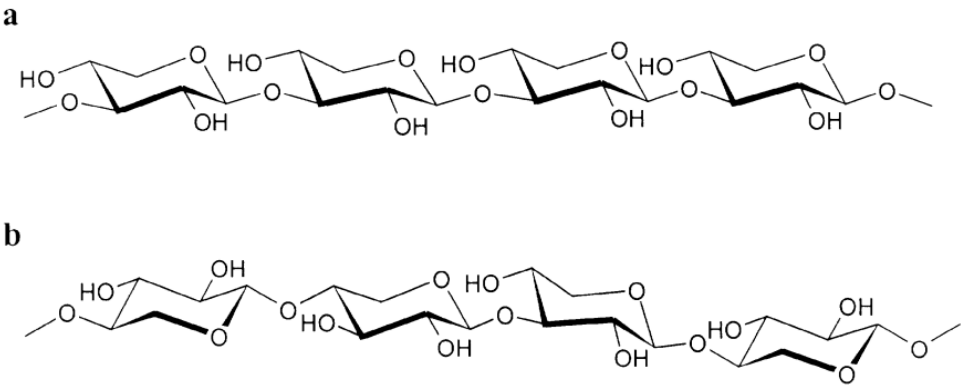

Figure 6. Hemicellulose chemical structure. (a) β-(1 → 3)-d-xylan type X3 and (b) β-(1 → 3, 1 → 4)-d-xylan (Ebringerová et al., 2005)

1.11.3.4 Lignin

Lignin (Figure 7,Figure **8**) is a high molecular weight aromatic polymer, consisting of numerous aromatic rings with methoxyl and hydroxyl functional groups. Due to its multifunctional side groups, lignin can serve as a free radical scavenger, making it a natural antioxidant. However, its antioxidant activity is influenced by extraction conditions, source species, and structure. As a relatively safe and

natural antioxidant, lignin finds applications in foods, pharmaceuticals, cosmetics, and industrial materials. lignin's structural characteristics, its radical scavenging abilities allows its commercial use as an antioxidant (Qin et al., 2020).

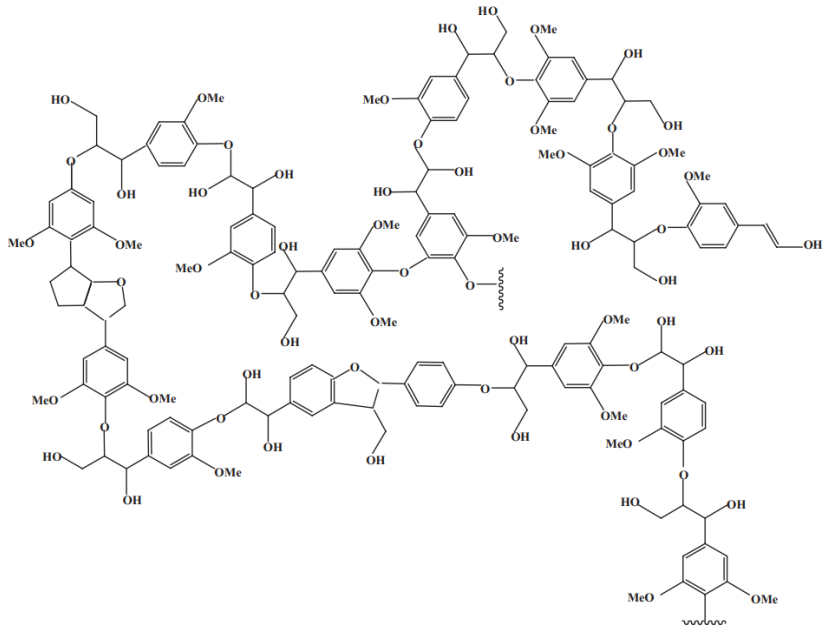

Figure 7. Lignin chemical structure. (Qin et al., 2020)

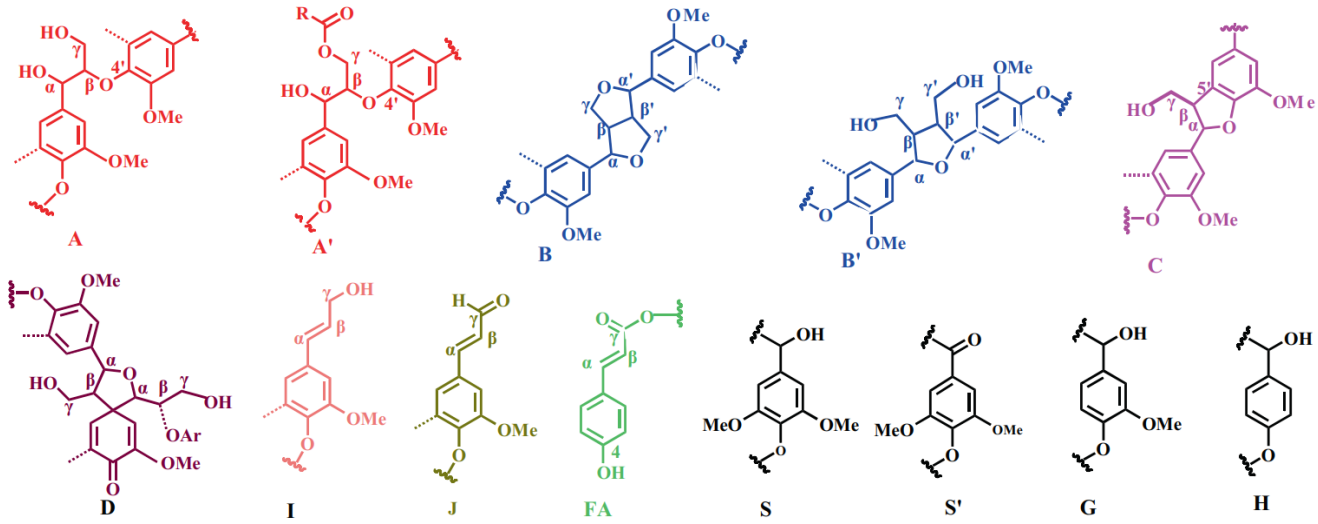

Figure 8. Main substructures present in lignin: (A) β-O-4 alkyl-aryl ethers, (A′) β-O-4 alkyl-aryl ethers with acylated γ-OH, (B) β-β resinols, (B′) tetrahydrofuran, (C) phenylcoumarans, (D) spirodienones, (I) cinnamyl alcohol end-groups, (J) cinnamyl aldehyde end-groups, (FA) ferulates, (S) syringyl units, (S′) oxidized syringyl units bearing a carbonyl at Cα, (G) guaiacyl units and (H) p-hydroxyphenyl units. (Qin et al., 2020)

1.11.4 Fiber extraction methods

There are various methods for extracting fiber from citrus fruits, each influencing sensory properties, physicochemical properties, and physiological functions (Table 7). Generally, the steps include drying (if the starting product is fresh peels), crushing, extraction, precipitation, separation,

purification, filtration, and further drying.

Table 7. Fiber extraction tecnique from citrus

Extraction method	Process	Advantages	Disadvantages	Source
mechanical	Shredding, grinding and sieving of peel and pulp.	- Does not use chemical solvents. - It retains many of the nutritional characteristics.	- Low efficiency in complete fiber extraction. - May require subsequent treatments.	(Li et al., 2023)
aqueous solvents	The fiber is extracted from the plant matrix using hot water or steam	- Non-toxic. - No chemical solvent residues.	- Requires high amount of water. - Variable efficiency depending on process conditions.	(Gallina et al., 2022; Wang et al., 2023)
organic solvents	Using organic solvents (ethanol) to extract fiber from the matrix.	- Fiber extraction with specific properties. - Efficient in removing unwanted substances such as essential oils.	- Requires removal of solvents. - Limited use for food.	(Yi et al., 2024)
enzymatic	Treatment with enzymes (pectinase, cellulase) to degrade components of the peel/pulp.	- Preserves the functional properties of the fiber. - High purity of the extracted fiber.	- High cost of enzymes. - Controlled conditions needed.	(Chandel et al., 2022)
ultasound	Ultrasonic waves are used to disrupt cell walls and release the fiber	- Does not use toxic solvents. - High extraction efficiency.	- Requires specialized equipment.	(Sengar et al., 2020)
microwave	Microwaves are used to heat the plant material and facilitate fiber release.	- Fast and efficient. - Low energy consumption. - Does not require chemical solvents.	- Potential thermal degradation over extended times.	(Liew et al., 2016)
supercritical fluids	Use of supercritical CO_2 to separate fibers from the plant matrix.	- Non-toxic. - No chemical residues. - Highly selective method.	- High equipment costs. - Suitable only for certain fibers.	(Tanaka et al., 2012)
microbial fermentation	Microorganisms are used to degrade unwanted components and release the fiber.	- Natural and sustainable method. - Does not require the use of chemicals.	- Potential microbial residues.	(Yi et al., 2024)

The extraction method strongly influences the functionality of pectin, affecting its molecular integrity, purity, and specific properties (e.g., gelling, emulsifying, and antioxidant activities).

Techniques like enzyme-assisted and microwave extractions preserve pectin's bioactive qualities, making it ideal for food, pharmaceutical, and industrial applications, while harsher chemical methods can degrade its structural integrity, limiting its functionality.

Aqueous-Based and Enzyme-Assisted Extraction: they are favorable for maintaining the purity of pectin. These techniques enhance pectin's gelling and emulsifying properties, by preserving a high degree of methylation and uniform molecular weight. Acidic or alkaline treatments can alter pectin's degree of esterification and reduce its functional properties, such as gelling strength (Riyamol et al., 2023). Impact on Functional Applications: Pectin extracted with these methods has high compatibility with food products, acting as a natural thickener and stabilizer without toxic residues preserving the antioxidant capacity.

1.11.5 The role of pectin

In fruits, protopectins are naturally present. These protopectins transform into pectins through a process involving extraction and precipitation using diluted acid and ammonium hydroxide. Once extracted, the pectins are dried and ground. To enhance their effectiveness for various applications, they are standardized with additives such as sugar, calcium salts, or organic acids (Riyamol et al., 2023). Commercially, they are divided based on the level of esterification (% of methoxylation, number bonds occupied by methoxyl groups instead of hydrogen) into low methoxyl and high methoxyl pectin. Low methoxyl pectins have less than 50% methyl ester groups. They have greater hydrophilicity and acid stability compared to high methoxyl pectins, as well as the ability to form reversible gels at low temperatures. They are further subdivided into:

- Conventional low methoxyl: less than 50% of the carboxyl groups of the molecule are esterified with methyl groups $-CH_3$. They form gels without requiring high sugar concentrations, in the presence of calcium ions (Ca^{2+}) through the "egg-box" mechanism (Figure 9).

- Amidated low methoxyl: presence of NH_4^+ amide groups that are larger and mask the effects of methoxyl groups. There is a limit, the degree of amidation (DA), otherwise steric hindrance is created. It is expressed as the percentage of amide groups on the total galacturonic acids present in the pectin molecule and can vary from a minimum of 2% to a maximum of 25%. Higher amidation results in stronger bonds between charges with less need for sugar and calcium.

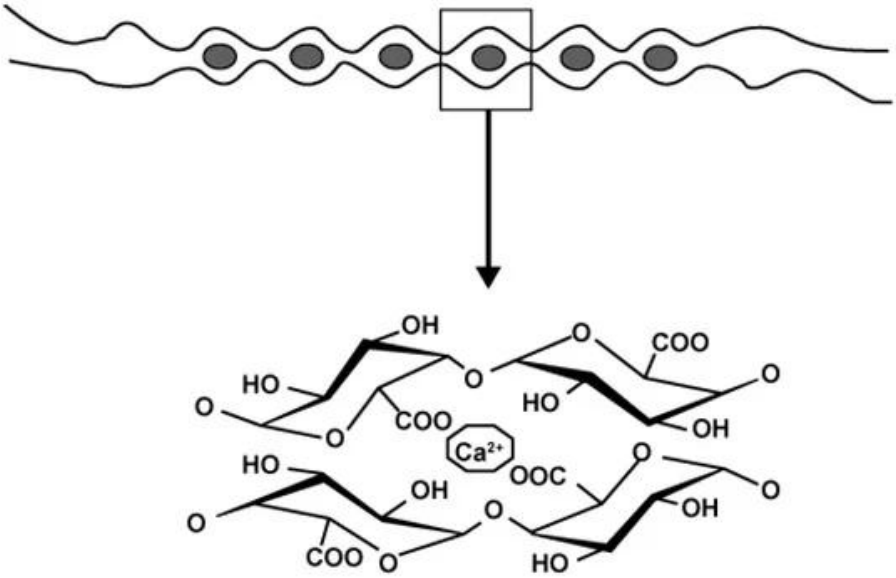

Figure 9. Egg box structure.

High methoxyl pectins have more than 50% methyl ester groups. They do not require calcium but need a significant amount of sugar to create bonds.

Pectins have been used for their gelling ability, creating a structure similar to an egg box (Figure 9) where the methoxyl groups are in contact, and calcium ions with their charges regulate the structure. This depends on the concentration of Ca2+ and the pH of the solution, as well as hydrogen bonds that form between amide groups (the latter allowing the creation of the gel and its thermoreversibility), making amidated pectin an interesting ingredient for the food industry (Freitas et al., 2021). A pectin gel is a three-dimensional network of macromolecules that includes the dispersant. It forms through physical or chemical changes that reduce pectin solubility, leading to local crystallizations. The physicochemical and functional properties of pectins, such as their gelling abilities, are closely related to their structures, including molecular weight, degree of esterification, galacturonic acid content, and monosaccharide composition, which vary based on plant sources and extraction methods (Riyamol et al., 2023). Pectin can form gels through different mechanisms, regardless of their degree of methylation (DM). For high methoxyl (HM) pectin, the higher DM results in a faster gel formation. Low methoxyl (LM) pectin forms gels by strongly binding divalent ions. Commercial HM pectin, typically with 8–11% methoxyl content, can form gels with high sugar content (over 65%) and acidic pH (2.20–2.80). The low pH reduces electrostatic repulsion, and the sugar helps bring the chains closer together, facilitating hydrogen bond formation and reducing water activity (Chandel et al., 2022). The creation of the three-dimensional network is further stabilized by hydrophobic interactions among methyl groups. Gel formation depends on time, temperature, and the type of sugar used. LM

pectin gels form when coordination bonds are established between carboxylate groups (in homogalacturonic unesterified zones) and divalent cations (such as calcium). This process is characterized by the "egg box" model. LM pectins with less than 7% methoxyl content can form gels at lower sugar content than HM pectins, making LM pectins suitable for a wider range of applications (Williams, 2020).

1.11.5.1 Different types of pectin gel

Pectin gels can be formed through various types of junction zones, which are the points where pectin molecules interact to create a network. These junction zones can be categorized into several types based on the nature of the interactions:

1. Ionotropic Gels: These gels are formed by the interaction between divalent cations, such as calcium ions, and pectin molecules. The pectin used in ionotropic gels typically consists predominantly of homogalacturonan, which can have a low or high degree of methylesterification (DM). The unmethylesterified (charged) regions of the pectin are arranged in a pattern along the polymer backbone. At pH values where the carboxyl groups of the galacturonic acid residues are charged, these regions interact with divalent cations to form stable junction zones. This type of gelation is commonly observed in nature, such as in the cell walls of growing pollen tubes, where calcium concentration and enzyme-induced demethylesterification control the mechanical properties of the network (Chandel et al., 2022).

2. Acidic Gels: These gels are typically formed in high-sugar systems, such as jams and confectioneries, where the interactions are driven by hydrogen bonding between hydroxyl and carboxyl protons, and some degree of hydrophobicity enhanced by reduced water activity. High DM pectin substrates are usually used for these gels. However, it has been shown that low DM pectins with charge distributions can also form gels simply by reducing the pH, without the addition of sugar. The reduction in pH modifies the polymer charge density, leading to changes in the local conformation of the pectin chains and promoting interchain hydrogen bond formation (Belkheiri et al., 2021).

3. Other Pectin Gels: There are also pectin gels formed through other mechanisms, such as:
    - Covalent Linkages: These gels are formed by chemical coupling of groups that have been pre-incorporated into the pectin components or are naturally occurring, such as ferulic acid substituents (Williams, 2020).

    - Changes in Solute Composition: Gels can be formed by introducing alcohol or large

amounts of monovalent salt, which drive the assembly of the polymer (Said et al., 2023).

- Interactions with Other Polyelectrolytes: Specific interactions with other biological polyelectrolytes, such as alginate, can also lead to gel formation (Williams, 2020).

- Exotic Pectic Components: Components like rhamnogalacturonan I (RG-I) and rhamnogalacturonan II (RG-II) have unique self-associating properties and can form gels through interactions with sidechains or boron, respectively (Gutierrez-Alvarado et al., 2022).

1.11.5.1 Different assembly procedures in pectin gelation:

The assembly process of pectin gels can significantly affect their properties. Two main methods are used to prepare these gels:

1. Heating and Mixing at High Temperatures: This method involves heating solutions of free calcium ions (typically calcium chloride) and pectin separately, then mixing them vigorously at the highest temperature possible to avoid chemical changes to the polymer. The mixed solution is then cooled, allowing gelation to occur. This method can sometimes result in precipitation or microgel formation, especially from the smallest chains with the most calcium-sensitive charge distributions. The process requires timely mixing and transfer of the solution to avoid premature gelation (Gutierrez-Alvarado et al., 2022).

2. Controlled-Release Protocols: These protocols introduce a slower, rate-limiting step into interactions between ions and ion-binding groups, allowing for more homogeneous mixing before gelation. One common approach uses glucono-delta-lactone (GDL), which hydrolyzes over time to release protons. These protons interact with calcium salts (typically calcium carbonate), releasing free calcium ions without lowering the pH. This method ensures that the effects observed in the network assembly result only from introducing free ions. Controlled-release gels tend to have a more homogeneous appearance and fewer issues with precipitation compared to those formed by heating and mixing (Williams, 2020).

The choice of assembly method can influence the final properties of the gel, such as its mechanical strength and homogeneity. For example, gels formed by controlled release at room temperature may have different melting behaviors compared to those formed by heating and cooling, due to differences in the binding energies and spatial extents of the junction zones formed. By carefully considering the

type of junction zones and the assembly procedures, it is possible to tailor the properties of pectin gels for specific applications, whether in food, pharmaceuticals, or other industries (Morales-Medina et al., 2022).

1.12 Positive Effects of Fiber Consumption on Health

Fiber, obtained not only from oranges or citrus fruits but also from other types of vegetables, plays a fundamental role in the health of the body (Fan et al., 2022). According to recommendations, its consumption should be between 25 and 35 grams per day, with at least 30-50% being soluble fiber (Kendall et al., 2010).

Regarding the benefits of fiber, the following are well-known:

- Antioxidant activity (Fuller et al., 2016).
- Action in counteracting the onset of certain types of cancer (Hua et al., 2017).
- Anti-inflammatory properties (Sawicki et al., 2017).
- Ability to reduce blood lipid levels, lowering cholesterol levels (Xue et al., 2019).
- Ability to improve intestinal health (Fan et al., 2022).

Additionally, fiber has beneficial effects in counteracting diabetes, infections, and cardiovascular problems (Kaur et al., 2023) and in preventing diseases caused by oxidative stress (Martínez-Las Heras et al., 2017).

1.13 Technological Properties of Citrus Fiber and Effects on Emulsion Formation

As described in several studies (Maqbool et al., 2023; Martínez-Las Heras et al., 2017; Zha et al., 2009), fiber has been added to various foods, resulting in improvements in both structure and shelf-life. In meat-based products, the use of fiber has yielded excellent technological results, particularly by inhibiting lipid oxidation and thus increasing the stability of the product itself. Other foods in which fiber has been integrated include cakes, cereal-based products, pasta, soups, and some types of beverages, where it has improved viscosity, texture, and shelf-life (Martínez-Las Heras et al., 2017; Sáyago-Ayerdi et al., 2009). Among the technological properties of fiber, WHC (water holding capacity) is crucial, as it describes the fiber's ability to hydrate and retain water. It can adsorb surface water and absorb it, thanks to the insoluble fraction that has a capillary structure capable of swelling (Zhang et al., 2023). Therefore, the greater the amount of insoluble fiber present, the higher the capacity to retain a significant amount of water. Additionally, some types of fibers can form a

structure with gel-like properties, even if very weak (Fan et al., 2022), which occurs when the fiber is hydrated with water. This capability is also useful for retaining oil, an aspect that can be exploited in emulsion formation (He et al., 2023). Indeed, fiber can be used in the previously mentioned food products, as well as in other types of products, functioning as an emulsifying agent improving texture and stability (Yang et al., 2023). In Ruan et al., (2019) study, an emulsion made with citrus fiber was compared to commercial mayonnaise. The fiber emulsion results in a creamier, softer, and more fluid product. The structure formed using citrus fiber has the characteristic of being both an emulsion and a weak gel, making it suitable for formulating products where fluidity, structure, and compactness are essential. It can be stated that the emulsifying capacity of fiber depends precisely on WHC (Water Holding Capacity). A study conducted by Yuan et al. (2023) demonstrated that the ability to retain more water is closely linked to the formation and maintenance of the emulsion. Citrus fiber also plays an important role in defining the shelf-life of products, providing stability to the emulsion. Through electrostatic repulsion phenomena, it prevents the coalescence of oil droplets and consequently the phase separation of the emulsion due to structural breakdown (Huang et al., 2020). Citrus fiber is a valid alternative to commonly used emulsifiers. Being pectin gel hydrophilic, they cannot solubilize or incorporate lipophilic elements due to the lack of chemical compatibility between hydrophilic molecules (pectin) and lipophilic ones (fats or oils). To stabilize systems containing both hydrophilic and lipophilic elements, emulsifiers are usually used to form stable mixtures (Said et al., 2023). This emulsifying agent is insoluble citrus fiber, a by-product of pectin extraction, as it has shown the ability to stabilize the emulsion through a Pickering effect (stabilizing the interface between two incompatible liquids by adding solid particles in powder form) and has led to the creation of a network capable of reducing the creaming effect (or phase separation), providing high resistance to thermal treatment and pH (Qi et al., 2021). Citrus fiber-based emulsions have shown superior creaminess and softness compared to egg-based mayonnaise products. This suggests that citrus fiber has the potential as a plant-based egg substitute. Additionally, these emulsions retain flavors like whipped cream, making them suitable for low-fat product formulations while providing pleasant palatability (Ruan et al., 2019). They also play a role in reducing glucose diffusivity during digestion (Miehle et al., 2022). The process for orange processing, generally applied by the industry, is as follows: whole oranges are juiced; the juice and pomace (a mixture of juice, peels, seeds, and essential oils) are obtained. The juice is sold, and the pomace is washed with hexane to dissolve hydrocarbons and distilled to obtain a white, odorless puree. The pH is lowered with hydrochloric acid, then heated to solubilize and extract low methoxyl pectins (Fakayode & Abobi, 2018). The properties of the fiber depend on the content of three components: pectin, hemicellulose, and cellulose. As the pectin content increases, the viscosity of the structure increases; as the hemicellulose content increases, the water-holding

capacity improves, but the oil-holding capacity worsens. As the cellulose content increases, the oil-holding capacity improves, but the water-holding capacity worsens (He et al., 2023).

1.14 Emulsion Filled Hydrogel

Emulsion-filled hydrogel particles are systems where oil droplets are embedded within a hydrogel matrix and dispersed in an aqueous phase. These particles are made from proteins or polysaccharides that form a gel under controlled conditions, like heating, cooling, pH adjustment, or enzyme addition. They can be created using various methods such as injection, molding, gel disruption, and controlled biopolymer phase separation (Chung & McClements, 2014). Gels are advanced materials characterized by three-dimensional networks that can incorporate large amounts of water, oil, or air, resulting in hydrogels, oleogels, and aerogels, respectively. These materials possess unique properties such as high surface area, porosity, and loading capacity. Emulsion gels, or emulsion-filled gels or emulgels, are a specific type of gel where at least one emulsion phase forms a three-dimensional network. Compared to traditional emulsions, this structure provides superior stability against chemical reactions, physical processes, and environmental changes (Cao & Mezzenga, 2020; Lin et al., 2021). The formation often involves mixing an oil-in-water emulsion with a biopolymer solution and adjusting conditions to promote gelation. Hydrogel particles can form through segregation-based or aggregation-based phase separation due to thermodynamic incompatibility between biopolymers. This incompatibility causes the system to separate into two phases, each rich in one type of biopolymer. The hydrogel particles are then cross-linked by adjusting temperature, pH, salt, or enzyme activity, ensuring oil droplets are within the biopolymer phase (Fu et al., 2019). These particles have a higher viscosity than conventional emulsions with the same oil concentration, making them suitable for reduced-fat products. They also help control the release of flavor compounds, matching the flavor profile of full-fat products.

Biopolymer-based emulsion gels, from polysaccharides and proteins, can form complex microstructures and serve as efficient delivery vehicles for various industrial applications. They are handy for encapsulating and protecting functional food additives and bioactive compounds, such as carotenoids, phenolic acids, flavonoids, vitamins, and unsaturated fatty acids, which exhibit health-promoting characteristics but are difficult to incorporate into food matrices due to their low chemical stability, limited water solubility, and poor cell adsorption (Abdullah et al., 2022). Recent developments have highlighted the potential of emulsion gels in encapsulating and delivering nutraceuticals, controlling the release of bioactive molecules, reducing fat, sugar and salt in foods, and delivering probiotics with improved viability. These gels are also being explored for designing complex food structures using 3D printing, offering new possibilities for creating safer, healthier, and

more sustainable food products (Godoi et al., 2016). Emulsion gel preparation involves various methods such as emulsification, heating, enzymatic treatment, and pH adjustment. The gel properties are influenced by factors like biopolymer type, processing conditions, and emulsifiers. Emulsion gels can be classified into protein-based, polysaccharide-based, and mixed emulsion gels. The future of emulsion gels in the food industry looks promising, with potential applications in creating tailored food breakdown behavior, sensory perception, and targeted release of functional ingredients (Light & Karboune, 2022). The interest in mixed gels (protein and polysaccharide) has grown because they offer enriched gelling behaviors and more precise control over physicochemical, rheological, and functional properties than individual emulsion gels. Mixed gels had high water-holding capacity and could produce a diverse range of microstructures that can be further exploited to bring desirable textures and sensory attributes (Le et al., 2017). The polysaccharide part imparts better stability against environmental conditions such as pH, temperature, and ionic strength, while the protein part contributes to producing fine droplet sizes through its emulsifying capacity, leading to a homogenous structure. Network structure, texture, and perception of food gels are extremely relevant, thus a better understanding of gel structure and strength is vital for designing food gels. Chain flexibility and fractal dimensionality are two important structural parameters of food gel networks. Polymers can be recognized as flexible, semiflexible, or rigid, by comparing the persistence length and contour length (Burla et al., 2019). The fractal dimensionality connects the mass and size of the aggregate. Gel building blocks (flexible polymers, semiflexible polymers, or fractal colloids) can be connected by point junctions (a chemical crosslinker) or zone junctions (an egg-box zone in alginate or coiled-coil helices in carrageenans), leading to the formation of a percolated network (Cao & Mezzenga, 2020). Although polysaccharide chains are inherently flexible, purely flexible networks are uncommon in food gels. This is due to the formation of junction zones during gelation, which involves the lateral aggregation of helical structures (Zhang et al., 2013). Semiflexible networks include those established by protein nanofibrils, nanocellulose, and chitin nanofibrils. Fractal colloidal networks, on the other hand, are formed by random protein aggregation, such as protein gels formed under high salt contents or pH levels close to the isoelectric point. Junction zone networks can manifest in at least two distinct forms: pseudo-flexible networks and pseudo-semiflexible networks (Mackintosh et al., 1995). In pseudo-flexible networks, the junction zones are formed by the remaining flexible sections of the polymer chains. In pseudo-semiflexible networks, a longer portion of the contour length of the polymers is involved, with junction zones formed by helical associations or egg-box structures. This creates a semiflexible fibrous network, a structure commonly observed in many polysaccharide gels (Broedersz & MacKintosh, 2014). Coacervation is a commonly employed method in the formation of mixed gels from oppositely charged biopolymers (e.g., protein-protein, polysaccharide-

polysaccharide, and protein-polysaccharide) by regulating the mixture ratio (biopolymer type and concentration), temperature, pH, ionic strength, etc. (Diener et al., 2019). During this process, the charged species adsorbed on biopolymer surfaces interact through electrostatic complexation and develop 3D networks leading to gel formation. Mixed emulsion gels can be created using various combinations, such as protein-protein, polysaccharide-polysaccharide, and protein-polysaccharide. For instance, sunflower oil combined with xanthan gum and guar gum has been used to deliver *Lactobacillus plantarum* (Pandey et al., 2016). These gels' mechanical strength and disintegration have shown significant improvements in stability and resistance to gastric acid, thanks to the xanthan gum and guar gum in the dispersed phase. Additionally, when stored at different temperatures (4°C, −20°C, and −196°C), these natural gum-based emulsion gels demonstrated higher survival rates of encapsulated probiotics compared to the control. Developed mixed emulsion gels using an enzymatic gelation method, incorporating flavored corn oil and stabilizing with complexes of soy protein isolate and sugar beet pectin (Hou et al., 2016). They presented more compact structures due to the formation of strong interfacial networks ascribed to higher emulsifier absorption at the oil-water interfaces.

Elasticity is another crucial aspect of hydrogels, characterized by storage moduli dominating loss moduli over a wide oscillatory frequency range. The network elasticity is the plateau value of G' at low frequency. For flexible (rubber-like) polymer networks, the elasticity is essentially of entropic origin and arises from the thermal energy contained within a unit volume of the network, that is, the network mesh size (Prince & Kumacheva, 2019). Instead, the elasticity of semiflexible polymer networks arises from the bending energy of the polymer chains and is influenced by the bending modulus, mesh size, and cross-link length. This simplifies a relationship where a semiflexible network exhibits a stronger dependence on mesh size than a flexible network and has stronger elasticity at comparable mesh sizes. The network elasticity can be enhanced by decreasing the mesh size and promoting the transition from flexible to semiflexible chains. Many food gels show a similar scaling exponent, including semiflexible amyloid fibrils, cellulose fibrils, and junction zone networks formed from agar and gellan (Picone et al., 2017), this implies that junction zone networks can be modeled as pseudo-semiflexible networks. Some authors (Diba et al., 2017; Prince & Kumacheva, 2019) claim that elasticity can be further increased by bundling semiflexible fibrils at a fixed polymer concentration. However, this approach is not inherently justified, as it also introduces a competing effect: an increase in mesh size, which reduces the elasticity of the network. Cao et al. (2019) developed a model to address the competing effects of bending modulus and increasing mesh size during filament bundling in the semiflexible regime. The model reveals non-monotonic behavior: at low levels of bundling, bending rigidity dominates, enhancing elasticity, while at higher bundling levels, mesh size effects prevail, leading to reduced elasticity. In fractal colloidal networks, elasticity

arises from the bending energy of the structural chains within the network volume. Given the fractal dimensionality of both the structural chains and all objects within a mesh, the elasticity of the network scales accordingly (Mezzenga & Fischer, 2013). This highlights how the mechanical properties of fractal protein gels are intrinsically linked to their structural characteristics. Additionally, this scaling is frequently used to uncover structural details of protein aggregates. The fractal dimensionality depends on two primary aggregation kinetics: diffusion-limited and reaction-limited cluster aggregation. Consequently, the microstructure and thus the elasticity of food gels can be precisely adjusted through control of the gelation kinetics. Strain stiffening is a crucial characteristic of filamentous networks (Burla et al., 2019; Goldenberg & Goldhirsch, 2005). Numerous experimental and theoretical studies have shown that semiflexible polymer networks, such as those formed by actin and intermediate filaments, become stiffer as they stretch along the direction of applied strain. This stiffening effect is due to a reduction in polymer conformational entropy under strain.

1.15 Gel-Body Interactions

Gel-body interactions play a main role in the sensory experience of food consumption and physiological processes of digestion, absorption, and nutrient delivery. During oral processing, texture perception is a complex, multi-stage experience shaped by food properties such as chemical composition, structural organization, and the various mechanical, enzymatic, and physicochemical changes occurring in chewing and swallowing. It is also closely connected to the various conditions within our body, both due to the physical stress it may undergo and its interaction with enzymes and other substances it comes into contact with inside the body (Figure 10). The texture of gels is primarly studied by two disciplines: rheology and tribology (Krop et al., 2019), which allow to define attributes, including hardness and creaminess.

1.15.1 Oral Phase

Texture, which involves the sensations of hardness and brittleness, is experienced during the initial chewing phase and is closely related to a food's fracture stress and strain properties. Tribology is associated with later stages of oral processing like swallowing and lubrication. Smoothness and creaminess perceived as food lubricates the mouth, a sensation largely determined by friction coefficients. The texture and sensory profile can be fine-tuned by adjusting biopolymer type, concentration, structural arrangement, and mesh size (Srivastava et al., 2021). It's also possible to replicate sensory feeling of fats, salts, or sugars, reducing the need for these components without sacrificing flavor or mouthfeel. Emulsion gels are increasingly employed in the food industry to mimic the mouthfeel of fat without raising the fat content (Hayakawa et al., 2014). Lowering friction

creates a creamy sensation that mimics fat while masking undesired flavors of bioactive ingredients by delaying their release until after the food has passed the taste buds. For instance, gelatin-based gels that melt at mouth temperature can reproduce the perception of fat, providing a full sensory experience while reducing caloric content (Taktak et al., 2021). By adjusting gel structure and composition, it is possible to create textures that replicate specific microgels in semi-solid foods and mimic creaminess by lowering the friction coefficient through mechanisms such as the "ball-bearing" effect. This capability enables the development of foods that deliver reduced fat, salt, or sugar while retaining desired sensory qualities (Liu et al., 2016).

1.15.2 Digestion phase

Structural aspects of food gels, like mesh size, can control the digestion kinetics by slowing gastric emptying, which prolongs satiety, enhances blood sugar regulation, and supports cholesterol control. Certain gels break down within the digestive tract due to the acidic environment, making them ideal carriers for the targeted delivery of bioactive nutrients or drugs, they are released at specific locations, such as the stomach or small intestine. Through controlled release, food gels can be designed to protect these substances from early degradation and promote their bioavailability at optimal locations within the digestive system (Guo et al., 2015). The digestion of polymer-based gels is influenced by their gelation process, modulating breakdown rates, and impacting nutrient release. Protein-based gels are digested by gastrointestinal peptidases, whereas the digestion of polysaccharides varies; for example, fiber-rich polysaccharides depend on gut microbiota for their breakdown. Acid- and heat-gelled milk proteins, exhibit slower digestion rates and longer gastric retention, while polysaccharide gels prolong gastric emptying through thickening (Abdullah et al., 2022). Surface features of food gels can be engineered to enhance bioavailability allowing them to adhere to the mucous layer, which prolongs residence time, or by facilitating direct absorption into the circulatory system. Gels can slow down the diffusion of digestive enzymes, which delays the release of bioactive compounds. This process helps to prolong feelings of fullness and manage glucose levels (Mudgil & Barak, 2013). The digestion of gel-based systems involves disintegration, swelling, molecular interactions, and erosion. These mechanisms interact with enzymes and pH changes throughout the digestive tract, controlling the release of encapsulated molecules at precise sites, like the small intestine or colon. They protect nutrients from environmental stress and enable controlled release over time. Encapsulation within emulsion gels shields sensitive nutrients from oxidation and degradation, allowing their targeted release within the digestive tract. By manipulating the ionic strength and pH conditions within gels, targeted release systems can be created to transport compounds effectively to specific parts of the gastrointestinal tract. For example, protein-loaded calcium alginate gels are designed to release at the

neutral pH of the small intestine, where both the protein and alginate acquire negative charges, facilitating an efficient, controlled release (Lin et al., 2021). Naturally derived polymers, including cellulose, alginate, chitosan, hyaluronic acid, agarose, gelatin, and protein fibrils, generally exhibit high biocompatibility and are safe when used in medical or cell culture settings. After bioactive compounds are released in the gastrointestinal tract, their efficient absorption is essential to maximize bioavailability. The mucus layer, a dense network of mucin fibers, can hinder nutrient absorption, as only compounds smaller than approximately 100 nm can pass through easily. Emulsion gels, designed with specific surface properties such as optimal size, shape, charge, and hydrophobicity, improve permeability by facilitating better transport across this barrier (Wang et al., 2024). Chitosan-based gels are especially effective, as they can interact with and permeate mucosal surfaces without damaging epithelial cells. Chitosan's ability to increase cellular permeability through temporary depolymerization of the cellular structures allows bioactive compounds to reach target cells more effectively. For instance, gelatin-based emulsion gels loaded with omega-3 fatty acids increased plasma levels of eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) compared to standard gelatin capsules. This efficiency in delivering essential nutrients and enhancing absorption through targeted structural design makes gels promising carriers for many compounds (Haug et al., 2011). Emulsion gels and hydrogels are proving to be highly valuable in both food and biomedical fields. Emulsion gels enhance the texture, bioavailability, and nutrient absorption in clean-label foods. They protect bioactive compounds and enable targeted release, making them essential for advanced food systems. Different polymers offer different texture perception, degradation rate, and preserve differently the bioactive compounds in a supermarket shelf or inside human body.

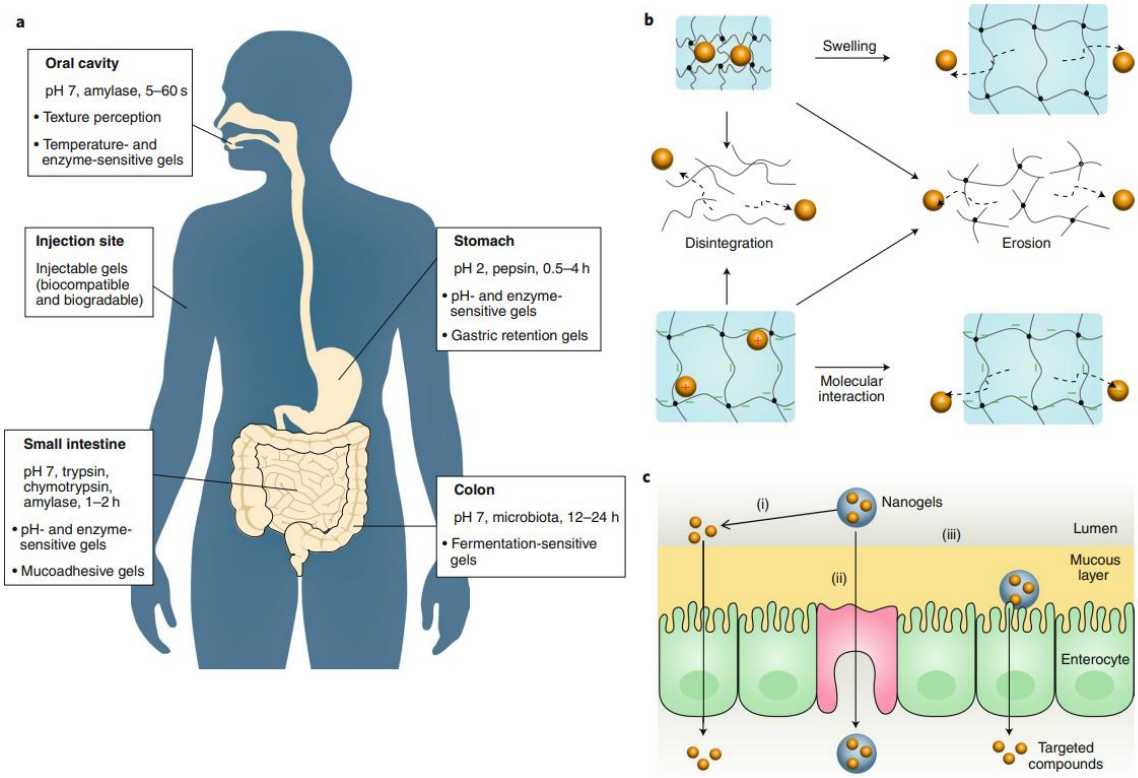

Figure 10. Physiological conditions such as pH, enzymes, and retention time (a) and gels' functional molecules release in various sections of the gastrointestinal tract and tissues. Potential mechanisms for the release of targeted compounds from hydrogels include (b) swelling, which increases interchain repulsion; disintegration, involving gel melting and dissociation of electrostatic coacervates; erosion, through digestion by enzymes and fermentation by microbiota; and molecular interactions, which modulate the electrostatic interaction between the building block and the encapsulated agent. Gel particles can enhance the bioavailability of encapsulated compounds by delivering to targeted points (i), direct uptake into the circulatory system (ii), and adsorption to the mucous layer to extend residence time (iii) (Cao & Mezzenga, 2020).

1.16 Dysphagia

Dysphagia, derived from the Greek words "dys" (disorder) and "phago" (eat or swallow), is a condition characterized by difficulty in swallowing. Dysphagia is a dysfunction of the digestive system characterized by difficulty swallowing and the proper transit of the bolus through the upper digestive tract. It most commonly occurs because of other obstructive or motor disorders, such as neoplasms or achalasia. It affects both solid and liquid foods (Smithard et al., 2007). It is commonly associated with damage to the structures and functions of the jaw, lips, tongue, soft palate, throat, esophagus, and other related organs. Dysphagia is a significant public health issue, particularly among the elderly and individuals with certain medical conditions, such as Parkinson's disease. The prevalence of dysphagia is increasing globally, affecting millions of people and significantly reducing their quality of life (Liu et al., 2024). There are classifications based on etiology and location. Symptoms include difficulty controlling the bolus in the oral cavity with loss of saliva or food from the mouth, coughing, a sensation of choking due to aspiration into the airways, nasal regurgitation, as well as fatigue during meals, multiple swallows for the same bolus, and adoption of certain postures

during swallowing (Boczko, 2006).

In cases of esophageal narrowing due to intrinsic muscle abnormalities (achalasia), pharmacological treatment aims to promote muscle relaxation using muscle relaxants such as calcium antagonists. Surgical treatment focuses on dilating the affected area (usually the lower esophageal sphincter) through pneumatic dilation or myotomy. In cases of tumors compressing or infiltrating the esophagus, treatment involves surgical removal of the tumor, possibly with adjuvant chemotherapy. For psychogenic disorders, treatment is psychological or psychiatric. The rehabilitative intervention of a speech therapist is crucial, as they can determine the most suitable bolus consistencies for the individual patient and any facilitating postures. This is followed by a rehabilitation process with partial or total recovery, in which the patient and their family members must actively participate to ensure the best possible outcome. Local vibration therapy, which also allows intraoral treatment, is often used for rehabilitative treatment (Easterling, 2018). To manage dysphagia, texture-modified foods and thickened fluids are often recommended. These modifications help ensure that food and liquids are easier to swallow, reducing the risk of choking and aspiration. Various Countries have established standards for texture-modified foods to improve patient safety and care. For instance, the International Dysphagia Diet Standardisation Initiative (IDDSI) provides global guidelines, but there are variations in classification and definitions across different regions. The IDDSI framework categorizes foods and liquids into levels based on their texture and thickness, ranging from regular foods to extremely thick liquids (Liu et al., 2024). The role of biopolymers in the development of texture-modified foods is crucial. Biopolymers, such as starch-based and gum-based thickeners, are used to modify the rheological properties of foods and liquids, making them easier to swallow. Starch-based thickeners are commonly used due to their availability and cost-effectiveness (Yang & Lin, 2021). However, they may leave residues that increase the risk of post-swallow aspiration, making them less ideal for some patients. Gum-based thickeners, on the other hand, offer several advantages. They increase the viscosity of liquids by creating entanglements that trap water, maintaining a stable viscosity over time. These thickeners are less digestible by salivary amylases, resulting in fewer residues and a lower risk of aspiration (Hansen et al., 2022). Xanthan gum, for example, is widely studied and used in dysphagia diets due to its high viscosity at low shear rates and stable viscosity across a wide range of pH levels, temperatures, and ionic strengths. Other gum-based thickeners include cellulose derivatives, pectin, guar gum, gellan gum, κ-carrageenan, and flaxseed gum (Yang et al., 2022). As already stated in the previous chapter, the use of biopolymers in texture-modified foods not only improves the safety and ease of swallowing but also enhances the sensory properties and nutritional value of the foods. By incorporating these biopolymers, food products can be tailored to meet the specific needs of individuals with dysphagia, ensuring they receive adequate nutrition

while minimizing the risk of choking and aspiration. In conclusion, the advancements in biopolymers application for texture modification represent a significant step forward in dysphagia treatments. These materials offer innovative solutions that improve the quality of life for individuals with swallowing difficulties, making it easier for them to consume a variety of foods and liquids safely and enjoyably.

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Chapter 2

Objectives of the work

The objective of this research is to develop a nutritionally enriched and easily swallowable food product tailored for individuals requiring texture-modulated foods. The research will be structured into four progressive stages (supported by collaboration with industry partners), each addressing critical components of formulation and processing. In the first stage, a detailed analysis of various nuts will be conducted to determine their nutritional properties: particular attention will be given to tocopherol profiles, and protein content. To preserve their natural synergies, the nuts will be cold-pressed, isolating components to optimize their incorporation during the formulation of emulsion-filled hydrogels. This approach aims to strategically utilize these components to maximize functional and nutritional benefits throughout the process. The second phase will focus on the fibrous byproducts of citrus juice production, specifically isolating pectin from insoluble citrus fiber to harness their respective functionalities. Pectin will act as a structuring agent, while citrus fiber will serve as an emulsifier. The interaction between these two components will be studied under thermal treatments to understand how their synergy contributes to stability, consistency, and resilience. This exploration seeks to develop a flexible and robust matrix that integrates oils and other components without compromising the overall structural integrity. The third stage will emphasize the rheological evaluation of citrus fiber-based emulsions in two dispersing media: water and apricot puree. This comparative analysis aims to uncover how citrus fiber forms networks in different environments and how apricot matrix effect enhances the emulsion properties. The results will clarify the role of fruit intrinsic components in improving texture and structural cohesion, paving the way for broader applications. These findings will contribute valuable insights into the mechanisms underpinning stability and texture in emulsions designed for food use. In the final phase, insights from the previous stages will be synthesized to create an advanced emulsion-filled hydrogel combining citrus fiber, apricot puree, cold-pressed hazelnut oil, and hazelnut defatted cake. This formulation will be optimized for swallowability, stability, and tribological performance. Hazelnut oil, rich in tocopherols, will be evaluated for its stability under processing conditions, while hazelnut cake will enhance emulsification and structural reinforcement. By integrating pectin and citrus fiber, the hydrogel's texture will be modulated for a pleasant and manageable mouthfeel. This phase will also focus on ensuring the product meets the tribological standards for easy swallowing without compromising nutritional quality. The final product will serve as a platform for delivering targeted

nutrition through innovative textural solutions, addressing the dual challenges of palatability and functional nutrition. These efforts will contribute to advancing the field of texture-oriented food science while opening pathways for tailored, sustainable, and nutrient-rich food applications.

Chapter 3

"Unlocking cold-pressed nut potential: focus on tocopherols content of oils and defatted cakes"

Abstract

The research aimed to provide a survey on the composition of oil and partially defatted cakes obtained by cold-pressing of various tree nuts to enable their use as ingredients for modulating the nutritional properties of final food products. Different types of pistachios (*Pistacia vera)*, hazelnuts *(Corylus avellana)*, and apricot kernels *(Prunus armeniaca)* were evaluated in terms of colour, water activity, moisture, ash, fat, protein, fibre, total phenolic, and tocopherol contents. They were extracted by hydraulic press giving oils rich in vitamin E and defatted cakes with high nutritional potential: the cakes preserved significant antioxidant compounds, as well as fat, protein, and fibre levels based on the oil extraction yield. Products derived from cold-pressed nuts revealed promising compositions that could be exploited to develop healthy foods with improved sensorial and techno-functional properties, increasing the sustainability of the process and zeroing waste.

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1. Introduction

Thanks to their organoleptic and structural characteristics, tree nuts are suitable for being consumed in their original form or as an ingredient in various food preparations. In addition, they represent an important source of nutrients, unsaturated and polyunsaturated fatty acids, vitamins, and fibre (Brufau et al. 2006). Pistachios and hazelnuts are some of the world's most consumed and produced tree nuts (Alalwan et al. 2022). Although not as popular as them, apricot kernel is the by-product of one of the most produced fruits in temperate areas (Gómez et al. 1998). The main issue about apricot kernel seed and oil use is the presence of amygdalin (Akinci Yildirim and Atilla Askin 2010). This can be easily solved by using a sweet variety that contains a small quantity of it, compared to the bitter one (Gorrepati et al. 2015). Dried nuts are generally constituted of 50 to 70% fat with unsaturated fatty acid (UFA), mono-unsaturated fatty acid (MUFA) and poly-unsaturated fatty acid (PUFA), proportionally more present than saturated fatty acid (SFA) (Astrup et al. 2011; Tvrzicka et al. 2011). Fats should constitute 30% of the nutritional energy requirements in a healthy and balanced diet (Kaya et al. 2008). Since the maximum recommended amount of SFA in a diet is 10%, PUFA and MUFA must be most of the intake, in this way the probability of chronic heart disease can be reduced as much as LDL cholesterol concentration in blood (Król and Gantner 2020). The apricot kernel contains 7% of SFA and 93% of UFA (Mandalari et al. 2021), in hazelnut the amount of SFA is always lower than 10% (Lobo et al. 2010) while in pistachio there are 14 % of SFA and 86% of UFA (2015a). The fatty acid profile is not the only factor influencing the nutritional quality of the dried nuts: they can also contain micronutrients such as tocopherols, with antioxidant activity (Cherif et al. 2021). Considering their importance, EFSA suggests their daily assumption, for a healthy lifestyle, evaluated as α-tocopherol equivalent (α-TE) (EFSA, 2015a). In α-TE calculation is considered the nutritional value of the four homologues (α, β, γ, and δ) for being able to sort them according to their importance and effect (D'Evoli et al. 2015). Vitamin E's most present homologue in apricot kernel and pistachio is γ – tocopherol, while hazelnut contains predominantly α – tocopherol (Maestri et al. 2020; Özcan et al. 2013). Nutritional values of the fat fraction, thanks both to fatty acids composition and the micronutrients contained, explain the importance of oil extraction. It's also fundamental to preserve them during the process to obtain a high-value product. According to Özcan et al. (2013) and Ahmed et al. (2019) there are three main methods for oil extraction: by pressure, by solvent or with a combination of both (Ajibola et al. 2002). The most used industrial technique is by solvent but, as demonstrated, this is not the best for preserving the quality in terms of fatty acids composition and tocopherols (Oyinlola et al. 2004). The nutritional value loss is a result of the high temperature applied during the process (Ghiasi et al. 2022). In recent years, top quality oil industry has been developing

an interest in the cold-extraction technique thanks to its simplicity, quickness, and safety (Catalán et al. 2017). Cold-pressed extraction is a process in which the temperature never goes over 30°C (Fantino et al. 2020). The two main pressure systems for cold extraction are the screw press and the hydraulic press. Even though being considered cold extraction, screw press can generate heat and the temperature can go way over 30°C (Sena-Moreno et al. 2015), because of friction and pressure required for yield optimization (Álvarez-Ortí et al. 2012). With a hydraulic press, no heat is generated and, as a consequence, the product never goes over room temperature having a positive impact on the oil, which will achieve a minor level of K270 and peroxides compared to a screw press (Sena-Moreno et al. 2015; Roncero Heras et al. 2022). However, temperature reached by screw-press can also have a positive impact on the final product's sensory profile if the raw material is not roasted (Celenk et al. 2020). On the other hand, roasting nuts before extraction with hydraulic pressure leads to improved organoleptic and physicochemical characteristics (Zhang et al. 2022). The main issue regarding mechanical cold-press extraction is the yield, which can be around 80% with maximum optimization (Helstad et al. 2022). Thanks to the higher yield and the capacity to work continuously, during time screw-press has replaced hydraulic press in industries and laboratories (Senkoylu and Dale 1999; Aldobouni et al. 2015; Ozyurt et al. 2021). The extraction process generates a by-product that consists of a significant amount of solid, called defatted cake (DFC), which has been used as feed (Deshmukh et al. 2022) or biofuel (Calvo et al. 2011) in the past years. Unfortunately, the progressive abandonment of hydraulic press took place without considering its potential. With no heat, and only by pressure, it can generate a high-quality product (Sena-Moreno et al. 2015; Roncero Heras et al. 2022) and a by-product with a potentially higher value than the oil. In the present study three different types of tree nuts, for a total of five samples including hazelnuts, pistachios, and apricot kernels, were studied with the respective cold-extracted oil and de-oiled cake aiming to evaluate the main changes in the nutritional composition occurring after the oil extraction, by focusing on content and quality of tocopherols. The characterization will allow the future use of different combinations of oils and DFC to achieve the desired nutritional composition in a food product. DFCs are an ideal solution to increase the protein content of nut-based spread creams or, in general, of products for elderly and sports people (without adding different protein sources); they can also exert an important role on the modulation of food structural/lubricant performances.

2. Materials and methods

Five different nut kernels (BASE) with the corresponding oils and defatted cake (DFC) were kindly provided by Pariani S.r.l. (Givoletto, Torino, Italy). In detail, samples from two types of hazelnuts *(Corylus avellana*) (a mix of Turkish *Tombur and Palaz cvs.,* and a Piedmont P.G.I. *cv. Tonda Gentile*

delle Langhe), two types of pistachios (*Pistacia vera*) (a mix of pistachio types from Sicily *cv.Napoletana*, and a Bronte P.O.D. *cv. Napoletana*), and apricot kernels *(Prunus armeniaca)* (by different types from Turkey) were supplied.

Extractions were performed following the industry's parameter: different kernels were roasted and cold-pressed under different pressures and times allowing to separate oils and DFCs. BASEs and DFCs were milled (Retsch GM 200, Retsch, Düsseldorf, Germany) and then analysed for moisture, water activity (aw), ash, fat, protein, soluble and insoluble dietary fibre, total phenolics, tocopherols content, and colour. After the grinding, all samples were stored in vacuum-sealed bags at -21°C without exposure to light. Oils were analysed for tocopherol and colour and have been conserved at -21°C inside glass bottles with synthetic seals, without light exposure.

2.1 Process conditions:

The Pariani company receives the already shelled nuts and performs the roasting by itself with specific parameters for each type of nut, as described in

Table **8**:

Table 8. Roasting parameters applied by the company on different nut kernels. *Apricot kernels are only dried and not roasted.

Samples	Temperature (°C)	Time (min.)
Piedmont hazelnut P.G.I.	165	38
Turkey hazelnut	165	30
Apricot kernel*	-	-
Bronte pistachio P.O.D.	150	18
Sicilian pistachio	150	18

After the roasting treatment, the BASEs are cold extracted with a hydraulic press that can reach 400 bar of pressure. The different extraction conditions are summarized in Table 9:

Table 9. Extraction parameters applied by the company on different nut kernels.

Samples	Pressure (bar)	Time (min)
Piedmont hazelnut P.G.I.	350	130
Turkey hazelnut	350	130
Turkey apricot kernel	400	140
Bronte pistachio P.O.D.	300	100
Sicilian pistachio	300	100

2.2 Characterization analysis

2.2.1 Water Activity (a_w)

A water activity meter for the analysis of solid samples (HygroPalm HP23-AW-A, Rotronic, Bassersdorf, Switzerland) was used to measure a_w at room temperature (25°C). Before the analysis, the frozen sample has been removed from the freezer and left sealed, under vacuum, until reaching room temperature.

2.2.2 Moisture and ash

Moisture and ash contents were determined according to 925.40-1925 and 950.49-1950 official AOAC methods for nuts and nuts products, respectively.

2.2.3 Fat content

For fat determination, the 963.15 AOAC method was used as a reference with some modifications. Samples were subjected to a first 8h Soxhlet extraction with petroleum ether; the residual solid fractions underwent an acid hydrolysis with HCl 4N, and they were further extracted by an additional 8h Soxhlet. All chemicals used were purchased from Carlo Erba (Cornaredo, Milano, Italy).

The oil extraction yields were calculated with a mass balance on the extraction process calculated on the percentage of fat before and after the extraction.

2.2.4 Protein content

Protein contents were estimated following the 950.48 AOAC method. The mineralization process was performed by SpeedDigester K-436 coupled with Scrubber K-415 (Buchi). Samples were distilled (Udk 127, Velp Scientifica SRL, Usmate Velate, Italy) and then titrated with sulphuric acid 0.1 N (AT1000Series, TitraLab).

2.2.5 Soluble, and Insoluble Dietary fibre Content

The analysis has been assessed on BASEs and DFCs previously defatted by 8h Soxhlet extraction with petroleum ether (Carlo Erba, Cornaredo, Milano, Italy). Samples were analysed with K-TDFR-200A Kit (Megazyme, Wicklow, Ireland) in reference to the AOAC method 991.43.

2.2.6 Total phenolic content

The analysis was performed following the method reported by Bassani et al. (2020) using a micro-volume version of the Folin's assay. The absorbance was read at 750nm using a spectrophotometer, Jasco V730 (Jasco Europe S.r.l., Cremella, Lecco, Italy).

2.2.7 Tocopherols

2.2.7.1 Oil extraction:

Five grams of solid sample were weighed into Falcon tubes and 25 mL of n-hexane (Sigma Aldrich, Milan, Italy) were added; tubes were then covered with aluminium foil to avoid light exposure and left in an orbital incubator (SKI 4 ARGO LAB) at 25°C for 1 h at a shaking speed of 180 rpm. Falcons were centrifugated at 3000 g, at 15°C for 15 minutes (Thermo Scientific SL16R Centrifuge, Thermo Fischer Scientific, Waltham, USA). Supernatants were filtered through pleated paper filters (Whatman No. 595) inside flasks, previously placed in the freezer to cool, and then covered with aluminium foil. Oil was collected after vacuum hexane evaporation. The so extracted oil was diluted with the mobile phase and injected. Cold-pressed oil samples were directly diluted into the mobile phase, filtered with paper filters (Whatman No. 595), and then injected.

2.2.7.2 HPLC analysis:

Analyses were carried out according to Calvo et al. (2011) procedure with an HPLC system composed of a Perkin Elmer (Norwalk, CT, USA) 200 Series pump equipped with a Perkin-Elmer 650-10S fluorescence detector, Jasco LC-Net II/ADC (Oklahoma City, OK, USA) communication module and ChromNAV Control Center as a software. As an injection column LiChrosorb Si60-5 column 250 mm×4.6 mm, 5 µm (Supelco, Bellefonte, PA, USA) was used, the volume injected was 20 µL, and the mobile phase was hexane:isopropanol:ethanol (98.5:1:0.5) with a flow of 0.6 mL/min. The fluorescence detector was set at 290 nm excitation and 330 nm emission wavelengths. Each run had a duration of 25 min. The homologue α; γ; β; and δ were identified and quantified in comparison with commercial standards (Sigma Aldrich, Milan, Italy). The results were expressed as mg/100g of oil and mg on 100g of product.

2.2.8 Colour Analysis

Colour analyses were performed on milled solid products (BASE and DFC) and on the oil samples (Konica Minolta CR-310). The results were expressed according to CIEL*a*b* colour space. The colour was measured through the three-dimensional colour diagram (L*, a* and b*), where: L* indicates lightness (L* = 0 (black), L* = 100 (white), a* indicates (−a* = greenness, +a* = redness) and b* chromaticity indicates (−b* = blueness, +b* = yellowness).

The mathematical description of colour difference was established to quantify the visible difference between the colours of two samples. Values of L* a* and b* were used to calculate the colour difference (ΔE) with the following equation:

$$\Delta E^* = \sqrt{(\delta L^*)^2 + (\delta a^*)^2 + (\delta b^*)^2}$$

ΔE can be evaluated in the following way:

− 0 < ΔE<1 – the difference is imperceptible,

− 1 < ΔE<2 – the difference is perceptible only for experienced evaluators,

− 2 < ΔE < 3.5 – the difference is noticeable also for inexperienced evaluators,

− 3.5 < ΔE<5 – observable colour difference,

− 5 < ΔE − observers notice two different colours (Mokrzycki and Tatol 2011)

2.2.9 Statistical Analysis

Cold-press extractions were threefold performed, and each sample was analysed in triplicate. The mean and standard deviations (SD) of the experimental data were calculated. The results obtained for each sample were evaluated and ranked using a one-way analysis of variance (ANOVA) followed by Tukey's post-hoc test for means discrimination ($p \leq 0.05$). Statistical analyses were executed via the IBM SPSS Statistics 27 software (SPSS Inc., Chicago, IL, USA).

3. Results and discussion

Pariani's extraction parameters have been optimized for obtaining the maximum organoleptic evaluation in both DFCs and oils, so different BASEs are submitted to different pressures and times to maintain a good organoleptic evaluation, not only in the oil but also in the DFC making it an interesting ingredient for the food's industry.

3.1 Moisture and water activity (a_w)

Moisture and a_w were measured to assess the microbiological safety of raw materials and to analyse the variations that may occur during the extraction process (Table 10).

Table 10: Moisture and a_w values for nut kernels (BASE) and corresponding defatted cake (DFC) samples. Values reported within the same column with different lowercase letters are significantly different ($p \leq 0.05$)

Samples	BASE		DFC	
	Moisture (g/100g)	**a_w**	**Moisture** (g/100g)	**a_w**
Piedmont P.G.I. hazelnut	0.91±0.00^a	0.40±0.02^a	2.17±0.15^a	0.30±0.01^a
Turkish hazelnut	2.47±0.04^c	0.50±0.01^b	5.36±0.05^d	0.47±0.00^b
Apricot kernel	3.93±0.07^e	0.55±0.00^c	7.80±0.11^e	0.55±0.00^c
Sicilian pistachio	2.18±0.03^b	0.42±0.01^a	4.86±0.10^c	0.50±0.00^c
Bronte P.O.D. pistachio	3.64±0.01^d	0.49±0.00^b	4.59±0.00^b	0.49±0.00^b

As shown in Table 10, roasted nuts had a lower and significantly different moisture value than apricot kernels, which were only dried. The roasting and drying processes generated a decrease in a_w bringing all values to be less than 0.55. The water activity had a trend that followed the humidity: the lowest value was related to Piedmont P.G.I. and the highest value was for apricot kernel. With the previous consideration, this was a consequence of the different heat treatments applied to the raw materials. From a microbiological point of view, these values represent a safety limit for the growth of bacteria, moulds and yeasts that are unable to duplicate in that condition (Grant, 2004).

After the extraction, there was a general increase in moisture, due to the removal of the oil and the consequent percentage redistribution of the other constituents. All increments were related to the extraction yield (Table 13). The DFC apricot kernels showed the highest value, while Piedmont P.G.I. DFC resulted as the least humid. Before and after extraction, both the hazelnut samples showed a reduction in water activity (Piedmont P.G.I. switched from 0.4 to 0.3), both the pistachio types showed an increase, while the apricot kernel remained unchanged. In general, they all remained below the critical safety threshold of 0.55 (Grant, 2004).

3.2 Nutritional evaluation

To better evaluate the nutritional modifications that occurred during the extraction process, a comparison between the five BASEs and the respective DFCs was necessary. Values, reported in Table 11 are related to BASEs characterization.

Table 11. Proximate composition of the BASE samples. Results are reported as g/100g of product. Values reported within the same column with different lowercase letters are significantly different ($p \leq 0.05$).

Samples	Ashes	Fats	Protein	Insoluble fibre	Soluble fibre
Piedmont P.G.I. hazelnut	2.01±0.04^{a}	76.17±0.82^{c}	13.43±0.40^{a}	10.93±0.32^{b}	2.56±0.02^{a}
Turkish hazelnut	2.21±0.05^{b}	67.50±0.23^{b}	17.88±0.77^{b}	11.81±0.78^{bc}	2.48±0.24^{a}
Apricot kernel	2.04±0.04^{a}	59.48±0.38^{a}	24.96±0.13^{c}	12.46±0.04^{c}	3.54±0.22^{b}
Sicilian pistachio	2.99±0.00^{d}	61.19±1.66^{a}	25.84±0.20^{c}	9.02±0.48^{a}	5.48±0.13^{c}
Bronte P.O.D. pistachio	2.89±0.00^{c}	57.69±2.94^{a}	25.95±0.59^{c}	9.83±0.32^{a}	3.19±0.11^{b}

The sample of Piedmont P.G.I. hazelnuts had a slightly higher fat content than that one reported by CREA (2019) (64.1 on 100g of product). The apricot kernel also showed a higher fat content than those described by Femenia et al. (1995) (43.4-53.3%). As for Sicilian and Bronte pistachios the values were quite in line with those described by Celenk et al. (2020) (45-59% on 100g), while the sum of insoluble and soluble fibre values was higher than the total dietary fibre content found by Mandalari et al. (10.6%) (2021). By correlating data related to the DFC composition (Table 12) with oil extraction yields (Table 13), it can be confirmed that a lower extraction pressure applied on the

BASE during processing induced a lower decrease in the oil content and, therefore, a lower yield. This was the case, specifically of both pistachio samples. Instead, the other three samples underwent a large reduction in fat content leading to a redistribution of the other components within the DFCs.

Table 12. Proximate composition of the DFC samples. Results are reported as g/100g of product. Values reported within the same column with different lowercase letters are significantly different ($p \leq 0.05$).

Samples	Ashes	Fats	Protein	Insoluble fibre	Soluble fibre
Piedmont P.G.I. hazelnut DFC	4.82 ± 0.10^{c}	31.77 ± 0.48^{b}	37.30 ± 1.39^{c}	17.22 ± 0.75^{c}	7.26 ± 0.22^{c}
Turkish hazelnut DFC	3.92 ± 0.06^{b}	31.06 ± 0.63^{b}	34.66 ± 0.07^{b}	20.23 ± 0.36^{d}	5.53 ± 0.28^{b}
Apricot kernel DFC	3.74 ± 0.02^{ab}	23.24 ± 0.91^{a}	43.91 ± 0.46^{d}	16.76 ± 0.48^{c}	4.87 ± 0.06^{d}
Sicilian pistachio DFC	3.43 ± 0.18^{a}	43.21 ± 0.46^{c}	32.55 ± 0.48^{a}	13.52 ± 0.60^{b}	4.43 ± 0.25^{a}
Bronte P.O.D. pistachio DFC	3.46 ± 0.14^{a}	45.71 ± 0.07^{d}	32.04 ± 0.01^{a}	10.79 ± 0.44^{a}	5.00 ± 0.23^{a}

Table 13. Oil extraction yield obtained from the different nut kernels (BASEs).

Samples	Extraction yield (%)
Piedmont P.G.I. hazelnut	85.6
Turkish hazelnut	78.1
Apricot kernel	79.3
Sicilian pistachio	50.2
Bronte P.O.D. pistachio	38.4

Li et al. (2015) identified 150 °C for 20 min as an optimal time-temperature combination to apply to peanuts before extracting. The authors noted an increase in free oil in peanuts which reached its maximum value under the previously mentioned conditions. The roasting treatment involves a reduction of the emulsification layer optimizing the yield. However, exceeding the temperature can lead to the formation of insoluble protein aggregates which trap the oil and reduce the yield. The same was observed by Ahmed et al. (2019) on hazelnuts: increasing the roasting time also improved the yield but at the same time gave a strong increase in K232 and K270 for treatments over 20 min. Therefore, optimizing the roasting step can be considered as quality-leading for the entire oil extraction process. This was the only heat treatment to which nut kernels were subjected before being pressed and during which the major transformations of the raw product took place.

Apricot kernel DFC showed the highest protein concentration after oil removal (Table 12). However, the most evident change was in Piedmont P.G.I. DFC whose protein content switched from the lowest value among samples before extraction, 13.43±0.40% w/w to 37.30±1.39% w/w in the DFC, thanks to the higher extraction yield. Pistachios offer the opposite example: while overall they were the most protein-rich BASEs, after extraction with the lowest pressure they turned out to have the lowest

concentration. These considerations also apply to the other components (i.e., fibre) and can be useful for evaluating the use of DFCs in the formulation of new products to improve their nutritional properties.

3.3 Total phenolic content

It was possible to observe that pistachios were the samples containing the highest amount of total phenolics (Table 14) and those in which the highest quantity was found in the oil. Among hazelnut samples, the phenolic content of Turkish hazelnuts stands out, because the skin was still present in the sample. In both hazelnut types, there was minimal transfer of phenolics from the base to the oil, which, for the Piedmont PGI hazelnut sample, was since the quantity was already reduced at the outset.

Table 14. Total phenolic content (mg GAE/100g of product) in BASE, oil, and DFC samples. For the same nut sample, values reported within the same column with different lowercase letters are significantly different ($p \leq 0.05$).

Samples		**Total phenolic compounds** (mgGAE/100g of product)
Piedmont P.G.I. hazelnut	Base	11.11 ± 0.52^{b}
	Oil	7.00 ± 0.20^{a}
	DFC	14.61 ± 0.41^{c}
Turkish Hazelnut	Base	64.41 ± 1.45^{b}
	Oil	9.59 ± 0.73^{a}
	DFC	141.70 ± 4.45^{c}
Apricot kernel	Base	58.62 ± 1.59^{b}
	Oil	15.32 ± 0.01^{a}
	DFC	98.77 ± 0.58^{c}
Sicilian Pistachio	Base	167.56 ± 3.39^{b}
	Oil	35.13 ± 0.08^{a}
	DFC	199.89 ± 10.13^{c}
Bronte pistachio	Base	$150.07 \pm 0,73^{b}$
	Oil	34.02 ± 0.07^{a}
	DFC	173.64 ± 8.77^{c}

It can be observed that in DFCs the total phenolic content increased due to oil extraction, as detected by Ojeda-Amador et al. (2019) and Melo et al. (2021) who also noted that a minority of phenolic compounds were transferred to the oil during extraction. The information on nutritional values per 100 g of product relating to DFCs highlighted a lower tocopherol content (see Table 15), but an increase in total phenolic content (Table 14) with a consequent positive effect on the residual antioxidant activity.

3.4 Tocopherol quali-quantification

Alpha-tocopherol was the major homologue in Piedmont's P.G.I. and Turkish hazelnuts, while γ-tocopherol was predominant in apricot kernel, and in Sicilian and Bronte's pistachios (Table 15), as reported by previously cited studies (Turan et al. 2007; Evoli et al. 2015).

Table 15. Tocopherols content (mg/100g of oil, and mg/100g of product as is) in BASE, oil, and DFC samples: α, β, γ, δ homologues and total phenolic content of BASEs and DFCs. For the same nut sample, values reported within the same column with different lowercase letters are significantly different ($p \leq 0.05$).

		Homologue							
		Alfa		**Gamma**		**Beta**		**Delta**	
		mg/100g of oil	mg/100g of product	mg/100g of oil	mg/100g of product	mg/100g of oil	mg/100g of product	mg/100g of oil	mg/100g of product
Piedmont P.G.I. hazelnut	Base	21.75±2.64^{a}	16.13±1.61^{b}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Oil	31.75±0.27^{b}	31.75±0.27^{c}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	DFC	32.74±1.03^{b}	10.40±0.23^{a}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Turkish Hazelnut	Base	21.00±0.05^{a}	13.80±0.67^{b}	5.30±0.01^{c}	3.48±0.17^{c}	n.d.	n.d.	n.d.	n.d.
	Oil	19.95±0.97^{a}	19.95±0.97^{c}	3.03±0.07^{a}	3.03±0.07^{b}	n.d.	n.d.	n.d.	n.d.
	DFC	25.34±3.07^{b}	7.87±0.68^{a}	5.19±0.09^{b}	1.61±0.02^{a}	n.d.	n.d.	n.d.	n.d.
Apricot kernel	Base	0.35±0.02^{b}	0.21±0.01	29.38±2.16^{b}	17.57±1.15^{b}	n.d.	n.d.	3.05±0.18^{c}	1.81±0.08c
	Oil	0.27±0.00^{a}	0.27±0.00	19.80±1.05^{a}	19.80±1.05^{c}	n.d.	n.d.	1.45±0.03^{a}	1.45±0.03^{b}
	DFC	0.42±0.02^{c}	0.10±0.00	30.94±2.18^{b}	7.00±0.24^{a}	n.d.	n.d.	2.81±0.01^{b}	0.65±0.00^{a}
Sicilian Pistachio	Base	1.00±0.01^{b}	0.61±0.01	25.51±0.82^{c}	15.61±0.36^{b}	6.66±0.07^{b}	4.08±0.03^{b}	1.54±0.02^{b}	0.94±0.01^{b}
	Oil	1.20±0.02^{c}	1.20±0.02^{c}	22.80±0.02^{b}	22.80±0.02^{c}	n.d.	n.d.	1.86±0.04^{c}	1.86±0.04^{c}
	DFC	0.88±0.04^{a}	0.38±0.01	19.85±0.20^{a}	8.58±0.06^{a}	4.35±0.27^{a}	1.88±0.08^{a}	1.42±0.06^{a}	0.61±0.02^{a}
Bronte P.O.D. pistachio	Base	1.07±0.08^{b}	0.62±0.03	28.38±0.36^{b}	16.38±0.15^{b}	4.35±0.15^{a}	2.51±0.06^{b}	1.46±0.01^{a}	0.84±0.00^{a}
	Oil	0.86±0.00^{a}	0.86±0.00	25.66±0.51^{a}	25.66±0.51^{c}	5.39±0.04^{b}	5.39±0.04^{c}	1.49±0.03^{a}	1.49±0.03^{b}
	DFC	1.24±0.10^{c}	0.56±0.05	29.56±1.85^{c}	13.51±0.84^{a}	4.45±0.03^{c}	2.04±0.02^{a}	1.77±0.01^{b}	0.81±0.01^{a}

In the lipid fraction of DFCs and oils (

Table **15**), the most present homologues were the same which also appeared to be predominant within the BASEs. The results showed an increase in the concentration of some tocopherols from BASE to DFC samples: in terms of α-tocopherol, for example, Piedmont's and Turkish hazelnut DFCs reached values of 32.74±1.03 and 25.34±3.07 mg/100g oil, respectively. Gamma-tocopherol had a similar trend: apricot kernel and Bronte Pistachio DFCs contained 30.94±2.18 and 29.56±1.85 mg/100g oil, both higher values concerning their BASE samples

.

Table 16. Alfa-tocopherol-equivalents (α-TE on 100g of oil, and on 100g of product) referred to the different samples.

Samples	α-TE				
	on 100g of oil	on 100g of product	on 100g of oil	on 100g of oil	on 100g of product
	BASE		**oil**	**DFC**	
Piedmont P.G.I. hazelnut	21.75	16.57	31.75	32.74	10.40
Turkish hazelnut	21.53	14.53	20.25	25.86	8.03
Apricot kernel	3.38	2.01	2.30	3.60	0.84
Sicilian pistachio	6.93	4.24	3.54	5.08	2.2
Bronte P.O.D. pistachio	6.13	3.54	6.16	11.82	5.40

There are few studies correlating tocopherols in oils and their respective cakes. Ojeda-Amador et al. (2018b) studied the changes that occurred in the cold oil extraction from pistachios and found no particular variations in the concentration of tocopherols expressed as tocopherol in 100 g of oil. The 400-bar pressure applied for extraction falls into the medium-high pressure category (between 100 and 1000 bar). In this condition the plant tissues are destroyed, the cell wall is disrupted and so is the membrane, facilitating the release of oil (Mwaurah et al. 2020). The changes in tocopherol concentration and the apparent increase in the sum of DFC and oil contents, relative to BASE, could be explained as increased extractability due to pressure treatment. Similar results in tocopherol concentration have been reported by Ojeda-Amador et al. (2018a) describing an increase in the concentration of the α-homologue, in partially defatted flour. A very interesting perspective is offered by Melo et al. (2021), who observed an unexpected distribution of tocopherols, particularly the α- and γ- homologs, among oil, DFC, and BASE. They found lower values of α-tocopherol in the oil compared to the residue cakes and an increase in the quantity of γ-tocopherol present in the cold-pressed oil compared to the original BASE. Seeking an explanation, they noted that Bermúdez et al. (2018) highlighted a different distribution of tocopherols based on certain tocopherol-binding proteins found in tomato cells' chloroplasts. Moreover, the different distribution and quantification may be due to the extraction solvent, which uses hexane for HPLC analysis while the oils are extracted with a hydraulic press, potentially resulting in a different distribution of homologs. Further studies are needed to better evaluate the possible variations that occur by solvent extracting the oil fraction from the BASE and DFC samples for tocopherol HPLC analysis (Rodríguez et al. 2023). However, tocopherols (in particular the α-homolog) are generally thermostable (Amaral et al. 2006): as a matter of fact, the concentration of α-tocopherol remained high even in the Piedmont hazelnut sample subjected to long roasting treatment at high temperatures. It should be considered that the roasting process is fundamental in creating the aromas of the final product. With a screw press it is possible to extract the oil and at the same time heat the sample creating a toasted flavour; conversely, with a hydraulic press, there is no heat involved in the extraction process so the final product will taste just

like raw. Roasting nuts before extraction represents an effective method to increase the flavour of derived products (oil and DFC) (Rabadán et al. 2017). If the final aim is to enhance the quality of the final products not only for the aroma but also for the nutritional point of view, nuts containing the most α-tocopherols are preferable. This fact is associated with the role of tocopherols as antioxidant agents, being their antioxidant capacity in vivo α > β > γ > δ (Rodríguez et al. 2023).

Table 16. Alfa-tocopherol-equivalents (α-TE on 100g of oil, and on 100g of product) referred to the different samples.

Samples	α-TE				
	on 100g of oil	on 100g of product	on 100g of oil	on 100g of oil	on 100g of product
	BASE		oil	DFC	
Piedmont P.G.I. hazelnut	21.75	16.57	31.75	32.74	10.40
Turkish hazelnut	21.53	14.53	20.25	25.86	8.03
Apricot kernel	3.38	2.01	2.30	3.60	0.84
Sicilian pistachio	6.93	4.24	3.54	5.08	2.2
Bronte P.O.D. pistachio	6.13	3.54	6.16	11.82	5.40

Each sample was also stated and evaluated as α-tocopherol-equivalent (Table 15) according to EFSA definition (EFSA, 2015b). This conversion allows for a better assessment of the total antioxidant capacity and is not just the sum of the total value of the homologues. The samples rich in α - tocopherol had an advantage, compared to the poor ones, this was evident by comparing the two hazelnuts with the other nuts. As noted for individual homologues, a higher concentration of α-TE can be found in DFCs than in BASEs and oils as a general trend. The data, such as α-TE, showed a general increase in concentration in the DFCs that can be almost double that originally present, as in the case of Bronte where BASE had a α-TE value of 6.13 while the DFC had 11.82; the only exception was for the Sicilian pistachio where there was a slight reduction in the DFC and a more significant one in the oil. The extracted oil generally showed a lower α-TE value than the related BASE and DFC, except for Bronte which had a similar value and the Piedmont hazelnut which showed a higher value than the BASE.

3.5 Colour

The colour differences between BASE and correspondent DFC samples were evaluated by calculating the ΔE value. As they all were greater than 3 (Table 17), it can be stated that the differences in the colours between each BASE and the respective DFC sample were perceptible to the human eye (Mokrzycki and Tatol 2011). It is possible to make a point on the brightness value (L*): the tendency of L* was to increase on the transition from BASE to DFC with a negative correlation between DFC values and the fat content. Furthermore, the final value of L* was the main factor influencing the ΔE

values. A comparison between the oils obtained by pressing the same types of nuts was performed showing a perceptible difference between the two pistachios and the two hazelnuts with a ΔE value bigger than 7. The colour of the DFC was affected by the removal of the oil, resulting in a whitening effect. It is important to also consider the visual changes in the final product. The use of DFCs as ingredients will have a visual impact important for the consumer's perception. If DFCs are intended for direct consumption, colour, especially for pistachios, is a determining factor. Instead, if they are intended as an ingredient, consumers expect the product to display the typical green colour that characterizes them.

Figure 11. Cold-pressed oil samples

Table 17. CIELAB values for oils, and colour differences (ΔE) between DFC and BASE of the related tree nuts. Values reported within the same column with different lowercase letters are significantly different ($p \leq 0.05$).

	Oil			**DFC vs. BASE**
	L	**a**	**b**	**ΔE**
Piedmont P.G.I. hazelnut	98.41±0.14^{d}	-2.68±0.14^{a}	36.39±0.09^{b}	31.48±0.53
Turkish hazelnut	96.57±0.05^{c}	-1.48±0.05^{b}	45.02±0.10^{c}	11.92±0.30
Apricot kernel	98.31±0.28^{d}	-1.48±0.00^{b}	30.64±0.05^{a}	9.92±0.07
Sicilian pistachio	53.67±0.04^{b}	3.03±0.06^{c}	85.38±0.01^{e}	8.83±0.15
Bronte P.O.D. pistachio	47.94±0.06^{a}	2.87±0.04^{c}	80.90±0.01^{d}	6.47±0.03

4.Conclusions

Cold oil extraction carried out using hydraulic presses has been able to preserve the nutritional value of nuts, giving rise to precious derived products: oils rich in tocopherols and defatted cakes (DFCs) with interesting nutritional properties. The DFCs maintained a valuable amount of fat and an increased concentration of protein and fibre, proportional to the extraction yield. The DFCs of Piedmont and Turkey hazelnuts showed the highest values of α-tocopherol equivalents (α-TE) denoting the best biological activity as an antioxidant. The apparent increase in the total amount of tocopherols per 100g of oil (from BASE to cold-extracted oil and DFC) is due to a combination of causes. In DFC there is better extractability because of the hydraulic press treatment. The hexane used to extract the oil from DFCs and BASEs has a different affinity for tocopherols than cold-extracted oil without the use of solvents. There is a different affinity of the tocopherols for the components of the raw material, in particular proteins, and this leads to a behaviour that varies between nut types. Therefore, considering DFC on/100g of product as is, appears depleted in lipophilic antioxidants (tocopherols) but at the same time sees an increase in the polar antioxidant component (hydrophilic phenols) due to the concentration effect resulting from oil removal. The results pave the way for further analysis of the technological application for DFCs in the food industry. In particular, by separating the phases as a part of a fractionation and recombination process it will be possible to ensure greater control over the process and the derived products. DFCs will undergo an evaluation of their functional properties to formulate new products.

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Chapter 4

"Exploring citrus fiber as an emulsifying agent: synergy with low methoxyl pectin and amidated pectin for advanced food formulations"

ABSTRACT

Citrus fiber consists of the residue remaining after primary citrus processing and pectin extraction. While the emulsifying properties of this byproduct and the gelling abilities of pectins are well known, research has primarily focused on their interactions within emulsions. However, the technological properties of a gelled emulsion system had never been investigated. This study focused on the synergistic interaction of citrus fiber, mango puree, sunflower oil, and four distinct low-methoxyl pectins within an emulsion-filled hydrogel. Low-methoxyl pectins were chosen for their gelling ability at low sugar concentrations, allowing the formulation of products aligned with specific dietary needs. Mango was selected as an illustrative fruit-based dispersing phase to assess the applicability of citrus fiber in a realistic food system. First, the research engaged in homogenization conditions and resilience to heat treatment at 90°C. Various combinations of fiber and oil were tested to minimize both droplet size and phase separation, identifying 5% (w/w) citrus fiber and 20% (w/w) oil as the most stable formulation. The emulsifying ability of citrus fiber was found to be linked to the water-to-fiber ratio, which had to be lower than the water binding capacity. Then, the emulsion-filled hydrogel was created from the previously optimized emulsion using four different pectins (1% w/w). Among them, only the amidated low-methoxyl pectin with a higher degree of methoxylation was capable of forming a self-standing gel. The findings indicate that the texture of a hydrogel comprising insoluble citrus fiber and pectins is primarily influenced by the citrus fiber rather than the pectin. However, when citrus fiber acts as a heat-resistant emulsifier, the addition of pectin imparts unique characteristics, allowing the modulation of the final product's consistency.

1.INTRODUCTION

The agro-industrial sector greatly relies on the citrus processing industry, which holds significant importance. Citruses are the most extensively cultivated fruit globally (Satari et al., 2016). While domestic waste typically cannot be reused, the one that originates from the juice industry is utilized to produce fiber and food ingredients, such as pectin, mucilage, and flavonoids (Boukroufa et al., 2015). After juice extraction and essential oil distillation, the industrial by-products offer cost-effective resources of sustainable ingredients. Finding a use for this leftover will drastically reduce both the volumes and disposal costs, enabling the production of valuable nutritional goods (Naviglio et al., 2022; Pasandide et al., 2017). From the fibrous residue, it's possible to extract pectins, a soluble dietary fiber, and the so-called citrus fiber, which represents all the water-insoluble components.

Pectins serve as a versatile gelling and stabilizing agent. Moreover, they positively affect human health and find multiple biomedical applications. Commercial pectins are divided into low methoxy (LM) pectin and high methoxy (HM) pectin, based on the level of esterification. LM pectins have less than 50% methyl ester groups, while HM pectins have over 50% methyl ester groups (Caroço et al., 2019). The LMs are further subdivided into two groups: amidated LM (LMA) and conventional LM. LMs exhibit superior hydrophilicity and higher acid stability, compared to HMs. Also, LMs can form thermally reversible gels at lower temperatures. Among LMs, the LMAs demonstrate the highest gelling capacity (Feng et al., 2023). After extraction and precipitation, treating pectins with diluted acid and ammonium hydroxide yields LMA (Adetunji et al., 2017; Lootens et al., 2003). After drying and milling, all pectins are usually standardized with sugar and sometimes with calcium salts or organic acids to perform optimum in a particular application (Sriamornsak, 2011). The gelation of LMs depends on Ca^{2+} concentration and pH of the solution, originating the so-called 'egg-box' 3D configuration. The egg box, alone, cannot describe the LMA gel structure; it needs to be integrated considering the hydrogen bonding promoted by the amide groups along the chain (Racape et al., 1989; Wan et al., 2019). Hydrogen linkages are the primary interaction for the LMA gel mechanism and enable their thermo-reversibility (Feng et al., 2023). Pectins are universally known for preparing hydrogels (Kwan & Davidov-Pardo, 2018; Mekala et al., 2022) but in this type of structure with pectin only, it is impossible to incorporate lipophilic elements. By employing an emulsifying agent, an emulsion can be successfully incorporated into their network, resulting in an emulsion-filled hydrogel (Feng et al., 2023). The insoluble components of citrus peel (citrus fiber) showed the capacity to stabilize an emulsion not only through a Pickering effect, but also by creating a network that reduces the creaming effect with high resistance to thermal treatment and pH (Zhai et al., 2018). As a by-product of pectin extraction, citrus fiber is ideal for developing an environmentally

sustainable system with innovative properties (Liu et al., 2012). Citrus fiber-based emulsions have shown superior creaminess and smoothness compared to egg-based mayonnaise. Additionally, these emulsions retain flavors like whipping cream, making them suitable for low-fat product formulations, while providing enjoyable palatability (Ruan et al., 2019; Shin et al., 2021). Citrus fiber plays a role in reducing the diffusivity of glucose during digestion (Miehle et al., 2022) with positive effects on our digestive system (Mudgil & Barak, 2013). This study investigates the two main components of citrus peel, after being separated and purified: pectin and insoluble citrus fiber (CF). The focus is on the interactions between standard LMs and LMAs with CF. The use of different types of LMs enables the achievement of diverse consistencies, resulting in the creation of a wide range of semi-finished products with extensive applications in the food industry. Further objective of the study is to develop a process using mango puree, without any added sugar, that could be processed by industrial-style mixers. The project aims to scale up and demonstrate the benefits of using citrus fiber (CF) not only in laboratory simulations but also in the industrial formulation of products. These products will be suitable for both general consumers and those with specific dietary needs.

2.Materials and methods

2.1 Raw Materials.

The hydrogel was prepared using four different types of low-methoxyl pectins (Table 18), with less than 5% w/w of insoluble fiber on 100g. Namely, two types of LM (LM-12 and LM-18) and two LMA variants (LMA-10 and LMA-20). The emulsifying agent (CF) is a mixture of citrus insoluble dietary fiber, a co-product of the pectin extraction industry. Citrus fiber (CF) and pectins were kindly gifted by JRS Silvateam Ingredients S.r.l. Bergamo (BG) Italy. The sunflower oil used for emulsion making was bought at the local market. Mango puree (kindly provided by DEcorgel Productos Alimentares S.A. Braga (PT)) was used as a dispersing phase to simulate a food application of the emulsion-filled hydrogel. Mango puree had 15,5±1,0 °brix, a specific gravity of 1,064±0,001, and a pH of 3.72±0,01.

Table 18. Pectin main composition provided by the producer.

	POLYGALACTURONIC ACID MIN	DEGREE OF METHOXYLATION	DEGREE OF AMIDATION
LM-12	65%	31±3%	n.d.
LM-18	65%	39±3%	n.d.
LMA-10	65%	30±3%	21±3%
LMA-20	65%	23±3%	24±3%

2.2 The production process:

To develop a process suitable for industrial scale-up, a strategy of progressively optimizing various parameters was adopted. A constant mixing speed of 1200 rpm was utilized FOR all trial preparation (HEi-Tec mechanical mixer, Heidolph Instruments GmbH & Co. KG, Schwabach, Germany). As an initial step, the optimal mixing time was identified to test various ingredient combinations and achieve the most suitable emulsion for subsequent steps. With the ideal emulsion combination established, four different pectins were tested as texture modifiers for the emulsion-filled hydrogels.

2.2.1 Mixing time optimization.

Emulsions were prepared at room temperature using the same amount of oil but with varying mixing times (2.5-5-7.5-10-15-20 minutes). The results were compared with the counterparts subjected to thermal treatment consisting of heating the just prepared emulsions inside a water bath at 90 °C for 15 minutes. The oil droplet sizes of treated and untreated samples were compared (optical microscopy) in order to determine the emulsion's stability. The emulsion was considered stable if there were no statistically significant differences in oil droplet size between treated and untreated samples (Huang et al., 2001).

2.2.2 Mango puree emulsifying capacity.

To determine the emulsifying capability of mango puree independently from citrus fiber (CF), it was tested alone with varying oil concentrations (5%, 7.5%, 10%, and 15% w/w) using a fixed mixing time. The samples were then compared with their thermally treated counterparts. The thermal treatment involved heating to 90°C over 14 minutes of mixing and maintaining this temperature for an additional minute. Oil was considered stably emulsified if there were no statistically significant differences in oil droplet size between treated and untreated samples (Huang et al., 2001).

2.2.3 CF emulsion optimization.

Emulsions containing different concentrations of sunflower oil (20-25-30% w/w) and CF (3-4-5% w/w) were prepared to identify the most stable combination. They were analyzed for oil droplet sizes using optical microscopy and examined for phase separation after centrifugation. The emulsions were compared by phase separation quantification. Trials were also conducted to evaluate the emulsion stability under heat treatment, consisting of reaching 90°C over 14 minutes and maintaining the temperature for an additional minute.

2.2.4 Emulsion-filled hydrogel formulation.

Before the preparation of the emulsion-filled hydrogel (

Figure 12), two distinct solutions were prepared:

- Solution **(1)**: Mango puree mixed with pectin in an 18.2:1 ratio. This mixture was heated to 80°C while continuously stirring to prevent pre-gelation.
- Solution **(2)**: Mango puree with a 1.67% w/w of $CaCl_2$.

For the preparation of 100g of emulsion-filled hydrogel, the following procedure was selected.

An initial mixture was prepared by combining 45g of mango puree and 20g of sunflower oil, pre-mixed for 1 minute without heating. Then, 5g of CF were added. After 10 minutes of mixing, 19.2g of preheated solution **(1)** were gradually added to the emulsion. This addition took place at around 65°C to promote pectin solubilization. At the 12th minute of continuous mixing, when the temperature reached 80°C, 10.8g of pre-heated solution **(2)** was incorporated to allow gel formation. Maintaining the temperature at 90°C is crucial to prevent undesired pre-gelation. Once the mixture reaches 90°C, it is maintained at this temperature for 1 minute to ensure thermal treatment and achieve effective pasteurization. The mixture is then left to cool overnight at room temperature.

All the samples have the same composition by weight: 74% mango puree, 20% sunflower oil, 5% CF, 1% pectin, and 0.18% $CaCl_2$ as suggested by Lupi et al. (2015) for optimal pectin gelation.

To assess the influence of individual ingredients on the final products, two blank samples were prepared for texture analysis using the same procedures employed for the emulsion-filled hydrogel:

- "P" (pectin and mango puree), involved heating 70g of mango puree to 65°C. Subsequently, a mixture of 19.2g of solution **(1)** was added, followed by 10.8g of **(2)** with the same timing as previously.
- "NO" was created by incorporating 5% w/w of CF into the "P" sample. Initially, a mixture of 65g of mango puree and 5g of CF was heated to 65°C. Then, 19.2g of solution A was added, and after two minutes at around 80°C, 10.8g of solution **(2)** was introduced.

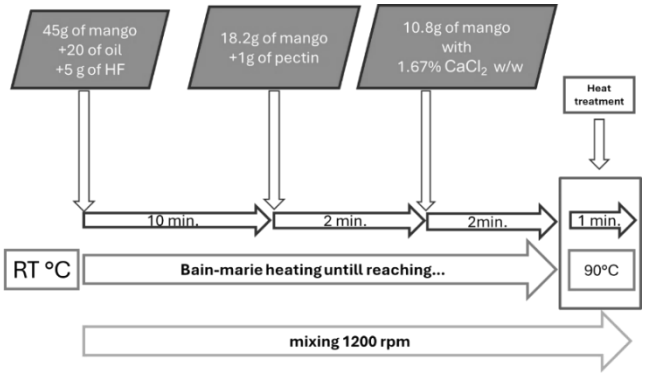

Figure 12. The emulsion-filled hydrogel production process for 100g of product.

2.3 Characterization analysis

Moisture, ash, and protein content of pectins and CF were determined by official AOAC methods 935.29, 942.05, and 2001.11 respectively. Soluble and insoluble dietary fiber were quantified with K-TDFR-200A Kit (Megazyme, Wicklow, Ireland) according to the AOAC method 991.43.

2.4 Water binding capacity (WBC), oil binding capacity (OBC), and swelling.

Swelling power, water binding capacity (WBC), and oil binding capacity (OBC) were determined in sixfold replicates according to the method described by Wang et al. (2014) with appropriate modifications. Approximately 0.5 g of CF was weighed into a 50 ml Teflon tube and 25g of water or sunflower oil was added. The lid was tightly screwed, and the mixture was heated in a water bath at 92.5 °C for 30 min with regular shaking to measure the swelling (HOT samples). The analysis was also performed using the same technique but with the water bath set at room temperature (COLD). After shaking, the samples (HOT or COLD) were divided into two equal groups. In one sample, the supernatant was immediately separated (0h), while in the other, it was left in contact for 24 hours (24h) to assess any differences. Due to the varying exposure times, it was possible to assess any additional absorption in the hours following preparation. All the samples were centrifugated at 13,000 g in 10 minutes. After supernatant removal, the deposit was weighted, and swelling (0h; 24h), WBC (0h; 24h), and OBC (0h; 24h) were calculated with equation (1):

$$Swelling, WBC\ and\ OBC = \frac{M_2 - M_1}{M_0} \quad (1)$$

M_0 represents the weight of the sample (g), M_1 is the weight of the centrifuge tube (g), and M_2 is the combined weight of the centrifuge tube and the sample after separating the supernatant (g).

2.5. Particle size distribution

The particle size distributions were determined using a Mastersizer 3000 laser granulometer (Malvern Panalytical, Malvern, UK) with an effective measurement range of 2000–0.02 µm. The size distribution analysis was performed at 25°C. Dry CF was analyzed using the Aero S dispersion unit, and hydration properties were assessed with the Hydro MV attachment. The hydrated samples (0h, 24h, COLD, and HOT) were stirred with the Hydro MV at 1000 rpm, with measurements taken after 1 minute. For CF, the refractive index was set to 1.460 (Jiang et al., 2022). Deionized water was selected as the dispersant, with a refractive index of 1.330. The lower and upper obscuration limits

were set to 10–20% for the wet dispersion unit and 1–10% for the dry dispersion unit. An obscuration value of around 15% was used for wet dispersion and 5% for dry units. Every sample was assessed 10^{th} DV(10), 50^{th} DV(50) and 90^{th} DV(90) percentile, SPAN, D[4;3], and Specific surface area (m^2/Kg).

2.6 Differential Scanning Calorimetry (DSC).

The thermal properties of pectins were evaluated using differential scanning calorimetry (DSC) measurements (Setline-DSC, Setaram, France) according to the method of Ma et al. (2020). The solid materials were accurately weighed (5mg) and placed in aluminum pans. Temperature was then increased from 30°C to 350°C at a rate of 10°C/min, nitrogen was employed as conveying gas at a flow rate of 20 mL/min. Simultaneously, an empty sealed pan was used as a reference under the same conditions.

2.7 Phase separation quantification.

The resistance of emulsion to phase separation was assessed through centrifugation, following the Gestranius et al. (2017) method with some modifications. The emulsions were examined: (A) Mango-based emulsions after heat treatment, produced by hot mixing to simulate the creation of the emulsion-filled hydrogel (mixed for 14 minutes at increasing temperatures up to 90°C and maintained for 1 min.); (B) Mango-based emulsions before heat treatment, not subjected to heating during the 15 minutes of mixing; (W) Water-based emulsions were not subjected to heating during mixing. Approximately 2g of emulsion was placed into a 2ml Eppendorf tube and then centrifuged at 4000 g for 2 minutes. After centrifugation, the tubes containing the emulsions were overturned onto absorbent paper to facilitate oil release and then weighted. The oil loss was expressed as a percentage of the initial oil weight. The calculation was performed using the following equation (2):

$$\left(\frac{Gross_{before} - Gross_{after}}{sample\ weight * oil\ percentage\ w/w}\right) * 100 \quad (2)$$

2.8 Confocal analyses

The structure of the mango puree emulsion, the citrus fiber (CF), and the influence of pectins on the overall structure were analyzed using confocal microscopy (LSM 410, Carl Zeiss, USA). In order to

visualize the arrangement of the citrus fiber, Beta-carotene (Sigma-Aldrich, USA) was used to stain the oil, and Calcofluor white (Sigma-Aldrich, USA) for cellulose.

2.9 Optical microscopy

Bright-field images of the emulsions were captured using a Nikon Wide-Field Upright Ni-E Microscope (Nikon, Tokyo, Japan) equipped with a Nikon digital camera. The NIS-Elements Microscope Imaging Software, also from Nikon, was utilized for image acquisition. The emulsions were diluted at a ratio of 1:10 with distilled water to be analyzed. Subsequently carefully placed on a glass support and covered with a cover glass, with care, to avoid any influence on the emulsion structure. The cover glass was laid over the sample. Image analyses were conducted using the ImageJ software, enabling the assessment of the oil droplet's diameter distribution (Schneider et al., 2012). Then thanks to the acquired data, $D_{[4,3]}$ and SPAN were assessed with the formulas (3) and (4) (ISO 9276-2):

$$D_{[4,3]} = \frac{\sum n_i D_i^4}{\sum n_i D_i^3} \quad (3)$$

$$\text{Span} = \frac{DV_{90} - D_{V10}}{DV_{50}} \quad (4)$$

Where "n_i" is the class abundance and "D_i" is the mean value of the class. Results are graphically shown as a cumulative particle-size distribution curve.

2.10 Texture analysis

All the texture analyses were performed using a Shimadzu AGX-10kN Texture Analyzer (Shimadzu, Japan) equipped with a 500 N load cell. The creamy samples analysis involved the use of a specialized probe called "jig set" (Shimadzu, Japan). This set consists of precisely matched acrylic 90° cones and supports. During the test, the procedure required moving 24 mm from a fixed starting point positioned 25 mm above the bottom of the lower cone. The tests were conducted at room temperature. The key parameters include the maximum force value, which corresponds to the highest compression force experienced during the test, indicating the 'firmness' of the material at the specified depth, and the negative force value (adhesiveness), which represents the force exerted by the sample on the probe

as it retracts. To perform the test, the hydrogel or emulsion-filled hydrogel samples were poured into the acrylic cup and allowed to equilibrate at room temperature overnight.

Single compression textural experiments were performed with a cylindrical stainless-steel probe of 50 mm diameter. The evaluation of the results was done sixfold. LMA-10 hydrogels were hot poured into an acrylic plate mold forming cylindrical samples with 32 mm diameter and 14 mm height. The experimental setup included compression tests at 0.5 mm/s speed, with equivalent pulling speed during the tensile phase. The applied strain reached a maximum of 70%. This specific strain value was determined to cause fractural damage in both the emulsion-filled hydrogel and the hydrogel.

2.11 Statistical analysis

All experiments were performed at least three times and analyzed in triplicate. The results obtained for each sample were evaluated and ranked using a one-way analysis of variance (ANOVA) followed by Duncan's multiple range test to evaluate the statistical significance between replicates ($p < 0.05$). The Pearson correlation analysis was conducted to assess the relationship between variables. The correlation coefficient (r) was calculated to be higher than 0,95 ($p < 0.01$). Statistical analyses were executed via the IBM SPSS Statistics 27 software (SPSS Inc., Chicago, IL, USA).

Results and discussion

3.1 Sample characterization

A preliminary characterization was performed for pectins (

Table **19**) and CF. Moisture values were between 10.60% and 10.85% for pectins, while CF contains 6.53±0.02%. The other parameter considered to verify the purity of both types of fibers was the ash content. CF contains 0.85±0.00%, and therefore it was not added with salts, which is a common practice for pectin standardization and to modify the pH of the solutions to which they are added (Sriamornsak, 2011). LM-12 contains 6.38±0.12% of ashes, and the other three pectins have a content of 9.16±0.01% always on a dry basis. CF was further characterized for protein (5.76±0.23%) and total dietary fiber (soluble 8.39±0.51% and insoluble74.74±0.89%). The low soluble fiber content can be attributed to CF being the final byproduct after pectin extraction, rather than comprising the entire peel flour. The high insoluble fiber content is due to the conventional pectin extraction method with acid hydrolysis for solubilizing them (Adetunji et al., 2017). Knowing the extraction method and/or the composition percentage of soluble and insoluble fiber allows the attribute of the main properties of CF to the insoluble component of CF as also stated by He et al. (2023).

Table 19. Characterization analysis results. Data were represented as percentage w/w by means ± SD. Data with different lowercase letters in the same row were significantly different ($p < 0.05$).

CHARACTERIZATION ANALYSIS (% W/W)					
	LM-12	LM-18	LMA-10	LMA-20	CF
MOISTURE	10.6±0.05^{b}	11.57±0.13^{e}	11.19±0.08^{d}	10.85±0.02^{c}	6.53 ±0.02^{a}
DRY MATTER	89.40±0.05^{d}	88.43±0.13^{a}	88.81±0.08^{b}	89.15±0.02^{c}	93.47 ±0.02^{e}
ASHES	6.38±0.12^{b}	8.12±0.08^{c}	8.21±0.09^{c}	8.24±0.09^{c}	0.85±0.00 ^{a}

Pectins were additionally characterized by DSC analysis (Ma et al. 2020**Error! Reference source not found.**) to test their heat resistance and predict their behavior under thermal stress in a food product subjected to a cooking treatment (Table 20).

Table 20. Pectin DSC analysis results. Data were represented by means ± SD. Data with different lowercase letters in the same row were significantly different ($p < 0.05$).

DSC (DEGRADATION PEAKS) °C				
	LM-12	LM-18	LMA-10	LMA-20
START	211.95±0.08^{a}	214.55±0.55^{b}	218.82±0.46^{c}	219.24±0.25^{c}
END	287.63±2.97^{c}	256.38±0.35^{a}	280.42±0.84^{b}	280.83±1.37^{b}
MAXIMUM	238.33±0.25^{a}	238.83±0.05^{b}	241.63±0.24^{c}	242.14±0.12^{d}

The exothermic peak that occurs around 238-240°C is due to pectin chain degradation. LM samples show lower heat resistance with degradation peaks that start at lower temperatures (211.95-214.55°C) and have a maximum peak at about 238°C compared to LMA where the degradation peak starts at about 219°C and has a maximum at about 280°C. The difference is probably due to the presence of ammonium groups in LMA samples. The smaller exothermic peak, present in all samples, preceding the melting peak of the crystalline structure of pectin is caused by impurities (Ma et al., 2020); it begins between 200°C and 209°C and ends when the main exothermic peak starts. Mango puree was subjected to pH analysis and a value of 3.83±0.02 was found, a parameter adequate for the gelation of all four types of pectins without requiring the addition of other compounds to lower the pH (Lootens et al., 2003). After being subjected to centrifugation with the same centrifugation conditions used for the fiber samples, the amount of supernatant led out was equal to 42.92±0.42%.

3.2 WBC, OBC, swelling, and particle size analysis

Analyses were conducted to quantify the ability of CF to bind water and oil (Table 21). As can be seen from Table 21, CF shows a significant difference in retaining oil or water. Regarding the OBC, there are no effects due to heating or contact times, and the very low values between 3.30 and 3.41. Even He et al. (2023) were unable to chemically increase the OBC by separating the major

components of citrus fiber. They found in the fiber microstructure the main factor influencing oil retention, with a positive correlation with the cellulose presence and a negative one with the hemicellulose content. As highlighted by Jiang et al. (2022), high-pressure homogenization is the only way to physically increase the OBC of citrus fiber by incrementing the surface area thanks to the unfolding of the fibrous structure, exposing the more lipophilic group. WBC instead varies in a range between 19.06 and 21.05 as a relative increase to the initial weight. In addition, CF is affected by both heat and contact time, finding a significant effect. Mantaining the same contact time but with different temperatures, there are no significant variations. Differences appear when comparing h_0 cold with the two temperatures at h_{24}. Comparing h_0 cold and h_{24} cold, we have an increase of 8.83%, while if we compare them to h_{24} hot, it rises to 10.44%. Jiang et al. (2022) reached a similar result with a dry powder with a D_{50} comparable with CF meaning that if the two samples have been extracted with a similar process leading to a similar composition and having a similar particle size if no homogenization is applied the two fibers will have a similar WHC. h_0 samples at different temperatures show no significant increases in WBC, indicating that applying heat causes CF to adsorb more water more quickly.

Table 21. Particle size analysis, oil binding capacity (OBC), and water binding capacity (WBC) were measured for CF samples at various conditions. The data are presented as means ± SD. Values within the same column that are marked with different lowercase letters indicate a significant difference ($p < 0.05$).

	D[4;3] μm	DV (10) μm	DV (50) μm	DV (90) μm	SPAN	SPECIFIC SURFACE AREA m^2/kg	OBC	WBC
DRY CF	138.47±3.33^{a}	28.39±0.20^{a}	111.76±1.92^{b}	291.58±8.95^{a}	2.36±0.06^{a}	93.17±1.04^{c}	/	/
COLD h_0	162.79±3.88^{b}	31.01±0.61^{b}	111.06±1.86^{b}	379.74±11.29^{b}	3.14±0.04^{c}	90.62±1.63^{c}	3.41±0.30^{a}	19.06±0.58^{a}
HOT h_0	139.05±6.15^{a}	28.96±0.70^{a}	97.68±2.84^{a}	314.41±18.26^{a}	2.92±0.10^{b}	97.07±1.68^{d}	3.32±0.24^{a}	20.01±0.90^{ab}
COLD h_{24}	163.15±2.86^{b}	32.73±0.44^{c}	115.1±1.51^{b}	374.85±7.62^{b}	2.97±0.02^{b}	85.29±1.32^{b}	3.33±0.25^{a}	20.74±0.49^{b}
HOT h_{24}	172.7±2.70^{c}	34.08±0.27^{d}	119.68±1.47^{c}	399.32±8.37^{b}	3.05±0.07^{bc}	80.31±1.92^{a}	3.38±0.20^{a}	21.05±0.55^{b}

The particle analysis trend measured reflects the trend found with WBC and swelling. CF dry has the smallest D[4;3], which is lower than both the samples with longer contact time and those subjected to heat treatment. When describing a particle size distribution, it is important to consider the shape of the distribution in addition to the size values. A key parameter used to assess the width or broadness of a statistical distribution is the Span value. Fibers of different sizes have different hydration rates as suggested by the SPANs data on the different treatments. Heat is a parameter that has an impact on WBC. Samples not subjected to heat treatment maintained a more constant distribution without significant differences in SPAN values between h_0 and h_{24}. Focusing on percentiles analysis, it's possible to note that the H-h_0 sample's D_{50} and D_{10} values are the only decreasing, compared to dry powder. H-h_0 has the largest surface area with 97.07±1.68 m^2/Kg indicating a high dispersion state, compared to the others. Microstructural examination, aligned with He et al.'s approach in 2023

describes citrus fiber's granules as big chunks majorly composed of a mix of soluble and insoluble fiber. The smaller particle size for H-h_0 compared with C-h_0 can be explained as a dissolution due to the mixing in hot water of the CF granules connected by the soluble fiber residues. Further insights into microstructure dynamics indicate that during cooling, the dissolved soluble fibers facilitate aggregation, resulting in increased particle size and reduced surface area for the H-h_{24} sample. This shift indicates a transition from dispersed particles to larger clusters, as evidenced by statistically significant values across various size classes in each test.

3.3 Phase separation

Experiments were carried out to find the ideal combination of oil, mango puree, and fiber to formulate the base emulsion for developing the emulsion-filled hydrogel. To quantify the impact of mango puree on phase separation, it was compared with the water-based version. As shown in Table 22, with a 3% w/w concentration of CF, mango puree appears to support the CF network, allowing for better oil retention. Mango fibers have a non-homogeneous length, and some of them (Figure 13) are longer than CFs (Table 21), supposedly acting as a backbone for the network at low CF concentration.

Figure 13. Optical microscopy images of mango puree fibers.

In water-based samples, 3% w/w CF alone did not allow the emulsion to be stable. The different behavior with the two dispersant phases suggests that it is necessary to reach a threshold concentration for using CF as a stabilizer. Overstepping the onset amount (depending on the dispersant) creates a sufficiently dense network, thus avoiding phase separation and preventing the coalescence of particles. In contrast, water-based samples show better results at high CF concentrations than mango-based ones even if the difference is small. At high concentrations, the network formed by CF could be disturbed by the presence of long mango fibers, which can interrupt the densely present net created by CF. The mango samples with the least phase separation are 20A and 20B. This suggests that an important parameter correlated with phase separation is the amount of water present in the final sample concerning the percentage of fiber. At the same CF concentration, a lower mango puree content results in greater phase separation

Table 22. Phase separation quantification. Data were represented by means ± SD. Data with different lowercase letters in the same column were significantly different ($p < 0.05$).

		SAMPLES	OIL RELEASE (%) W/W		
DISPERSANT	Heat treatment	Oil (%) w/w	CF 3% w/w	CF 4% w/w	CF 5% w/w
MANGO	Yes	30	16.93 ± 3.36^{b}	16.88 ± 1.72^{cd}	1.46 ± 0.13^{ab}
	No	30	19.81 ± 3.18^{cd}	21.21 ± 0.40^{d}	6.56 ± 0.12^{b}
	Yes	25	16.83 ± 2.78^{cd}	4.72 ± 0.60^{ab}	2.57 ± 0.26^{ab}
	No	25	14.67 ± 3.00^{cd}	6.62 ± 1.02^{b}	2.69 ± 0.39^{ab}
	Yes	20	5.19 ± 1.03^{ab}	4.55 ± 0.61^{ab}	0.00 ± 0.00^{a}
	No	20	6.13 ± 0.95^{b}	4.72 ± 0.69^{ab}	0.00 ± 0.00^{a}
WATER	Yes	30	90.37 ± 6.77^{g}	2.90 ± 0.98^{ab}	0.00 ± 0.00^{a}
	No	30	31.75 ± 3.44^{e}	$13,26\pm0.99^{c}$	0.00 ± 0.00^{a}
	Yes	25	$>100^{h}$	13.03 ± 2.02^{c}	0.00 ± 0.00^{a}
	No	25	62.17 ± 12.78^{f}	3.57 ± 1.74^{ab}	0.00 ± 0.00^{a}
	Yes	20	$>100^{h}$	14.25 ± 1.77^{cd}	0.00 ± 0.00^{a}
	No	20	91.26 ± 3.31^{g}	4.69 ± 1.27^{ab}	0.00 ± 0.00^{a}

It might seem that emulsifying ability increases with CF concentration, but the tests showed that a high CF content corresponds to a high viscosity (depending on WBC), and this is an obstacle for mixing. CF at 6% w/w was too viscous and formed lumps, having no emulsifications, 5% CF w/w formulation was fixed as the maximum CF concentration. Instead, the lower threshold (3% CF) is given by the minimum amount of fiber needed to create a sufficiently dense mesh, giving structure and retaining oil. CF at 3% w/w creates an emulsion dense enough to prevent a complete leakage from the Eppendorf when it's inverted for the test. Heat does not affect constantly the phase separation in mango puree samples. In water-based ones, it's possible to see a positive effect. Heat treatment impacts the particle size of CF (Table 21), allowing for greater separation of fibers and resulting in a more cohesive network. Consequently, this reduces the amount of oil separated into water-based samples at 3%CF. Qi et al., in 2021 found a similar trend when subjecting their emulsion to a heat treatment up to 70°C. They suggested a significant resilience to thermal treatment in fiber-based emulsions, specifically for those stabilized by citrus fiber, and attributed it to the cellulose content. Cellulose polymers can withstand thermal treatments up to 200°C before breaking down (Harini et al., 2018). Considering CF's OBC values, He et al., in 2023 research, positively correlated high values of OHC with their increasing cellulose content. The notable resistance to thermal treatment, both at high and low temperatures (Qi et al., 2021) stands as an additional advantage for emulsions based on citrus fiber. This highlights wide applicability in food production, offering an alternative to less effective ingredients with greater environmental impact, especially considering CF's status as a by-product. 25% w/w and 30% w/w oil gave little phase separations (Table 22). Despite being small amounts, it can cause problems with consumer acceptance, if the product after a period of storage

presents a thin layer of separated oil in the upper part. For the final formulation, the combination of 20% oil and 5% CF was chosen since it was the only one able to prevent phase separation even after heat treatment. In water-based samples at 3%, the released oil values exceed 100% of the initial oil content because after turning the samples over, they also released a small amount of water. Those samples had a water-to-fiber ratio of 26.67, 25,00 and 23.33 respectively, those values were higher than the WBC of CF (Table 21), which cannot completely bind all the water in the sample. Mango puree samples had a lower water-to-fiber ratio (20.50, 18.83, and 17.16 for 20%, 25% , and 30% oil respectively), this proportion of ingredients and the presence of mango fiber are the reason for the difference in the retained oil between the two phases.

3.4 Emulsion droplet size analysis:

Mango-based emulsions without the addition of CF were analyzed using optical microscopy to quantify the capacity of mango puree to form a heat-stable emulsion. The optimized mixing time and the evaluation of D[4;3] were used to assess the emulsions both before and after heat treatment.

3.4.1 Mixing time optimization.

D [4,3] volume-weighted mean is employed as a parameter for evaluating the average diameter of droplets in a way that considers the volume contribution of each. This approach considers the impact of larger oil droplets, as even a slight increase in their diameter can result in a significant exponential increase in volume. This formula gives greater importance to larger droplets, as they have a more substantial influence on the overall average. Considering that larger droplets destabilize the emulsion quicker than small ones it's possible to have an approximate idea of the emulsion resilience to time. The particle size of the samples subjected to WBC was also analyzed to correlate them. Initially, different mixing times were tested, for mango puree samples, maintaining a constant oil concentration at 7.5% w/w. The tested mixing times were 2.5 - 5 - 7.5 - 10 - 15 - 20 minutes, as Figure 14(a) shows the samples are divided into two groups. The first, on the right side of the graph, includes treatments from 2.5 to 7.5 min with D[4;3] values from 361.73 ± 7.50 µm to 282.5 ± 14.96 µm (Table 23a). The second group on the left, contains samples with mixing times from 10 to 20 minutes and are those that show a lower particle size. It was enough to go from 7.5 to 10 min to halve the value of D[4;3], without heat treatment, and by 40% if heat treated. Heat was the main factor in determining the optimal mixing times between 10-15 and 20 minutes, as there were no statistically significant differences between the A and B samples. The sample at 10 minutes of mixing had a more significant variation compared to 15 min. Improvements in terms of stability and reduction of particle size at 20 minutes weren't lower enough to justify the increase in processing times of 5 minutes. Considering

an industrial scale-up perspective, it was preferred to mix for a shorter time reducing potential production costs. Treatments less than 10 minutes, on the other hand, are not suitable for having a stable emulsion, as they have a D[4;3] significantly higher than that of the group composed of 10-15-20 min. (Liu et al., 2012).

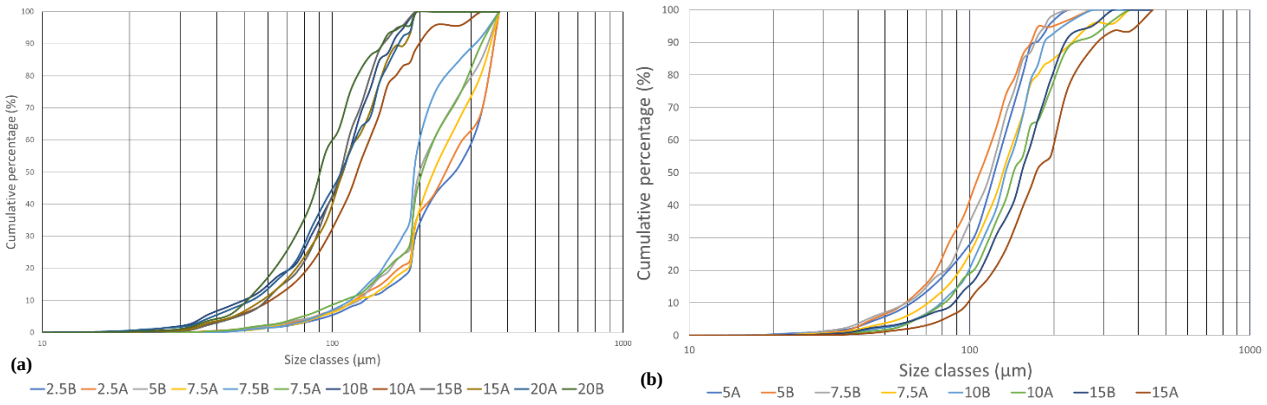

Figure 14. Cumulative particle size distribution of mango-based emulsion. **A** stands for "After heat treatment" and **B** for "Before heat treatment". **(a)** Mango puree-based emulsion with a constant oil content (7,5% w/w) and different mixing times (minutes). **(b)** Mango puree-based emulsion with a constant mixing time (10 min.) and different oil concentrations (w/w).

TABLE 23: D[4;3] values for mango-based emulsions. **A** stands for "After heat treatment" and **B** for "Before heat treatment". **(a)** Constant mixing time (10 min.) and different oil concentrations (w/w). **(b)** Different mixing times (minute) with the same oil concentration. Data were represented by means ± SD. Values reported with different lowercase letters are significantly different ($p < 0.05$).

3.4.2

(A) SAMPLES	D[4;3]
2,5 B	361.73±7.50^{g}
2,5 A	355.65±15.19^{fg}
5 B	314.63±13.97^{de}
5 A	334.81±5.17^{ef}
7,5 B	282.5±14.96^{c}
7,5 A	310.54±23.37^{d}
10 B	134.76±13.08^{a}
10 A	184.25±17.6^{b}
15 B	131.77±6,18^{a}
15 A	141.47±15.01^{a}
20 B	122.42±2.99^{a}
20 A	141.24±13.51^{a}

(B) SAMPLES	D[4;3]
5 B	140.61±4.82^{a}
5 A	135.86±15.58^{a}
7,5 B	134.76±13.08^{a}
7,5 A	184.25±17.68^{b}
10 B	156.33±6.81^{a}
10 A	198.93±12.66^{b}
15 B	186.18±13.04^{bc}
15 A	243.58±14.18^{c}

Mango puree emulsifying capacity.

The response of mango puree to increasing oil concentrations with the same mixing time was then assessed Figure 14 (b). While the oil content increases, so does the D[4;3] value, and the increase is even higher when subjected to heat treatment. The samples with 5% w/w oil do not have a significant difference between B and A, which is not the case for samples from 7.5% and above (Table 23b). It can be estimated that mango puree can originate a heat-stable emulsion with an amount of oil equal

to 5% w/w, in the final product, after heat treatment. Resuming the two trials, the increase in droplet size after the heat treatment can be reduced and almost eliminated by reducing the amount of oil and increasing the mixing times.

3.5 Fiber stabilized emulsion.

The addition of CF had the strongest impact on D[4;3], as reported in Figure 15 and Figure 16, with a large modification in the response of particle size to heat treatment and different oil concentrations.

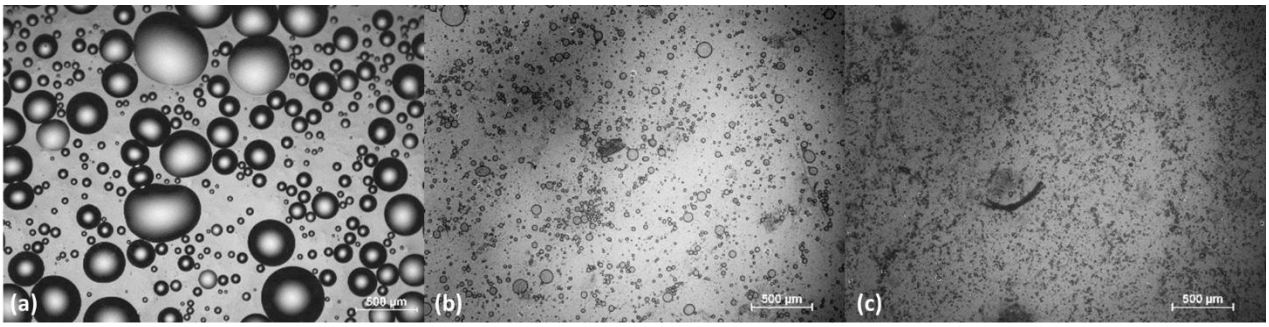

Figure 15. Optical microscopy images of mango puree emulsions (20% w/w oil) and different CF additions, respectively (a) 0% CF; (b) 3% CF w/w; (c) 5% CF w/w.

The 20%B sample that does not contain fiber (Figure 15(a)) has a D[4;3] of 219.55 ± 16.57µm, which decreases significantly to 37.02 ± 6.28µm (Figure 15(b)) with a size reduction of 83.14%, with a further halving of particle size when reaching 5% CF concentration (Figure 15(c)). It can therefore be stated that CF has an emulsifying power (Nomena et al., 2018; Qi et al., 2021), forming a network that stabilizes the emulsion. In samples containing fiber the correlation between heat treatment, oil content, and the increase in particle size is lost. Emerges that the most influential factor on D[4;3] is the fiber content, with an inversely proportional correlation of p = -0.918 and a significance level of 0.01. Therefore, the effect of adding CF to stabilize the emulsion on particle size is so strong that it makes the impact of oil and heat negligible. We also have a positive correlation between particle size and phase separation with a directly proportional correlation of p = 0.958. Consequently, identifying the sample with the lowest particle size also allows us to identify the most stable formulation even considering heated samples. Figure 16 represents cumulative particle sizes for all samples, it shows how great the difference is between samples with and without CF.

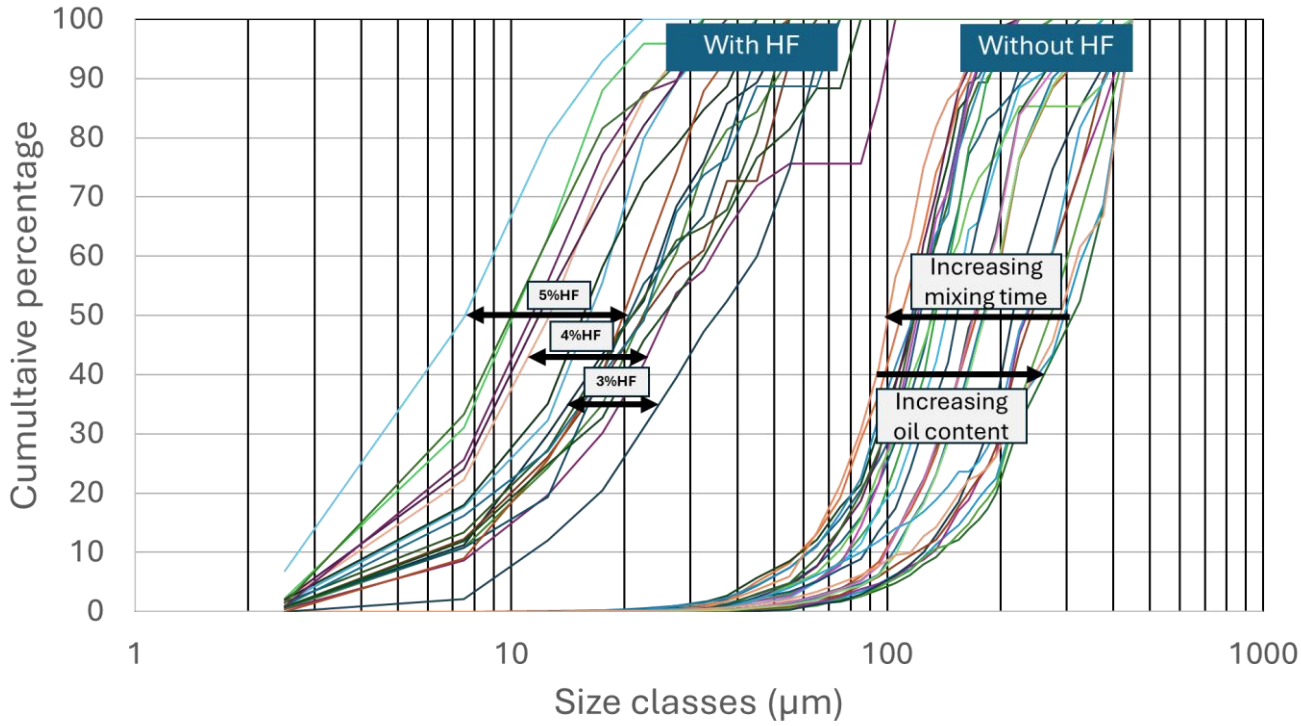

Figure 16. Cumulative particle size distributions of all emulsions before and after heat treatment.

The fiber content gradually increases from the right to the left of the graph (and therefore towards the samples with smaller oil droplets) having an inverse proportionality between the fiber content and the oil droplet particle size. The sample with the smallest droplet size in absolute terms is the 20% w/w oil with 5% w/w fiber sample (Table 24), which at the 10th percentile has a particle size of 2.04 µm while at the 90th it does not exceed 10.24 µm. The particle sizes obtained are comparable to those found by Qi et al. (2021), who, working with an Ultraturrax and high-pressure homogenizer, had to stop at a maximum concentration of Citrus fiber of 3% due to the excessive viscosity given by higher fiber concentration. Considering the whole homogenizing process, the particle size remained significantly larger compared to samples with 5% fiber in this study, suggesting that fiber probably has the most important impact than the rpm at which it mixed. In their study Nomena et al. (2018), obtained an emulsion with a particle size significantly higher than that reported by (Qi et al., 2021). Despite using a similar method, first Ultraturrax and then high-pressure homogenization, it is likely that the high-pressure treatment was not sufficiently intense to release the cellulose nanofibrils of Citrus Fiber. The nanofibrils allow a huge increase in the surface area of the fiber in the oil-water interface, making it able to stabilize emulsions containing a large amount of oil with modest amounts of fiber. High-pressure homogenization can release myofibrils, which then arrange themselves in direct contact with oil droplets. Small particle nanorods stabilize emulsions by forming a dense layer around droplets, as they can align around them, leading to high coverage. Intact citrus fiber contains

longer and stiffer particles within no myofibril's separation making it able to only provide partial coverage, stabilizing emulsions by forming an interconnected network in which droplets get trapped. Figure 16 visually shows the difference between this sample and all the others, clearly visible by the distance between the curves. Although the D[4;3] analysis shows that the 5% CF samples have the lowest values (compared to the other fiber concentrations), without having significant differences between 20-25 or 30% oil (Table 24). Combining this data Table 24 with phase separation data Table 22, it is possible to identify again the formulation with 5% fiber and 20% oil as the most stable in absolute terms of all those tested. It was selected as the base for emulsion-filled hydrogels.

Table 24. D[4;3] values mango-based CF emulsions. Letters **A** stands for "After heat treatment" and **B** for "Before heat treatment". Data were represented by means ± SD. Values reported with different lowercase letters with the same oil concentration (row) are significantly different ($p < 0.05$). Values reported with different uppercase letters with the same fiber concentration (column) are significantly different ($p < 0.05$).

			CF (W/W %)			
			0	3	4	5
OIL CONCENTRATION (%)	20	B	219.55 ± 16.57^{dA}	69.76 ± 4.95^{cD}	23.88 ± 1.46^{aAB}	16.16 ± 2.82^{aAB}
		A	230.38 ± 9.20^{dA}	37.02 ± 6.28^{bA}	19.15 ± 3.07^{aA}	13.6 ± 1.50^{aA}
	25	B	224.87 ± 5.51^{eA}	35.59 ± 1.73^{cdA}	27.62 ± 3.14^{bBC}	20.20 ± 2.35^{aB}
		A	237.42 ± 5.05^{fA}	41.34 ± 5.47^{dAB}	32.8 ± 4.63^{bcC}	39.1 ± 4.26^{cdC}
	30	B	304.80 ± 11.40^{dB}	51.53 ± 3.67^{cC}	49.64 ± 6.71^{cD}	18.26 ± 3.35^{aAB}
		A	354.76 ± 26.36^{eC}	42.18 ± 2.82^{bcAB}	27.57 ± 5.30^{abBC}	19.8 ± 2.86^{aB}

3.6 Confocal

Confocal microscopy confirms the stabilizing action of CF on the emulsion (Figure 17). However, due to the large size of the fibers, they do not cover the oil droplets to stabilize them directly. Instead, the branched structure they form creates a barrier or network of meshes, which becomes tighter as more fiber is present.

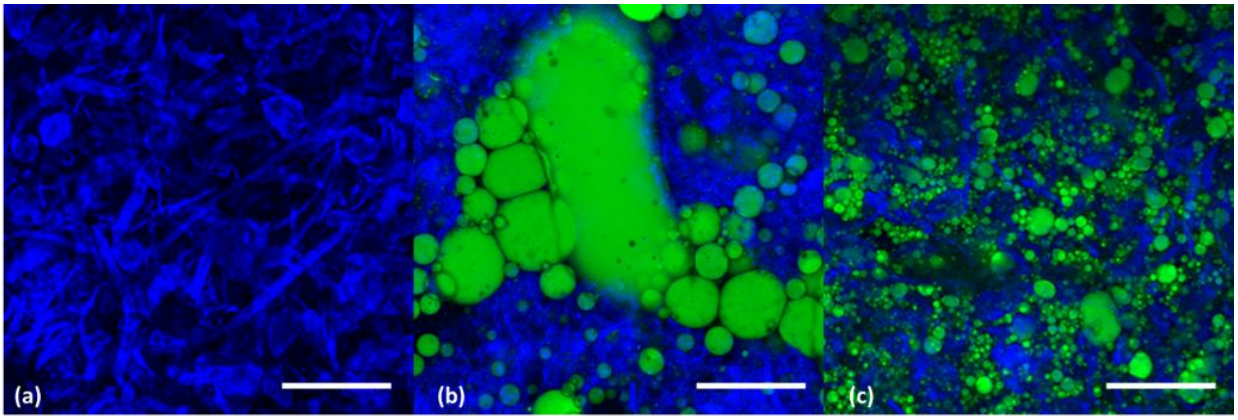

Figure 17. Confocal images of: (a) CF dispersion in water 5% w/w (b) 20% oil emulsion without CF and (c) emulsion containing 5% w/w CF and 20% w/w oil. The fiber is blue stained, and the oil is shown in green, scale bar is 50 µm

The net prevents the coalescence of the spheres, stabilizing the emulsion and preventing phase separation with a physical method, as also observed by Nomena et al. (2018). As can be seen in Figure 17(a), CF originates a mesh, and as reported in Figure 17(b) where the CF is not present, it does not originate any emulsion, also because the content of 30% w/w oil is higher than the 5% that mango can emulsify. In Figure 17(c) the oil micelles become embedded in the fiber mesh, distributing themselves close to their surface. CF alone, on the other hand, originates from a three-dimensional structure after absorbing all the water present in the sample, as also described by Lundberg et al. (2014), making a structure similar to a weak gel. It's possible to observe that in Figure 18(abcd), with the addition of pectins and the formation of the emulsion-filled hydrogel, the images of the four combinations show the structure given by the fibers in a second layer.

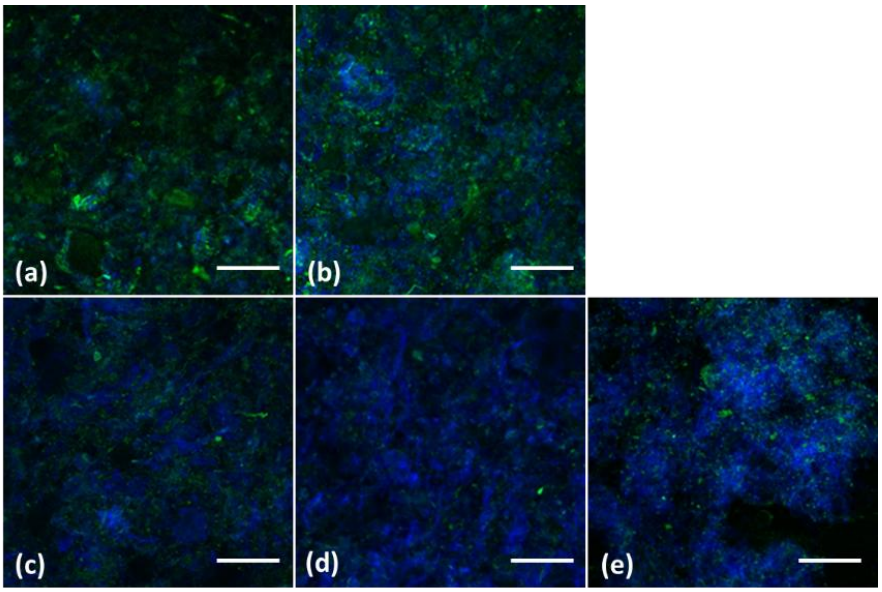

Figure 18. Confocal images of emulsion-filled hydrogels, respectively (a) LM-18x (b) LMA-20 (c) LM-12 (d) LMA-10 (e) mango puree only. Fiber is blue stained, and oil is shown in green, scale bar is 50µm.

However, the oil droplets remain scattered by the pectins, which prevent contact with the dye. This is why the presence of oil is not perceived. The analysis was performed before proceeding with the texture analyses of the four different formulations to confirm the presence of the desired structure and to confirm that pectin influences the structure of the emulsion. The images agree with what is said by Löfgren et al. (2006) who observed a similar microstructure for LMA or LM at a pH between 3 and 7. Additionally, it's possible to compare Figure 18(abcd) with those of the mango puree Figure 18(e), where the CF structure is absent.

3.7 Texture

The influence of the four pectins was studied by having different ingredient combinations:

- (P) Hydrogel (mango puree + 1% w/w pectin).
- (NO) Fiber reinforced hydrogel (mango puree + 5% w/w CF + 1% w/w pectin).
- (Final) Emulsion filled hydrogel (mango puree + 20% w/w oil + 5% w/w CF + 1% w/w pectin).

All the emulsion-filled hydrogels obtained were analyzed with confocal microscopy to verify the microstructure and then subjected to texture evaluation to better assess the differences. Depending on the pectin used in the Final samples, very distinctive consistencies were obtained. It was possible to divide the samples into two main groups: those originating a self-supporting gel (LMA-10, Figure 19) and samples with a creamy consistency that, once removed from the mold, were unable to maintain the mold shape (LMA-20; LM-12; LM-18,

Table 25). The comparisons between recipes were made to isolate the effect of pectin, fiber, and oil on the formulations. It can be generally observed that samples containing only mango puree and pectins gave the weakest structures with the lowest stickiness and firmness. On the other hand, the samples where 5% CF was added turned out to be firmer, overriding the influence of pectins, and by the fact making all the samples with it very similar. The further addition of oil, in the form of an emulsion in Final samples allowed to find new differences between similar recipes.

3.7.1 Creamy samples

Detailed analysis of the creamy samples (

Table 25) reveals that LMA-20, traditionally the least sticky, experienced a significant increase in stickiness in the NO recipe due to the addition of CF

In all three formulations, LM-12 exhibits the highest firmness and adhesiveness parameters, making it the most consistent among all creamy samples, even when considering the work of adhesion and the work for compression (Kamboj & Rana, 2014).

Table 25. Texture analysis on creamy samples. Data were represented by means ± SD. Data with different lowercase letters in the same column were significantly different ($p < 0.05$).

	FIRMNESS (N)	ADHESIVENESS (N)
P-LM-12	8.37 ± 0.66^{c}	-10.09 ± 0.80^{b}
P-LM-18	5.87 ± 0.17^{b}	$-3.34 \pm 0.19d^{e}$
P-LMA-20	3.13 ± 0.40^{a}	-2.08 ± 0.20^{e}
FINAL-LM-12	11.08 ± 0.21^{d}	-16.89 ± 1.28^{a}
FINAL-LM-18	10.29 ± 0.70^{d}	-7.07 ± 0.85^{c}
FINAL-LMA-20	7.80 ± 1.00^{c}	-5.39 ± 0.84^{cd}
NO-LM-12	12.99 ± 0.92^{e}	-15.58 ± 2.58^{a}
NO-LM-18	11.33 ± 0.46^{d}	-11.28 ± 0.36^{b}
NO-LMA-20	11.23 ± 0.05^{d}	-15.49 ± 1.15^{a}

The other two pectins produced samples with similar stickiness, except in the NO formulation, where LM-18 was the least affected by the addition of CF. Firmness analysis followed the trend of stickiness; in fact, if one parameter increased the other followed the trend. The pectin that consistently resulted in less consistent samples was LMA-20. As the degree of methylation decreases, the sequences of non-methylated galacturonic acid residues increase, which allows for the formation of more 'egg-boxes.' This rise leads to the development of a stronger gel (Chan et al., 2017). The use of mango puree without added sugars allowed the gelling effect optimization of LM and LMA: both are penalized by an excess of sugars that reduce the cross-linking power of calcium ions by binding water

(Fu & Rao, 2001). It can be hypothesized that the effect of CF is comparable across samples. By binding water and creating a three-dimensional network, CF can reduce the differences between pectins, thereby standardizing the consistencies. LMA are less sensitive than conventional to both sugar concentration (Löfgren et al., 2006) and CF, and for this reason, they can prevail over their effect. Recipes that can create structures more similar to self-supporting gels, thanks to the bonds formed by the ammonium groups originated from LMA. LMA-20 was able to give samples almost like gels with texture values that distance themselves from those of the other recipes. While LMA-10, despite the interferences, can give a self-supporting gel.

3.7.2 Self-sustaining gel (LMA-10)

LMA-10 originated with self-supporting gels. The differences between formulations were statistically significant, and the behavior between recipes is shown in Figure 19.

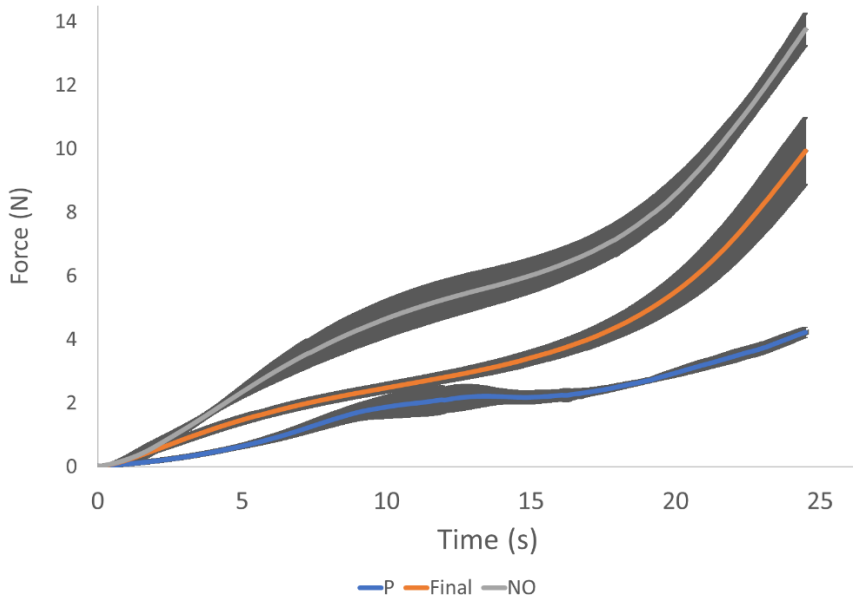

Figure 19. Firmness flow curves for LMA-10 samples are reported as the average flow curve ± SD as a grey banner.

Measuring the maximum force at equal time (25 sec) the P-LMA-10 (Figure 19, in blue) originated the weakest gels (4.22 ± 0,16N), followed by the FINAL-LMA-10 (13.75 ± 0.68N), and the most resistant were those where only fiber was added NO-LMA-10 (10.37 ± 0.51N). However, there were also significant differences in the firmness curves. Higher firmness values result in a wider area under the force versus time curve, indicating an increase in the overall area. It can be stated that in the blue curve, the widening of the standard deviation curve is correlated with the formation of cracks in the gel or chunk detachment. The chunks sliding against each other, or their separation, cause a decrease in the opposition force that the sample exerts on the probe. When the sliding stops or the probe reaches another undamaged section of the gel it starts again to exert a growing opposition force. This

phenomenon does not occur in the other two curves, a sign that the gel has greater resilience to compression and a more elastic structure, capable of resisting deformation without breaking into pieces. In all three recipes, the curves have slope changes that follow the breaking point. The slope variation can be used as an indicator of structure loss, whether this leads to visible changes with cracks and the formation of blocks, or whether no visible effect is present to the naked eye, this can indicate a variation or collapse of the microstructure internal to the gel. It is hypothesized that if the microstructure collapses it will not exert a growing opposition force until it reaches another point of stability, this happens in P samples with 30-35% height compression. The NO curve, despite being the one with the highest firmness, presents a slope change around values of 30-40% of compression too. CF makes a significant contribution to the gel consistency increase and improves its resilience. During tests, the sample did not show visible signs of cracking. Its curve, however, presents a change in slope between 30 and 40% height compression, the microstructure has still had a failure. To observe the minimum change in slope we need to move to the curve of the final formulation. The presence of the emulsion inside the hydrogel allows the exploitation of CF structuring power (see the increase in the maximum peak compared to samples with only pectin) in combination with the presence of oil. Compared to NO, emulsion reduces the maximum consistency but enhances the recipe's resilience at the microstructural level, without significant changes in slope or visible effects to the naked eye.

4.Conclusions

This study investigated the relationship between pectins, mango puree, citrus fiber, and oil. Each component of the emulsion-filled hydrogel was individually characterized for its main physicochemical properties and its ability to form a heat-stable emulsion with the smallest possible particle size. The results demonstrated that citrus fiber has emulsifying properties. At a concentration of 5% w/w, CF can stably emulsify 20% w/w oil, even under severe heat treatment. This ability to retain water and emulsify is attributed to the composition of the fiber insoluble fraction, particularly cellulose and hemicellulose.

Furthermore, the fiber content appears to be the primary factor influencing oil droplet size, more than the oil content itself. When CF and pectins are combined in a hydrogel (NO), a synergistic effect is achieved, resulting in a firmer product compared to a hydrogel made solely of pectin. Conversely, when pectins are used to formulate an emulsion-filled hydrogel, they can produce products with highly variable consistencies, thanks to the addition of oil and its interaction with CF. Emulsion-filled hydrogels, due to the thermal resistance of the emulsion and the simplicity of the production process,

are suitable for future use by the food industry or as ingredients for other preparations, either individually or in combination.

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Chapter 5

"Analysis of the interaction between citrus fiber and fruit-based system for emulsion formulation"

Abstract

This study explores the potential of citrus fiber and its integration with other food matrices, such as apricot puree, to develop innovative and sustainable food products. The research focuses on the rheological evaluation of citrus fiber emulsions in water and apricot puree dispersions. The findings highlight that citrus the network-forming ability of citrus fiber varies between these environments, influenced by particle size and matrix interactions. Apricot puree demonstrates a "matrix effect," altering emulsion stability and oil retention under stress. By applying physical stress, the microstructure of citrus fiber is examined to understand its applications in industrial food processing. The study also assesses the interactions between citrus fiber and other fibers within the apricot puree biopolymer matrix. By leveraging these underexplored ingredients and integrating them with sustainable practices, this study aims to contribute to the development of functional foods, addressing both nutritional and environmental challenges.

1.Introduction

Citrus represents worldwide the largest cultivated category of fruit. Their main use in the food industry is for juice extraction, a process generating waste for around 50-60% of the processed citrus. Considering global production, this is certainly a huge resource depletion (Mahato et al., 2018) In addition to juice, citrus fruits can also be used to extract essential oils, which results in many different applications inside and outside the food system (Mendelné Pászti et al., 2023). After essential oil extraction, citrus peels are still an interesting source of bioactive compounds and fibers, matching a lot of different applications (Liu et al., 2024). Peel can serve as a valuable source of active compounds and raw materials for the packaging industry (Fiorentini et al., 2022). Citrus peel extracts are utilized for the extraction of polyphenols (Kaur et al., 2024), known for their antioxidant properties. Fibers can also be added to dough and other food preparations in order to reduce their glycemic index (Miehle et al., 2024). Among these uses, the most widely diffused application for orange peel is as a substrate for pectin extraction. Pectin is a galacturonic acid polysaccharide that falls into the definition of soluble dietary fiber and found many applications in the food industry as a gelling and thickening agent (Kumar et al., 2023; Wedamulla et al., 2022). After oil and pectin extraction, the remaining part consists of an insoluble residue, primarily composed of fibers and other structural components of the peel like cellulose, hemicellulose, and lignin (Liu et al., 2012). Although numerous studies on the chemical and structural characterization of these fibers have been conducted in recent years, at present time the residue still has limited applications in the food industry (Tan et al., 2024; Viscusi et al., 2024). Moreover, the insoluble fraction seems to play an important role in fat absorption with interesting applications as a lipid absorption controller (Wang et al., 2024). A deeper understanding of their properties could lead to new opportunities for their use, particularly given the growing interest in sustainable and natural ingredients. Apricots are one of the most produced stone fruits in Europe, after cherries and peaches, and they occupy the third place as economically most important stone fruit

in global production (Mendelné Pászti et al., 2023). Since apricots are widely available in Italy, they were chosen as the example matrix for developing the emulsion. This study aims to investigate the properties of citrus fiber subjected to moderate-speed mixing treatment, simulating the type of mixer used in food industries. The objectives are to explore the microstructure of citrus fiber without subjecting it to intensive mechanical processes such as high-pressure fibrillation. It is important to understand the matrix effect with other fibers and components of whole fruits, using apricot puree as a model. The differing physicochemical composition and particle size of the puree compared to the fiber may significantly impact the final material properties, suggesting new potential uses for citrus fiber in innovative food products.

2.Materials and methods

2.1 Raw materials and emulsion preparation

The raw materials used in the emulsions are citrus fiber "CF" (Aglufiber FAS, JRS Silvateam Ingredients S.r.l. Bergamo, BG, Italy), and apricot puree (Fructus Meran S.P.A. Vilpiano, Bz, Italy). The sunflower oil was provided on a local market. Emulsions were prepared using either water (W) or apricot puree (A) as the continuous phase, the ingredients were emulsified with an IKA EUROSTAR 40 mixer (IKA-Works, Wilmington, North Carolina, USA) at 1200 rpm for 15 minutes at room temperature (T_{amb}).

2.2 Characterization analysis

Moisture, ash, and protein content of apricot and CF were assessed using the official AOAC methods 935.29, 942.05, and 2001.11 respectively. Soluble dietary fiber was quantified with K-TDFR-200A Kit (Megazyme, Wicklow, Ireland) according to the AOAC method 991.43. Identification and quantification of sugars and organic acids were performed by HPLC analysis.

2.3 Sugars

Sugars were identified and quantified with the following method. Respectively 4 g of the sample was dissolved in 16 g of water. The mixture was stirred to ensure the complete dissolution of sugars present in the sample. The sample was then transferred into centrifuge tubes, centrifuged, and placed into vials for HPLC analysis. The diluted sample was filtered using a 0.45 µm mesh filter. To quantify sucrose, a portion of the filtered sample was subjected to inversion. Specifically, 5 mL of the filtrate was taken and diluted in 50 mL of water, to which 5 mL of 32% v/v HCl was added. The mixture was stirred for 15 minutes at 70°C and then neutralized with NaOH. The sugars in the sample were

analyzed via HPLC equipped with a Jasco PU-4180 pump (Jasco, Halifax, Nova Scotia, Canada), with an Aminex HPX-87C column (300 x 7.8 mm, BIO-RAD, Hercules, California, U.S.), conditioned in an oven at 80°C. The mobile phase was: 100% water, with a flow rate of 0.6 mL/min and a runtime of 35 minutes. A refractive index detector (RI2031 plus, Jasco, Halifax, Nova Scotia, Canada) was employed in combination with the Jasco LC-Net II/ADC communication module (Jasco, Halifax, Nova Scotia, Canada). Data was analyzed using ChromNAV Control Center software (Jasco, Halifax, Nova Scotia, Canada). The quantification of sugars was carried out using a calibration curve that was previously established by injecting standard solutions.

2.4 Organic acid

Organic acids were identified and quantified with the following method. Respectively 10 g of samples was weighed into a beaker and diluted with 90 g of water. The solution was then stirred for 30 minutes and allowed to rest for 15 minutes. The diluted sample was filtered using a 0.45 µm mesh filter and placed into vials for HPLC analysis. The organic acids in the sample were analyzed via HPLC equipped with a Jasco PU-4180 pump (Jasco, Halifax, Nova Scotia, Canada) in combination with Rezex ROA-Organic Acid H+ column (300 x 7.8 mm, United States, Torrance, CA 90501-1430 USA). As mobile phase was employed a water-based solution with 0.005 N H2SO4, with a flow rate of 0.5 mL/min and a run time of 25 minutes. A UV detector at 210 nm (UV 2075 plus) was employed in combination with Jasco LC-Net II/ADC Communication module and data were elaborated thanks to ChromNAV Control Center Software (Jasco, Halifax, Nova Scotia, Canada).

2.5 Water activity (a_w)

The water activity (aw) of the emulsion was measured using a HygroPalm HP23-AW-A device (Rotronic, Bassersdorf, Switzerland) at a controlled temperature of 25°C.

2.6 pH

The pH evaluation of the emulsions was conducted on 10 g of sample in its original form, dissolved in 90 mL of distilled water. The pH was measured using a sensION™+ PH3 pH meter (Hach Company, Loveland, Colorado, USA).

2.7 Colour Analysis

Color analyses were conducted on water- and apricot-based emulsions. The results were expressed in accordance with CIEL*a*b* color space. The colour was measured through the three-dimensional colour diagram (L*, a* and b*), where: L* represents lightness (L* = 0 (black), L* = 100 (white), a*

represents (−a* = greenness, +a* = redness) and b* chromaticity represents (−b* = blueness, +b* = yellowness). The mathematical description of colour difference was established to quantify the visible difference between the colours of two samples. Values of L* a* and b* were used to quantify the colour difference (ΔE) using the following equation:

$$\Delta E^* = \sqrt{(\delta L^*)^2 + (\delta a^*)^2 + (\delta b^*)^2} \qquad (1)$$

ΔE can be evaluated in the following way:
− 0 < ΔE<1 – the difference is imperceptible,
− 1 < ΔE<2 – the difference is perceptible only for experienced evaluators,
− 2 < ΔE < 3.5 – the difference is noticeable also for inexperienced evaluators,
− 3.5 < ΔE<5 – observable colour difference,
− 5 < ΔE − observers notice two different colours (Mokrzycki Cardinal Stefan & Tatol, n.d.)

2.8 Water binding capacity (WBC), oil binding capacity (OBC), and swelling.

Swelling power, water binding capacity (WBC), and oil binding capacity (OBC) were determined in sixfold replicates according to the method described by Wang et al. (2014) with appropriate modifications. Approximately 0.5 g of CF was weighed into a 50 ml Teflon tube and 25g of water or sunflower oil was added. The lid was tightly screwed, and the mixture was heated in a water bath at 92.5 °C for 30 min with regular shaking to measure the swelling (HOT samples). The analysis was also performed using the same technique but with the water bath set at room temperature (COLD). After shaking, the samples (HOT or COLD) were divided into two equal groups. In one sample, the supernatant was immediately separated (0h), while in the other, it was left in contact for 24 hours (24h) to assess any differences. Due to the varying exposure times, it was possible to assess any additional absorption in the hours following preparation. All the samples were centrifugated at 13,000 g in 10 minutes. After supernatant removal, the deposit was weighted, and swelling (0h; 24h), WBC (0h; 24h), and OBC (0h; 24h) were calculated with equation (1):

$$Swelling, WBC\ and\ OBC = \frac{M_2 - M_1}{M_0} \qquad (1)$$

M_0 represents the weight of the sample (g), M_1 is the weight of the centrifuge tube (g), and M_2 is the combined weight of the centrifuge tube and the sample after separating the supernatant (g).

2.9 Particle size distribution

The particle size distributions were determined using a Mastersizer 3000 laser granulometer (Malvern Panalytical, Malvern, UK) with an effective measurement range of 2000–0.02 μm. The size distribution analysis was performed at 25°C. Dry CF was analyzed using the Aero S dispersion unit, and hydration properties were assessed with the Hydro MV attachment. The hydrated samples (0h, 24h, COLD, and HOT) were stirred with the Hydro MV at 1000 rpm, with measurements taken after 1 minute. For CF and apricot puree the refractive index was set to 1.460 (Jiang et al., 2022). Deionized water was selected as the dispersant, with a refractive index of 1.330. The lower and upper obscuration limits were set to 10–20% for the wet dispersion unit and 1–10% for the dry dispersion unit. An obscuration value of around 15% was used for wet dispersion and 5% for dry units. Every sample was assessed 10^{th} DV(10), 50^{th} DV(50) and 90^{th} DV(90) percentile, SPAN, D[4;3], and Specific surface area (m^2/Kg).

2.10 Phase separation quantification.

The resistance of emulsion to phase separation was assessed through centrifugation, following the Gestranius et al. (2017) method with some modifications. Approximately 2g of emulsion was placed into a 2ml Eppendorf tube and then centrifuged at 4000 g for 2 minutes. After centrifugation, the tubes containing the emulsions were overturned onto absorbent paper to facilitate oil release and then weighted. The oil loss was expressed as a percentage of the initial oil weight. The calculation was performed using the following equation (2):

$$\left(\frac{Gross_{before} - Gross_{after}}{sample\ weight * oil\ percentage\ w/w}\right) * 100 \quad (2)$$

2.11 Rheology

Rheological determinations of the samples were carried out in a controlled stress and strain rheometer (MCR 302, Anton Paar, Gratz, Austria), thermally regulated by a Peltier plate (CTD 180) and a circulating water bath (FP 50, Julabo, Milan, Italy) at 25°C. The geometry used for the analysis was the parallel rough plates (PP25\P2 mm in diameter, 1 mm in gap). Approximately 2 g of emulsions were placed on the lower plate. The samples were allowed to rest for 5 minutes to facilitate stress relaxation and achieve temperature equilibration. Mechanical properties were derived from amplitude and frequency sweep tests conducted at 25°C. An amplitude sweep was performed to determine the

linear viscoelastic region (LVER) for tested samples. For this purpose, a constant frequency of 1 Hz and a shear strain ranging from 0.01 to 100 were applied. Frequency sweep tests were then carried out at a controlled shear strain of 0.01% with frequency varying from 100 to 1 Hz and, similar to the previous method, a waiting period of five minutes is observed. The viscoelastic parameters, including the storage modulus (G′), loss modulus (G″), and loss tangent (tan δ), were plotted as functions of frequency.

2.12 Statistical analysis

All experiments were performed at least three times and analyzed in triplicate. The results obtained for each sample were evaluated and ranked using a one-way analysis of variance (ANOVA) followed by Tukey's post-hoc test for means discrimination ($p < 0.05$). Statistical analyses were executed via the IBM SPSS Statistics 27 software (SPSS Inc., Chicago, IL, USA).

3.Results and discussion

3.1 Samples characterization

A preliminary characterization was performed for apricot puree and CF (

Table **26**). The two products have distinct compositions. Citrus fiber (CF) has a high dry matter content, whereas apricot puree exhibits lower values. The most abundant component in CF is total dietary fiber as for citrus in general (Wang et al., 2024; Yang et al., 2023a; Zhang et al., 2024), which constitutes 91.68 ± 0.77% of the total dry matter. CF is distinguished by its high insoluble fiber content (80.36 ± 0.25) as for other types of commercialized citrus fiber (Miehle et al., 2024), a feature attributed to the production process (process from citrus fruits. A residue of soluble fiber remains, which influences its properties. proteins and ashes are considered minor components, and no sugars were detected (Miehle et al., 2024). The CF used in this study is the residue from the pectin extraction.

Table 26. Proximate composition of CF an apricot puree by means ± SD. Not detected (n.d.)

Analysis	**CF**		**Apricot puree**	
	on 100g	on 100g of d.m.	on 100g	on 100g of d.m.
Moisture	6.69 ± 0.06	\	86.76 ± 0.06	\
Dry matter	93.36 ± 0.06	\	13.24 ± 0.06	\

Ashes	2.67 ± 0.02	2.86 ± 0.02	0.54 ± 0.02	4.10 ± 0.11
Proteins	4.94 ± 0.60	5.29 ± 0.64	0.87 ± 0.12	6.59 ± 0.91
Total Sugars of which:	n.d.	n.d	10.54 ± 0.19	79.62 ± 1.43
Sucrose	n.d.	n.d	1.41 ± 0.12	10.65 ± 0.91
Glucose	n.d.	n.d	4.30 ± 0.13	32.54 ± 1.01
Fructose	n.d.	n.d	1.79 ± 0.03	13.53 ± 0.25
Sorbitol	n.d.	n.d	3.03 ±0.04	22.90 ± 0.32
Insoluble fibres	75.02 ± 0.23	80.36 ± 0.25	0.59 ± 0.00	4.52 ± 0.00
Soluble fibres	10.57 ± 0.78	11.32 ± 0.84	0.97 ± 0.02	7.32 ± 0.15

As for the apricot puree, its dry matter is mostly composed of sugars (79.62 ± 1.43), the main one being glucose, followed by sorbitol, fructose, and sucrose. The presence of sorbitol is considered a distinguishing feature of apricot puree. The values reported in the literature are either significantly lower (Voi et al., 1995) or slightly lower (Bassi & Selli, 1990) or similar (Levent & Alpaslan, 2018). Additionally, three main organic acids have been identified and characterized in apricots: citric acid (0.95 ± 0.003 g/100g), malic acid (0.56 ± 0.00 g/100g), and succinic acid (0.34 ± 0.01 g/100g) according to Bassi & Selli (1990) and Voi et al. (1995) these values are below average; this is another indicator of the level of ripeness or may be due to the type of cultivar used. Regarding the characterization of the CF, as shown in

Table **26**, the moisture content is relatively low, as it is an industrial product subjected to drying. The dry matter consists mainly of insoluble fiber (80.36 ± 0.03 g/100g) and soluble fiber (11.32 ± 0.01 g/100g), with the remainder comprising ash, proteins, and a minimal fraction of extractive.

3.2 WBC, OBC, swelling, and particle size analysis

The water and oil retention capacity of the fiber was evaluated both under hot conditions (>90°C to simulate thermal treatment) and at room temperature (cold conditions) at different contact times: after 10 minutes (h0) and after 24 hours (h24). This approach allowed the assessment of the impact of time exposure and processing temperature on the three most relevant physical properties. The data presented in Table 27 indicate that the fiber exhibits a higher WBC compared to its OBC, suggesting a stronger affinity for water than oil. Additionally, since CF is a blend of different citrus varieties, it is impossible to attribute its properties to a single variety. Furthermore, CF is a byproduct of pectin extraction, so the pectin extraction process influences the properties of the insoluble fraction (Liu et al., 2024). CF's tendency to retain oil compared to water was also noted by (Jiang et al., 2022) and is

considered to be due to the composition of the fiber itself (He et al., 2023). Regarding the OBC, the analysis performed at both hot and cold conditions did not reveal significant differences in the fiber's swelling behavior. Similarly, for WBC, neither temperature nor contact time caused substantial differences in the fiber's swelling. However, a greater swelling was observed in the hot analysis after 24 hours. This analysis confirmed that the fiber has a low oil retention capacity but a high water adsorption capability. Since the fiber was not subjected to any homogenization treatment that would lead to the release of the myofibrils that form the basic structure of cellulose in CF, as in other plants, it was not possible to exceed values of 3.78 ± 0.13bc ((Jiang et al., 2022; Liu et al., 2024).

Table 27. Particle size analysis, oil binding capacity (OBC), and water binding capacity (WBC) measured for CF samples with different water exposure conditions. The data are presented as means ± SD. Values in the same column marked with lowercase letters are significantly different ($p \leq 0.05$).

	D [4;3] µm	Dv (10) µm	Dv (50) µm	Dv (90) µm	Span	OBC	WBC
Apricot	269.37 ± 2.29^{c}	87.54 ± 0.31^{c}	225.65 ± 0.96^{d}	525.82 ± 9.16^{b}	1.94 ± 0.04^{a}	/	/
CF dry	92.98 ± 1.45^{a}	21.98 ± 0.06^{a}	72.05 ± 0.35^{a}	196.30 ± 3.90^{a}	2.42 ± 0.05^{b}	/	/
Cold h_0	101.31 ± 2.39^{b}	28.10 ± 1.34^{b}	81.60 ± 1.60^{b}	193.38 ± 39.92^{a}	2.03 ± 0.05^{a}	3.13 ± 0.08^{a}	24.97 ± 0.84^{a}
Cold h_{24}	102.27 ± 0.23^{b}	28.52 ± 0.23^{b}	86.23 ± 0.79^{c}	200.62 ± 6.45^{a}	2.00 ± 0.05^{a}	3.78 ± 0.13^{bc}	26.60 ± 0.93^{ab}
Hot h_0	101.53 ± 0.48^{b}	27.58 ± 0.48^{b}	85.30 ± 1.40^{c}	200.98 ± 5.57^{a}	2.04 ± 0.07^{a}	3.53 ± 0.25^{c}	26.50 ± 0.89^{ab}
Hot h_{24}	102.36 ± 0.42^{b}	27.94 ± 0.42^{b}	82.06 ± 1.73^{b}	197.68 ± 9.16^{a}	2.07 ± 0.07^{a}	3.30 ± 0.15^{ab}	28.29 ± 0.89^{b}

Particle size measurement was performed on various types of samples: apricot puree, dry CF powder, and CF kept in contact with water (cold and hot); the samples were further divided into h_0 and h_{24} based on contact time (as in the previous analysis). From the data, expressed as volume density in percentage, Figure 20 was derived:

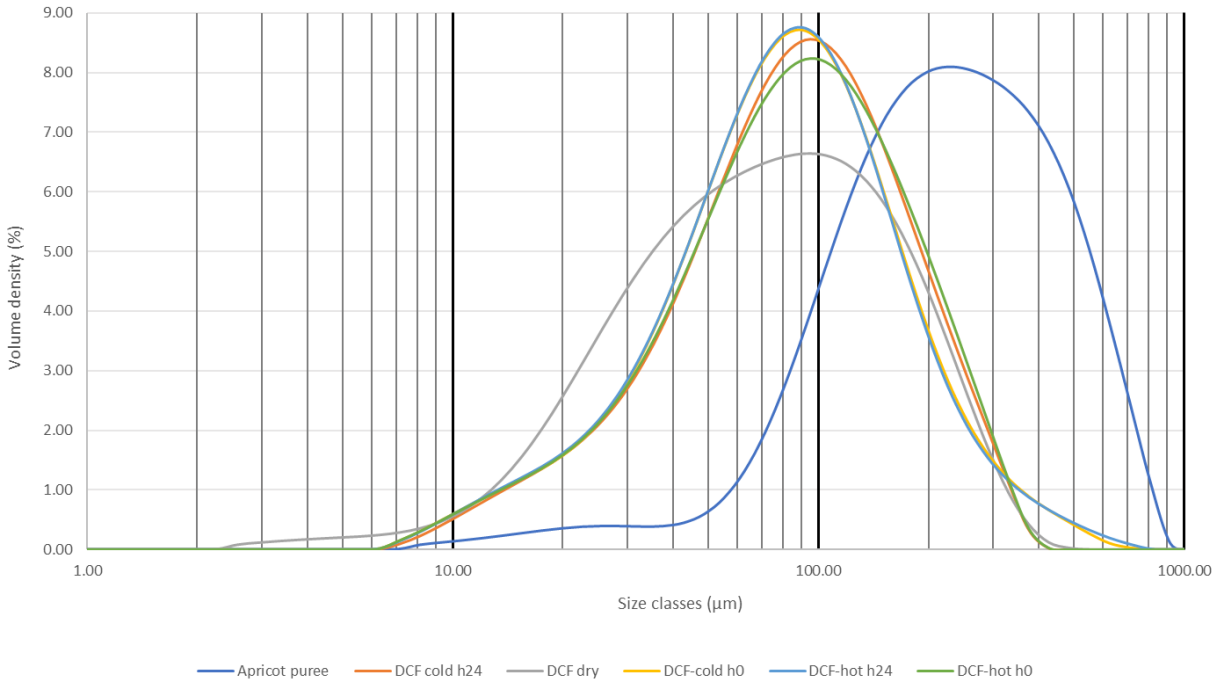

Figure 20. Particle size distribution of apricot and CF (with different exposure conditions to water)

It can be observed from the Span of the distributions that the particle sizes are less homogeneous in the case of CF dry due to the high difference between the dimensions of the smallest and the largest. CF dry also has the smallest particles in terms of D [4;3] µm and as can be expected because of the hydration there is a statistically significant increase with no difference between the other samples. There are slightly different statistical differences in the 50th percentile of the hydrated CF attributable to the uneven particle size of the original CF dry samples and not to an effective difference due to the treatment. Regarding the particle size of apricot puree, it shows the highest value for D [4;3] (Table 27). This measurement is largely influenced by the large insoluble parts, which can be attributed to the dietary fiber in the apricot puree (Table 27) and the intact pieces of apricot pulp.

3.3 A_w

Regarding water activity, no significant differences were observed in the emulsions produced with apricots (A) and those produced with water (W). In both types, the a_w reached a value of 0.99, regardless of the hydrated phase and the percentages of fiber and oil used. This a_w value is quite high, and therefore, if not properly treated (heat or preservatives), the a_w of the products is not a barrier against microorganism growth.

3.4 pH

The pH analysis reveals differences between the emulsions formulated with water and those with apricot (A). The results obtained from the pH analyses are reported in Table 28.

Table 28. Emulsion's pH with different continuous phases. Data are presented as means ± SD. Values within the same column marked with different lowercase letters are significantly different ($p \leq 0.05$).

CF (w/w)	Oil (w/w)	Water-based	Apricot-based
3%	30%	4.04 ± 0.01^{c}	3.43 ± 0.03^{ab}
	25%	4.11 ± 0.02^{d}	3.43 ± 0.03^{ab}
	20%	4.10 ± 0.01^{d}	3.42 ± 0.01^{ab}
4%	30%	4.03 ± 0.01^{c}	3.41 ± 0.02^{ab}
	25%	4.00 ± 0.01^{b}	3.39 ± 0.01^{a}
	20%	4.19 ± 0.02^{e}	3.42 ± 0.01^{ab}
5%	30%	3.96 ± 0.02^{a}	3.41 ± 0.02^{a}
	25%	3.96 ± 0.00^{a}	3.41 ± 0.03^{ab}
	20%	3.96 ± 0.00^{a}	3.47 ± 0.02^{b}

Between all samples, pH is primarily influenced by the dispersing phase rather than by the content of oil or fiber. In the water-based emulsions, the pH values ranged from 3.96 to 4.11, indicating that the concentration of CF has an effect. For the formulations with apricot puree, the pH was lower, with no statistical difference between samples: the lower average pH is due to the naturally present organic acids (

Table **26**).

3.5 Color

The emulsions were also assessed in terms of color to determine how different percentages of fiber or oil could affect changes in the coloration of the product using the ΔE to quantify the differences. The emulsions produced with water were compared to those containing different percentages of oil while keeping the fiber content constant (Table 29) Alternatively, the amount of oil was kept constant while varying the concentration of CF (Table 30).

Table 29. Color differences (ΔE) between emulsions with the same oil content but different CF concentrations.

Oil content w/w	Fiber content (w/w) comparison	Delta E	
		Water-based	Apricot-based
30%	5%-4%	1.40	3.25
	4%-3%	8.84	1.49
	3%-5%	10.08	4.22
25%	5%-4%	1.69	1.22
	4%-3%	6.60	2.35
	3%-5%	7.63	3.51

	5%-4%	3.24	1.65
20%	4%-3%	7.14	1.99
	3%-5%	10.26	3.54

Data highlight how CF content can influence the color with a major effect when emulsions with 3% are weighted with the other percentages, especially in water-based emulsions (Table 29). ΔE in apricot base emulsions has a lower value, meaning that the dispersant phase affects the final's product colour. When considering the emulsions produced with apricots and comparing them with equal fiber content, it can be stated that oil does not influence color, in this case (Table 30). Additionally, apricot can mask the color, overlaying the fiber effect. A similar situation can be observed by comparing emulsions with the same percentage of oil (Table 29).

Table 30. Color differences (ΔE) between emulsions with the same CF content but different oil concentrations.

Fiber content (w/w) comparison	Oil content w/w	Delta E	
		Water-based	Apricot-based
3%	30%-20%	1.57	1.01
	30%-25%	1.45	0.46
	20%-25%	2.58	0.67
4%	30%-20%	1.49	1.15
	30%-25%	1.49	1.21
	20%-25%	1.79	1.03
5%	30%-20%	1.44	1.68
	30%-25%	2.98	1.22
	20%-25%	2.47	0.57

The effect of oil content, given an equal amount of fiber Table 30, is shown to be more limited, with very low delta values, making the differences barely or not at all perceptible to the human eye (Mokrzycki & Tatol, 2011). It can be stated that the main factor influencing the final product's color is the amount of CF.

3.6 Phase separation

To evaluate the resilience to physical stress of the emulsions (Figure 21) phase separation was assessed by measuring the amount of oil separated from the emulsions compared to the initial oil content (Table 31).

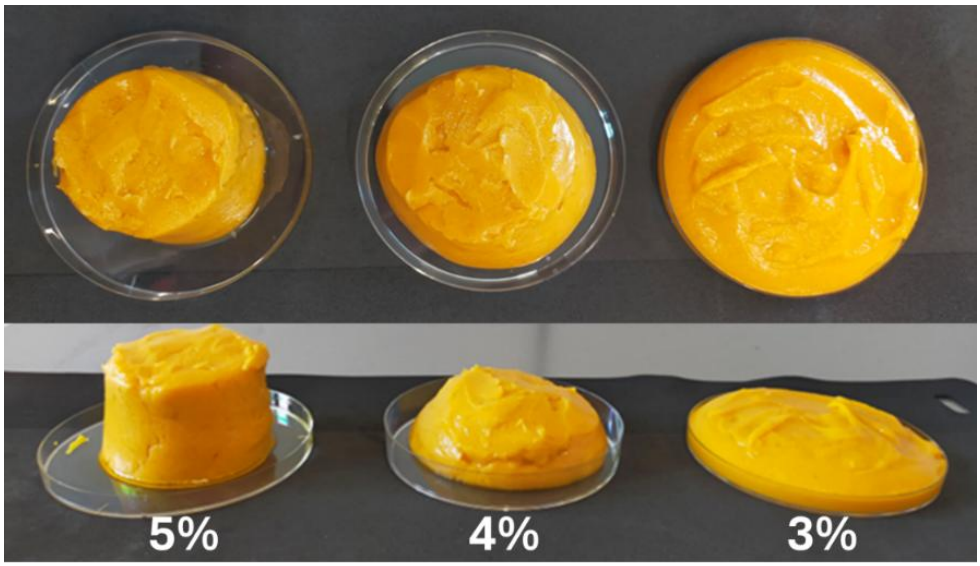

Figure 21. Apricot-based emulsions (20% oil w/w) with decreasing content of CF showed as % w/w.

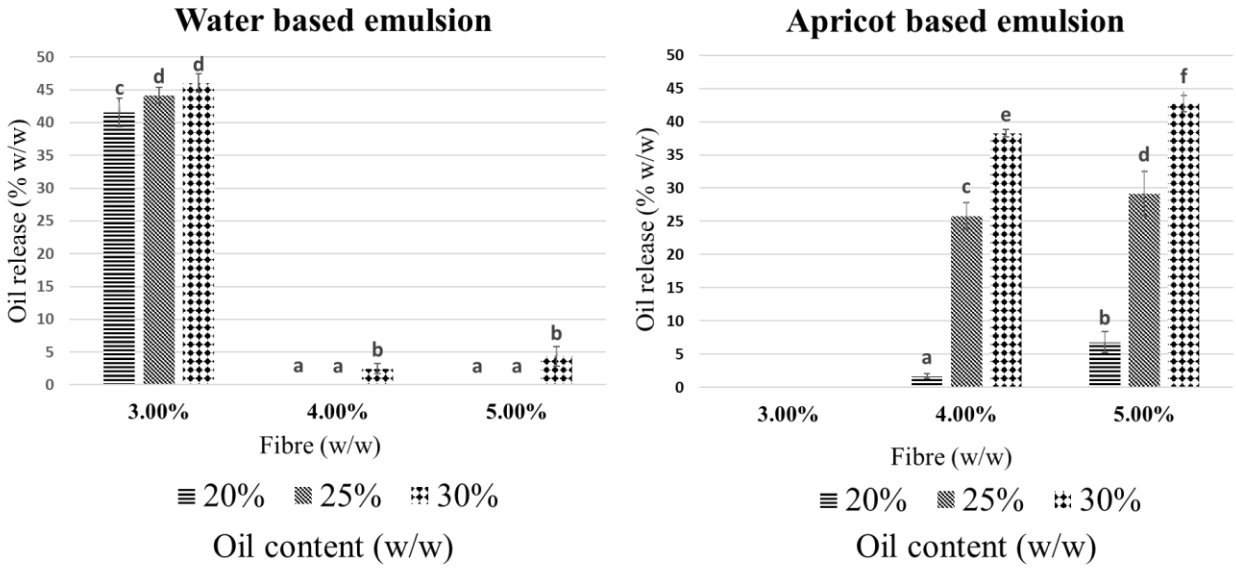

Figure 22: Oil released after centrifugation. Results are reported as a percentage (w/w) of the initial oil weight. Values with different lowercase letters for the same continuous phase are significantly different ($p \leq 0.05$).

Table 31. Oil release quantification on CF emulsions. Data were represented by means ± SD. Data with different lowercase are significantly different ($p < 0.05$).

	CF(w/w)					
	3%		4%		5%	
Oil (w/w)	**Water-based**	**Apricot-based**	**Water-based**	**Apricot-based**	**Water-based**	**Apricot-based**
20%	41.56 ± 2.17^{g}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	1.70 ± 0.39^{ab}	0.00 ± 0.00^{a}	6.81 ± 1.55^{c}
25%	44.16 ± 1.23^{gh}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	25.79 ± 1.99^{d}	0.00 ± 0.00^{a}	29.12 ± 3.41^{e}
30%	46.02 ± 1.39^{h}	0.00 ± 0.00^{a}	2.47 ± 0.77^{ab}	38.24 ± 0.58^{f}	4.34 ± 1.47^{bc}	42.67 ± 1.23^{g}

When treating water-based emulsion, the greatest phase separation occurred among all formulations containing 3% fiber, with more than 40% oil release. The result is due to insufficient CF amount, unable to create a stable structure, and a sufficiently tight network, achieved instead with 4% and 5% CF. Oil separation was also observed in emulsions containing 4% and 5% fiber with 30% oil, although to a lesser extent. In all other cases, no oil separation was noted. In water-based emulsions, it was found that an increase in CF concentration leads to a more stable emulsion as for Qi et al. (2021).
The behavior of apricot-based samples (Figure 21) despite having the same 3D structure had an opposite trend (Figure 22). The greatest oil separation occurred in formulations with higher fiber content, as well as more oil: with 4% fiber and 30% oil, 38% of the used oil separated, while with 5% fiber and 30% oil, 42% of the oil separated. A considerable separation also occurred with 4% and 5% fiber and 25% oil, with respective separations of 25% and 29%. The least separation was found in samples containing 4% and 5% fiber. In samples containing 3% fiber, however, no oil separation occurred. Overall result can be stated that In the Water-based emulsions, a higher percentage of fiber is required to prevent oil from separating from the emulsion. In contrast, for the A emulsions, the amount of fiber that maintained structural stability was exactly 3%. However, it is important to consider that if 3% fiber is combined with the fiber naturally present in apricots, the overall fiber percentage becomes similar to the value that provides stability in samples formulated with water. Consequently, a fiber content of 4-5% could be optimal for ensuring emulsion stability; however, exceeding this percentage may compromise structural stability, while not reaching it fails to guarantee maintenance of the structure. This consideration holds true as long as the oil percentage remains below 25%.

3.7 Rheological analysis

3.7.1 Frequency sweep

To categorize the type of emulsions produced, it is essential to define the stabilization mechanism that is activated during mixing. The CF used was not subjected to any high-pressure homogenization treatment, either during the manufacturing process at the production facility or during this study. High-pressure homogenization is known to separate individual cellulose nanofibrils, significantly increasing their surface area (Nomena et al., 2018). By contrast, treatments that reduce fiber particle size (like ball milling) without homogenization do not achieve this effect. These treatments may shorten fiber length, thereby reducing particle size without separating the nanofibrils (Jiang et al., 2022), and although this reduction in particle size is substantial (Jiang et al., 2022), it does not affect water-binding capacity (WBC) or oil-binding capacity (OBC). Additionally, such treatment decreases the fiber's insoluble fraction, negatively impacting both WBC and OBC. Therefore, it is necessary to

consider that the emulsion created through ingredient mixing alone preserves CF's original structure. Stabilization occurs through a hybrid mechanism between Pickering stabilization and physical stabilization, where a dense CF network forms, creating a three-dimensional structure that locks oil droplets in place (Qi et al., 2021). In this case, the primary stabilization mechanism is the formation of a three-dimensional network, which restricts the movement of oil particles within the structure, effectively reducing or eliminating oil mobility. The extraction process applied to the citrus pomace may significantly alter its structure (Liu et al., 2024). Given the pectin extraction treatment to which CF is subjected, it can be inferred that the cellulose structure is not identical to its native form. Furthermore, as the concentration of pectin decreases, an increase in fiber surface roughness has been observed (Jiang et al., 2022). The separated nanofibrils provide a weak level of Pickering stabilization, while the network prevents their aggregation by creating a physical barrier that also maintains the separation of electric charges. This repulsion between water and oil, facilitated by CF's water-adsorption capacity (Chen et al., 2023), functions similarly to a "wet sponge" that retains oil. The 18 emulsions produced with various combinations of fiber and oil were analyzed to identify their rheological properties. Each sample was examined in duplicate to compare the performances of the different formulations. Defining the flow curves (using rotational mode) was impossible because the samples were too rigid and compact. Therefore, oscillatory tests were conducted to obtain the parameters G' (elastic modulus) and G" (viscous modulus) to characterize the viscoelastic properties of the emulsions under examination. Specifically, amplitude sweep tests were performed to determine the linear viscoelastic region (LVER).

3.7.2 Viscoelasticity limit (LVER)

To better describe the differences in viscoelastic properties between the standard emulsion and the interactions between apricot fibers and CF, the linear viscoelastic region was measured Table 32.

Table 32. LVER real and suggested for the frequency sweep analysis. Data with different lowercase are significantly different ($p < 0.05$).

Water-based	CF (w/w)					
Oil (w/w)	3%		4%		5%	
	real	suggested	real	suggested	real	suggested
20%	0.03 ± 0.01^{a}	0.01	0.03 ± 0.00^{a}	0.01	0.03 ± 0.00^{ab}	0.01
25%	0.03 ± 0.00^{a}	0.01	0.04 ± 0.00^{ab}	0.01	0.04 ± 0.00^{b}	0.01
30%	0.03 ± 0.00^{a}	0.01	0.04 ± 0.00^{c}	0.01	0.16 ± 0.00^{c}	0.1
Apricot-based	CF (w/w)					
Oil (w/w)	3%		4%		5%	
	real	suggested	real	suggested	real	suggested
20%	0.40 ± 0.02^{b}	0.1	0.04 ± 0.00^{b}	0.01	0.02 ± 0.00^{a}	0.01
25%	0.37 ± 0.02^{ab}	0.1	0.03 ± 0.00^{a}	0.01	0.05 ± 0.00^{b}	0.01

30%	0.37 ± 0.01^{a}	0.1	0.03 ± 0.00^{a}	0.01	0.05 ± 0.00^{b}	0.01

As shown in To better describe the differences in viscoelastic properties between the standard emulsion and the interactions between apricot fibers and CF, the linear viscoelastic region was measured Table 32.

Table 32, the LVER values exhibit opposite trends in the two different dispersing phases. Specifically, the maximum LVER value for the water-based sample is observed in the formulation with 30% oil and 5% CF, whereas all other values range between 0.03 and 0.04. As the concentration of citrus fiber increases, the rigidity of the network also increases (Chen et al., 2023); at lower concentrations, the network remains more liquid, favoring oil release when subjected to centrifugation (Figure 22). The trend is reversed for the apricot fiber-based samples, where the highest LVER is observed in formulations containing 3% CF, which are also the only samples that did not exhibit oil release (Figure 22). This suggests that at low CF concentrations, a synergistic interaction with the apricot matrix is established. However, as CF concentration increases and the network structure becomes denser, the initial resilience of the structure is lost. This behavior can be attributed to the particle size of the apricot's insoluble compounds; particle size plays a crucial role in regulating interactions within complex systems like purees or fruit juices (Dahdouh et al., 2016). Similarly, the pectin in apricot puree may act as a binder with both the insoluble fiber from apricot and CF, reinforcing the network at 3% CF concentration (Dahdouh et al., 2016). As CF concentration rises, however, CF fibers increasingly bind with apricot components, reducing the number of hydrophobic groups available to bind oil (Julakanti et al., 2023). Higher CF concentrations also increase the dry matter content, and the high WBC of CF lends a visually more rigid and stable structure to the emulsion. However, due to the dispersed solids from apricot, the system cannot fully bind all the contained oil, resulting in a structure that is less resistant to external physical stress. Based on the results of the amplitude analysis and the determination of the LVER, frequency analyses were conducted on the samples under investigation. The resulting curves are shown in

Figure **23**, which enabled the identification of crossover points, providing a more precise characterization of each emulsion's resistance to stress (Figure 24).

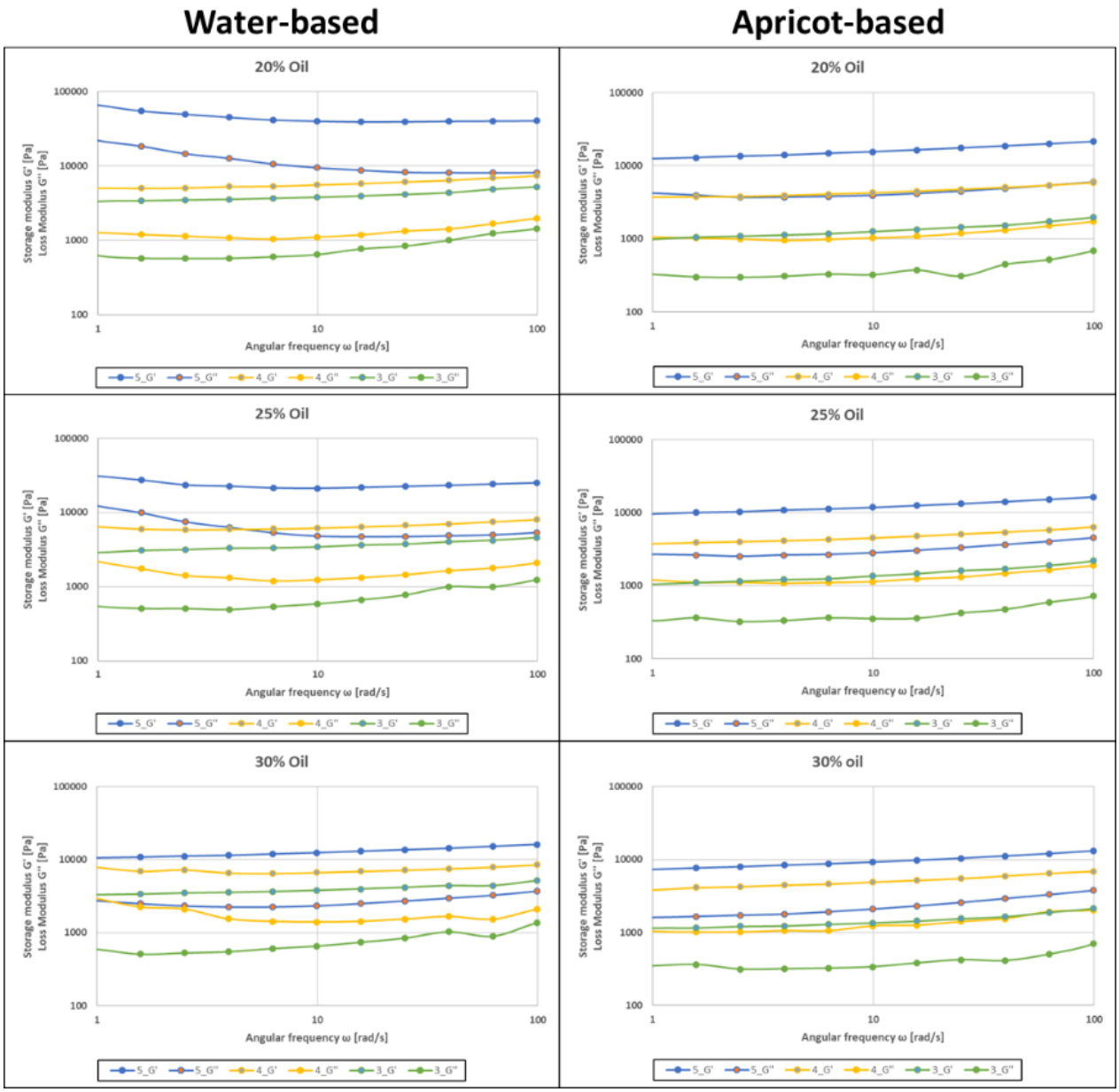

Figure 23. Frequency sweep test: comparison between emulsions with different continuous phases, CF, and oil concentrations.

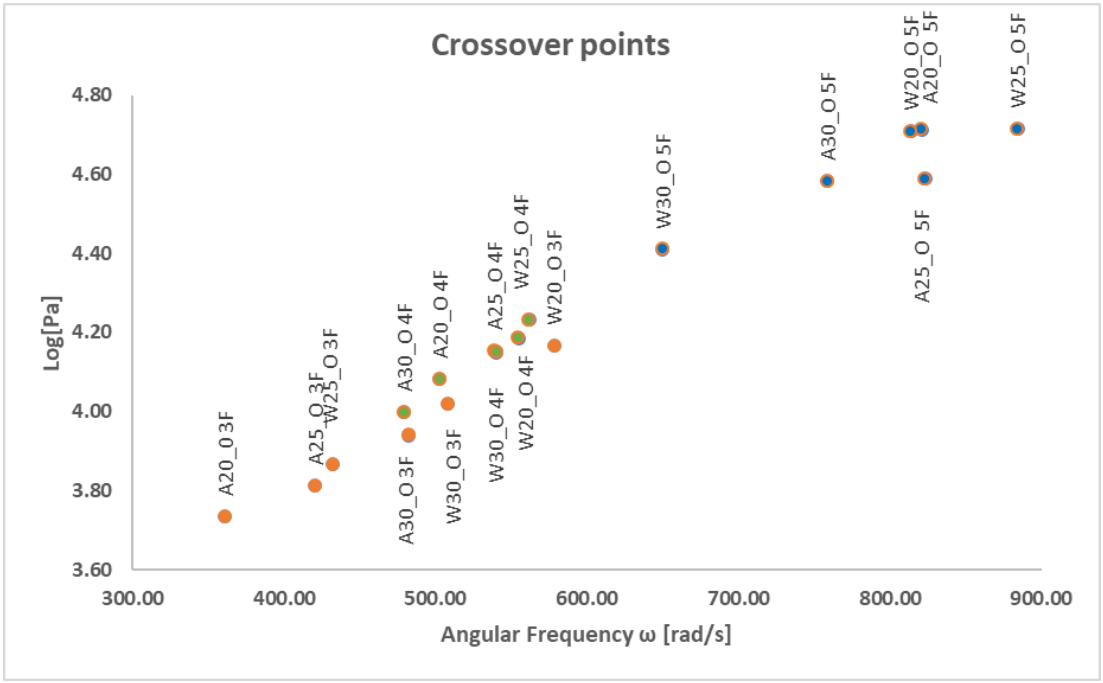

Figure 24. Crossover point of emulsion with different continuous phases (water "W" and apricot "A"), different oil concentration as percentage w/w (20_O, 25_O, 30_O), and CF concentration as percentage w/w (3F, 4F, 5F).

Figure 23 shows that varying CF or oil concentration across all samples does not significantly impact the material's viscoelastic properties. In all cases, the storage modulus G′ (indicative of elasticity) is greater than the loss modulus G″ (indicative of viscosity), reflecting an elastic, solid-like behavior without crossover within the observed range. When comparing water-based gels to their apricot-based counterparts with the same oil content, both G′ and G″ values are consistently higher in the water-based samples at equivalent fiber content. This suggests that structures formed in water are more rigid and exhibit a behavior closer to that of a solid. In contrast, in apricot-based samples, the dispersing phase destabilizes the network formed by CF. In the same dispersing phase, the most noticeable differences appear in samples with 5% CF comparing different oil concentrations. These differences, due to oil content, gradually diminish with decreasing CF levels until the values become nearly indistinguishable. This behavior can be attributed to the increased thickness of the interfacial layer and the densification and strengthening of the network formed by CF. Consequently, the 5% CF sample in apricot puree displays the highest rigidity within the same dispersing phase, likely causing the structure to appear stiffer. Over time, this rigidity may lead to an internal rearrangement of the structure and a slight release of oil when subjected to centrifugation. Generally, the upward trend of the curves, though slight, indicates the presence of a gelled structure (Zhang et al., 2024). The frequency curve analysis provides an alternative perspective on the results in Figure 22, suggesting that these two behaviors may stem from differing microstructural interactions. In the water-based samples, the network appears more cohesive and uniform since it is composed solely of CF, resulting

in a homogeneous particle size. With a stabilization mechanism that is a hybrid of Pickering and network stabilization (Qi et al., 2021), the oil droplets formed during the mixing phase remain trapped within the more uniform, rigid structure (

Figure **23**). By contrast, apricot-based samples exhibit a microstructure with significant particle size heterogeneity (Figure 20), as apricot contains larger particles. These suspended bodies may create discontinuities in the CF network, forming pathways through which oil escapes under centrifugation. The effect varies with CF concentrations: as shown in

Figure **23** and Figure 25, the 3% CF samples have the lowest viscosity and a less solid structure, which translates to greater microstructural mobility. In this case, following centrifugation, the CF network stabilizing the emulsion is not entirely constrained by the apricot's suspended solids, resulting in slight phase separation (image not shown). However, oil is not released because the network moves with the oil rather than remaining anchored to the apricot fiber. The emulsions with the same dispersing phase generally follow a similar trend across most points, indicating a stable structure (Figure 23): the higher the value of G', the more compact the product appears; the further the crossover point is, the greater the resistance over time. Therefore, it can be stated that there is a modification of the structure, but only with slight differences between the emulsions with the same dispersing phase. However, the curves for the emulsions formulated with apricot are consistently positioned lower than those with water, suggesting that they are structurally less stable compared to the latter. With 4% CF, the behavior in both dispersants is less discordant but the samples with water still exhibit a three-dimensional structure that proves to be more stable over time. 5% CF samples dispersed in water are characterized by an initially different structure, with particularly high elastic and viscous moduli. Notably, the water-based emulsion containing 5% fiber and 30% oil appears more like the samples with apricot. The samples with apricots are characterized by a weaker three-dimensional structure. Comparing cross-over point results with other studies (Chen et al., 2023; Yang et al., 2023) as they observed an increase in CF quantity brings to a thicker structure with a cross-over point at a higher angular frequency level. As Figure 24 shows there is a clusterisation between samples.

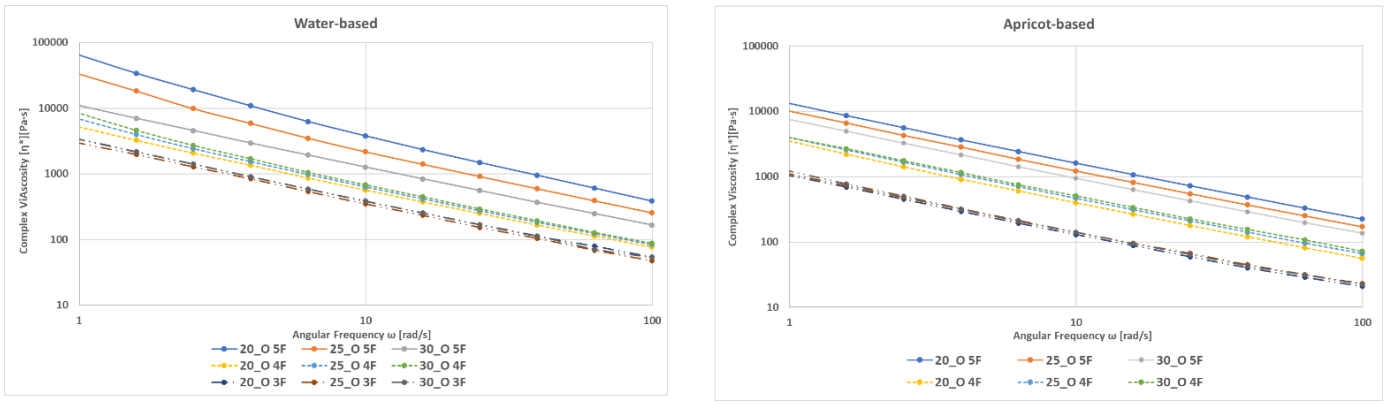

Figure 25. Complex viscosity comparison between emulsions with different continuous phases.

In all emulsions, complex viscosity decreases with increasing angular frequency, displaying a characteristic non-Newtonian shear-thinning behavior, even though flow curve measurements were not performed. Considering the gelled structure of the sample, it partially breaks down as the load increases indicating the previously stated behavior. As shown in Figure 25, the samples cluster based on similar complex viscosity values according to CF content, regardless of the continuous phase. The curves become increasingly similar as CF concentration decreases, eventually overlapping in the case of 3% CF, with greater differences observed at 5% CF. Additionally, when comparing different dispersing phases, apricot-based emulsions consistently show lower viscosity values at equivalent CF content. This may further indicate the disruptive effect of apricot puree on the CF network, reducing structural rigidity and increasing flowability.

4.Conclusions

The research conducted on citrus fiber and its application in fruit-based emulsions has yielded significant findings for the future development of functional foods. Studies demonstrated CF exhibits a high water adsorption capacity and serves as an effective emulsifying agent, showcasing varied behaviors depending on its concentration and the type of dispersing phase (water or apricot). In formulations containing water, it was noted that oil phase separation after centrifugation was more pronounced at lower fiber concentrations (3%). In contrast, apricot emulsions experienced the majority of oil separation at 4% and 5% citrus fiber concentrations. This opposing trend can be attributed to the larger particle sizes and differing composition of suspended solids in apricot, highlighting a significant matrix effect. While low concentrations of suspended solids can enhance stability, excessively high amounts may interfere with network formation. The analysis of the viscoelastic properties of the various systems confirmed that fiber is the primary ingredient influencing the viscosity and thickness of the emulsions. Notably, regardless of the continuous phase, the quantity of fiber (particularly at lower concentrations) has a more pronounced effect than oil content. At 3% CF, the results were most uniform; however, at 5%, the percentage decrease in the dispersing phase in favor of increased oil content resulted in less rigid samples as the presence of the fat phase increased. In conclusion, it can be affirmed that the fiber used is well-suited for the development and modulation of the consistency of fruit-based emulsions and can be effectively employed to formulate new functional products with high lipid content.

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Chapter 6

"Network-based structure for developing emulsion-filled hydrogels in food products for dysphagia management"

Abstract

This study explores the creation of a novel emulsion-filled hydrogel (EFH) designed to provide targeted nutrition and functional textures for individuals with dysphagia. Leveraging underutilized citrus fiber byproducts, apricot puree, cold-pressed hazelnut oil, and hazelnut press cake, the research highlights sustainable approaches to food innovation. Citrus fiber, rich in dietary fiber, was analyzed for its capacity to stabilize emulsions, while its synergy with pectin provided structural reinforcement. Apricot puree served as a dispersing medium, with its intrinsic sugars and phenolic compounds enhancing texture and providing oxidative protection. Citrus fiber's network-forming ability stabilized the oil phase, while pectin added a secondary layer of gelation. Hazelnut oil, a source of α-tocopherol, demonstrated stability during processing, retaining its antioxidant properties. Texture analysis confirmed the hydrogel's suitability for dysphagic individuals, with a structure that softened under mastication while maintaining integrity for safe swallowing. This research underscores the potential of combining sustainable ingredients to develop nutrient-dense, texture-modulated food products tailored for vulnerable populations. The findings offer valuable insights into the interplay between fiber networks, oil stabilization, and matrix effects, paving the way for future innovations in functional and therapeutic food applications.

1.Introduction

Citrus fruits constitute the most extensively cultivated category of fruit globally. Their primary application lies in juice extraction, with a proportionally large amount of biowaste generated by the citrus-processing food industry (Zayed et al., 2021). Given the scale of global citrus production, this leads to a waste of a sources of many bioactive molecules such as volatile oil, vitamins, flavonoids, coumarin/furanocoumarins and carotenoids (Fierascu et al., 2019) or polyphenols (Kaur et al., 2024). Citrus peels, even after the extraction of essential oils, remain a rich source of dietary fibers, both soluble and insoluble, offering diverse applications (Li et al., 2024). The fibers extracted can be incorporated into different products with many technological applications in the pharmaceutical (Bostancı et al., 2022; Eliaz et al., 2007) packaging (Roy et al., 2023) and functional food making, mainly added to food preparations to help lower the glycaemic index (Picot-Allain et al., 2022). Among these applications, the most prevalent use for orange peel is as a substrate for pectin extraction (Adetunji et al., 2017). Pectin is a polysaccharide having galacturonic acid as a monomer. It is classified as a soluble dietary fiber and plays different roles in the food industry, particularly as a gelling and thickening agent (Christiaens et al., 2016; Padma Ishwarya et al., 2022) but also as an emulsifier, especially in combination with protein (Du et al., 2021). After pectin extraction, the remaining material is the insoluble fraction of dietary fiber. This residue is primarily composed of fibers and other structural components, such as cellulose, hemicellulose, and lignin (He et al., 2023). This byproduct has limited use in the food industry, though recent years have seen a surge in research dedicated to chemically and structurally characterizing these fibers (Lundberg et al., 2014; Yang et al., 2023; Zhu et al., 2023). Additionally, the insoluble fraction appears to play a significant role in fat absorption, offering promising applications as a lipid absorption regulator (Yu et al., 2023) with the potential to also regulate lipid-soluble compounds. Gaining a deeper understanding of these properties may open new avenues for their use, especially in light of the increasing demand for sustainable and natural ingredients. Hazelnuts are known for their positive impact on human health (Michels et al., 2018), primarily due to their high content of alpha-tocopherol and their fatty acid profile, which is notably rich in polyunsaturated fatty acids (Taş & Gökmen, 2015). The beneficial effect of tocopherol is linked to its antioxidant capacity (Tey et al., 2011), which should be preserved as much as possible during industrial processing to maximize its effect on the consumer. By using the panel, we can add an important source of protein due to the concentration effect that follows the extraction (Panzanini et al., 2024). Apricots, given their known abundance in Italy (Bassi & Selli, 1990), were instead used as a representative matrix for developing the emulsion. The low pH and the presence of fibers have a significant effect on the properties of citrus fiber and the emulsion in general

(Chapter 4). This research aimed to develop a food product, an emulsion-filled hydrogel (EFH) designed specifically to meet several key criteria: it should be nutrient-dense, easy to prepare and consume, composed of readily available ingredients, and suitable for elderly individuals and those suffering from dysphagia. These groups are considered vulnerable and with overlapping dietary needs (Sodhi et al., 2024), require a diet rich in antioxidants and high-quality calories (Homem et al., 2020), ideally not derived from simple sugars. The developed product is envisioned as a cream or solid gel that satisfies nutritional and practical requirements. The citrus fiber's high water absorption capacity in combination with the emulsifying effect of protein from partially defatted cake (DFC) creates a synergy ideal for formulating highly stable food products. This functional characteristic is particularly beneficial for achieving desirable textures and enhancing the nutritional profile of food applications tailored to these sensitive populations.

2.Materials and methods

2.1 Raw materials, emulsion, and emulsion-filled Hydrogel (EFH) preparation.

The raw materials used in the emulsions are citrus fiber “CF” (Aglufiber FA, JRS Silvateam Ingredients S.r.l. Bergamo, BG, Italy) as emulsifier, apricot puree from Lucgel s.r.l (Spoleto, Perugia) as the continuous phase, hazelnut partially defatted cake (DFC) as an additional emulsifier, and the cold-pressed hazelnut oil as the dispersed phase both were kindly provided by Pariani S.r.l. (Givoletto, Torino, Italy). As a gelling agent for the emulsion-filled hydrogel making 4 different types of low methoxyl pectins were used, respectively, two standard types (LM-12 and LM-18) and two low methoxyl amidated variants (LMA-10 and LMA-20) kindly gifted by JRS Silvateam Ingredients S.r.l. Emulsions and EFH were prepared using either water (W) or apricot puree (A) as the dispersant phase; the ingredients were mixed and emulsified with an IKA EUROSTAR 40 mixer (IKA-Works, Wilmington, North Carolina, USA) at 1200 rpm for 15 minutes at room temperature (T_{amb}). For EFH preparation, refer to the recipe in Chapter 4.

2.2 Characterization analysis

The moisture, ash, protein, and fat content of apricot and CF were assessed using the official AOAC methods 935.29, 942.05, 2001.11, and 948.22 respectively. Soluble dietary fiber was quantified with K-TDFR-200A Kit (Megazyme, Wicklow, Ireland) according to the AOAC method 991.43. Identification and quantification of sugars and organic acids were performed using HPLC analysis

Table 33. Pectins' gelation optimal pH range. pH of a pectin solution 1% w/w.

Pectin	Optimal pH	1% w/w solution
LM 12	3.0-3.5	3.5-4.5
LM 18	3.0-3.2	3.5-4.5
LMA 10	3.2-4.0	4-5
LMA 20	3.2-4.2	4-5

2.3 Sugars

Sugars were identified and quantified with the following method. Respectively 4 g of the sample was dissolved in 16 g of water. The mixture was stirred to ensure the complete dissolution of sugars present in the sample. The sample was then transferred into centrifuge tubes, centrifuged, and placed into vials for HPLC analysis. The diluted sample was filtered using a 0.45 µm mesh filter. To quantify sucrose, a portion of the filtered sample was subjected to inversion. Specifically, 5 mL of the filtrate was taken and diluted in 50 mL of water, to which 5 mL of 32% v/v HCl was added. The mixture was stirred for 15 minutes at 70°C and then neutralized with NaOH. The sugars in the sample were analyzed via HPLC equipped with a Jasco PU-4180 pump (Jasco, Halifax, Nova Scotia, Canada), with an Aminex HPX-87C column (300 x 7.8 mm, BIO-RAD, Hercules, California, U.S.), conditioned in an oven at 80°C. The mobile phase was: 100% water, with a flow rate of 0.6 mL/min and a runtime of 35 minutes. A refractive index detector (RI2031 plus, Jasco, Halifax, Nova Scotia, Canada) was employed in combination with the Jasco LC-Net II/ADC communication module (Jasco, Halifax, Nova Scotia, Canada). Data was analyzed using ChromNAV Control Center software (Jasco, Halifax, Nova Scotia, Canada). The quantification of sugars was carried out using a calibration curve that was previously established by injecting standard solutions.

2.4 Tocopherols

2.4.1 Oil extraction:

For the solid samples, five grams were weighed into Falcon tubes and 25 mL of n-hexane (Sigma Aldrich, Milan, Italy) was added. The tubes were then covered with aluminium foil to prevent light exposure and left in an orbital incubator (SKI 4 ARGO LAB) at 25°C for 1 h at a shaking speed of 180 rpm. The tubes were centrifugated at 3000 g, at 15°C for 15 minutes (Thermo Scientific SL16R Centrifuge, Thermo Fischer Scientific, Waltham, USA). Supernatants were filtered through pleated paper filters (Whatman No. 595) inside flasks, placed in the freezer to cool, and then covered with aluminum foil. Oil was collected after letting hexane evaporate under vacuum. The oil extracted was diluted with the mobile phase and injected. Cold-pressed oil samples were directly diluted into the mobile phase, filtered with paper filters (Whatman No. 595), and injected.

2.4.2 HPLC analysis:

Analyses were performed according to Calvo et al. (2011) procedure with an HPLC system composed of a Perkin Elmer (Norwalk, CT, USA) 200 Series pump equipped with a Perkin-Elmer 650-10S fluorescence detector, Jasco LC-Net II/ADC (Oklahoma City, OK, USA) communication module and ChromNAV Control Center as a software. As an injection column LiChrosorb Si60-5 column 250 mm×4.6 mm, 5 μm (Supelco, Bellefonte, PA, USA) was used, the injected volume was 20 μL, and the mobile phase was a hexane:isopropanol:ethanol (98.5:1:0.5) with a flow of 0.6 mL/min. The fluorescence detector was set at 290 nm excitation and 330 nm emission wavelengths. Each run had a duration of 25 min. The homologues α; γ; β; and δ were identified and quantified in comparison with commercial standards (Sigma Aldrich, Milan, Italy). The results were expressed as mg/100g of oil and mg on 100g of product.

2.5 pH

The pH evaluation of the emulsions was conducted on 10 g of sample in its original form, dissolved in 90 mL of distilled water. The pH was measured using the sensION™+ PH3 pH meter (Hach Company, Loveland, Colorado, USA).

2.6 Total phenolic content

The analysis was conducted following the procedure reported by (Bassani et al., 2020) using a micro-volume version of the Folin's assay. The sample's absorbance was read at 750nm using a spectrophotometer, Jasco V730 (Jasco Europe S.r.l., Cremella, Lecco, Italy).

2.7 Water binding capacity (WBC), oil binding capacity (OBC), and swelling.

Swelling power, water binding capacity (WBC), and oil binding capacity (OBC) were determined in sixfold replicates according to the method described by Wang et al. (2014) with appropriate modifications. Approximately 0.5 g of CF was weighed into a 50 ml Teflon tube and 25g of water or oil was added. The lid was tightly screwed, and the mixture was heated in a water bath at 92.5 °C for 30 min with regular shaking to measure the swelling (HOT samples). The analysis was also performed using the same technique but with the water bath set at room temperature (COLD). After shaking, the samples (HOT or COLD) were divided into two equal groups. In one sample, the supernatant was immediately separated (0h), while in the other, it was left in contact for 24 hours (24h) to assess any differences. Due to the varying exposure times, it was possible to assess any additional absorption in the hours following preparation. All the samples were centrifugated at 13,000 g in 10 minutes. After

supernatant removal, the deposit was weighted, and swelling (0h; 24h), WBC (0h; 24h), and OBC (0h; 24h) were calculated with equation (1):

$$Swelling, WBC\ and\ OBC = \frac{M_2 - M_1}{M_0} \quad (1)$$

M_0 represents the weight of the sample (g), M_1 is the weight of the centrifuge tube (g), and M_2 is the combined weight of the centrifuge tube and the sample after separating the supernatant (g).

2.8 Particle size distribution

The particle size distributions were determined using a Mastersizer 3000 laser granulometer (Malvern Panalytical, Malvern, UK) with an effective measurement range of 2000–0.02 μm. The size distribution analysis was performed at 25°C. Dry CF was analyzed using the Aero S dispersion unit, and hydration properties were assessed with the Hydro MV attachment. The hydrated samples (0h, 24h, COLD, and HOT) were stirred with the Hydro MV at 1000 rpm, with measurements taken after 1 minute. For CF, apricot puree and DFC the refractive index was set to 1.460 (Jiang et al., 2022). Deionized water was selected as the dispersant, with a refractive index of 1.330. The lower and upper obscuration limits were set to 10–20% for the wet dispersion unit and 1–10% for the dry dispersion unit. An obscuration value of around 15% was used for wet dispersion and 5% for dry units. Every sample was assessed 10^{th} DV(10), 50^{th} DV(50) and 90^{th} DV(90) percentile, SPAN, D[4;3], and Specific surface area (m^2/Kg).

2.9 Phase separation quantification.

The resistance of emulsion to phase separation was assessed through centrifugation, following the Gestranius et al. (2017) method with some modifications. Approximately 2g of emulsion was placed into a 2ml Eppendorf tube and then centrifuged at 4000 g for 2 minutes. After centrifugation, the tubes containing the emulsions were overturned onto absorbent paper to facilitate oil release and then weighted. The oil loss was expressed as a percentage of the initial oil weight. The calculation was performed using the following equation (2):

$$\left(\frac{Gross_{before} - Gross_{after}}{sample\ weight * oil\ percentage\ w/w}\right) * 100 \quad (2)$$

2.10 Peroxide value (PV)

Peroxide number, as an indication of the degree of oxidation of fat, was measured according to AOAC 965.33 method.

2.11 Texture profile analysis (TPA)

Texture Profile Analysis (TPA) was performed using a Texture Analyzer (PerkinElmer Perten TVT 6700, Waltham, Massachusetts, US), equipped with a 75 mm flat probe (673075). Samples were 22 mm in height facing a 20% relative compression. The pre-test speed was set to 1 mm/s, the test and post-test speed was set to 3 mm/s. The maximum force reached during the first 20% compression is defined as "Firmness". "Springiness" represents the sample's elasticity, its ability to return to its original shape after the first compression. It is measured as the ratio between the compression distance of the second peak (X2) and the compression distance of the first peak (X1). "Resilience" is expressed as the ratio of the recovery work of the first peak to the compression work of the same peak. "Cohesiveness" is the ratio of the area under the second peak (A2) to the area under the first peak (A1). "Gumminess" is the product of Firmness and Cohesiveness, used to describe semi-solid foods, which are soft but resistant. "Chewiness" is the product of Gumminess and Springiness, is used for solid foods that require prolonged chewing.

2.12 Tribological properties

The friction coefficient associated with each EFH was measured using a tribo-cell attached to a Modular Compact Rheometer MCR 302 (Anton Paar, Gratz, Austria) paired with a stainless-steel ball-on-three-PDMS-plates geometry at 25°C. The EFH samples were equilibrated at 25°C for 1 h before analysis. Sections of the sample, each 10 mm in length, were used for the measurements. The parameters were set as follows: 20 min duration in log mode, constant applied force of 5 N, and sliding velocity varying from 0.0001 to 1,000 mm/s. The friction coefficient was plotted versus sliding speed in the Stribeck curve.

2.13 Statistical analysis

All experiments were performed at least three times and analyzed in triplicate. The results obtained for each sample were evaluated and ranked using a one-way analysis of variance (ANOVA) followed by Duncan’s multiple range post-hoc test for means discrimination ($p < 0.05$). Statistical analyses were executed via the IBM SPSS Statistics 27 software (SPSS Inc., Chicago, IL, USA).

3.Results and discussion

3.1 Samples proximate composition

The proximate composition characterization (Table 34) was conducted on DFC and apricot puree, allowing for the outlining of the properties and attributes of these two raw materials.

Table 34. Proximate composition of DFC and apricot puree. Not detected (n.d.)

	DFC		Apricot puree	
	g/100g	**g/100g of d. m.**	**g/100g**	**g/100g of d. m.**
Moisture	3.06 ± 0.03	\	89.84 ± 0.05	\
Dry matter	96.94 ± 0.03	\	10.16 ± 0.05	\
Ashes	4.03 ± 0.01	4.15 ± 0.01	0.47 ± 0.02	4.58 ± 0.17
Protein	29.11 ± 0.36	30.03 ± 0.37	0.59 ± 0.02	5.83 ± 0.20
Total Fats	37.48 ± 0.20	38.66 ± 0.21	n.d.	n.d.
Total Sugars of which:	5.00 ± 0.13	5.17 ± 0.13	7.43 ± 0.07	73.19 ± 0.65
Glucose	0.80±0.01	0.83±0.01	3.91±0.05	38.53±0.45
Fructose	0.27±0.00	0.28±0.00	2.60±0.03	25.55±0.34
Sucrose	3.93±0.13	4.06±0.13	0.35±0.03	3.49±0.29
Sorbitol	n.d.	n.d.	0.57±0.02	5.62±0.15
Insoluble fibres	14.17 ± 0.24	15.08 ± 0.25	0.45 ± 0.01	4.42 ± 0.07
Soluble fibres	2.64 ± 0.05	2.72 ± 0.05	0.67 ± 0.10	6.62 ± 1.02
pH	6.14 ± 0.01	\	3.47± 0.01	\

Table 34 shows that the DFC has very low moisture content, resulting in a high amount of dry matter. The main constituents are lipids and proteins. Total dietary fiber is predominantly made of insoluble fiber almost 5 times more than soluble fiber. Such a high content of protein and fiber is the result of the oil's cold press extraction process (Panzanini et al., 2024). The apricot puree is characterized by a low dry matter content (10.16 ± 0.05%) in line with Voi et al. (1995), and significantly higher moisture than the DFC but this is in line to be the dispersant of the emulsion system. The main puree's components are sugars, this puree shows some crucial differences compared to other apricots' sugar profiles (Levent & Alpaslan, 2018); it contains no sucrose and sorbitol, two of the four main sugars that can be found in such a fruit (Bassi & Selli, 1990). Moreover, the sugar concentration is also low compared to others and the previously used apricot at Chapter 5. The other components as ashes, protein, insoluble, and soluble fibers are present in minor quantities between 0,67 – 0,45 g/100g, lipids were not detected. The pH of a 10% solution w/w is 3.47 ± 0.01 thanks to the natural presence of organic acids (Aider & de Halleux, 2008). The high acidity will be the major factor defining the pH of apricot-based emulsions and EFH in this study.

3.2 WBC E OBC

The water binding capacity (WBC) and oil binding capacity (OBC) were determined both with different contact conditions, hot (90°C) and cold (25°C) temperatures, with varying times of contact, h_0 (no rest after shaking) and h_{24} (after 24h of contact), to evaluate the influence that time and temperature have on these two properties (

Table **35**). The analysis was performed individually on DFC, CF, and three combinations. In the CF:DFC mixtures, the amount of CF was kept constant while the DFC content was decreased (1:1, 2:1, 4:1).

Table 35. Oil binding capacity (OBC), and water binding capacity (WBC) results. Values marked with different lowercase letters are significantly different ($p \leq 0.05$).

			DFC	CF	CF:DFC 1:1	CF:DFC 2:1	CF:DFC 4:1
OBC	**Cold**	**h_0**	2.25±0.05^{a}	2.92±0.23^{fg}	2.56±0.04^{bcd}	2.80±0.14^{efg}	2.65±0.11^{cde}
		h_{24}	2.27±0.11^{a}	3.36±0.37^{hi}	2.54±0.11^{bcd}	2.73±0.09^{defg}	2.59±0.13^{bcde}
	Hot	**h_0**	2.44±0.05^{abc}	3.56±0.19^{il}	2.70±0.09^{def}	3.19±0.18^{h}	2.73±0.07^{defg}
		h_{24}	2.40±0.06^{ab}	3.70±0.14^{l}	2.96±0.03^{g}	2.94±0.07^{g}	2.77±0.12^{defg}
WBC	**Cold**	**h_0**	3.44±0.14^{a}	19.30±1.30^{i}	10.05±0.75^{ab}	12.95±0.42^{de}	12.23±0.19^{cd}
		h_{24}	3.60±0.28^{a}	19.91±1.22^{i}	11.18±0.16^{bc}	14.05±0.76^{ef}	12.78±1.55^{de}
	Hot	**h_0**	4.04±0.23^{a}	19.93±0.32^{i}	10.35±0.62^{b}	13.85±1.37^{e}	16.14±0.36^{gh}
		h_{24}	4.45±0.31^{a}	20.41±0.79^{i}	11.86±0.15^{cd}	16.84±0.76^{h}	15.24±1.51^{fg}

Table **35** shows DFC has a moderate affinity for both oil and water with a slightly better WBC than the OBC (Ulbrich & Flöter, 2014). Different conditions to which DFC was exposed did not affect retention properties. In terms of OBC, no significant differences were found between cold and hot analyses, nor were any differences observed between the contact time at zero (h0) and at 24 hours (h24) and the same for WBC. We can consider the water retention capacity of DFC underestimated, as CF contains no fats and has a very low moisture content (8.25 ± 0.03%), whereas DFC has an oil content of 37.48 ± 0.20%, which limits its further absorption and may act as a barrier to water uptake. Comparing CF with DFC, we observe that OBC values are higher in DFC, indicating a greater affinity of the fiber for oil. As shown in Table 34, DFC contains a high protein content but low fiber, as well as a high fat content, whereas CF primarily consists of insoluble fiber, with cellulose and hemicellulose as its main components (Lundberg et al., 2014). Cellulose, due to its structure and charge-compensating ability, enables effective oil retention, while hemicellulose, despite being

insoluble, has a high affinity for water. Its presence within CF allows for a remarkably high water-holding capacity (He et al., 2023). This highlights the fiber's extremely high capacity to retain water, indicating materials that create a highly hydrated weak hydrogel (Sze Wei et al., 2024). In the OBC of the fiber, an increase is observed from the contact time h0 to h24, both in the cold and hot analyses while WBC stays stable at all conditions denoting a minor effect of the contact condition on the main property of CF. Subsequently, it was decided to analyze the type of interaction that could arise from the combination of DFC and fiber within the same dispersing phase. As observed in Table 35, the OBC trend values of the three combinations vary compared to the individual ingredients. Previously, both CF and DFC showed no statistically significant differences in WBC, but now, with heat applied to the CF:DFC 2:1 and CF:DFC 4:1 samples, this becomes a distinguishing factor, leading to an increase in WBC. Heat likely promotes DFC dispersion, allowing for more contact points with CF and thus enhancing performance. If the amount of DFC decreases, both WBC and OBC improve, though not proportionally, as the 2:1 combination outperforms the 4:1 ratio in hot samples. This could indicate a competitive interaction, where DFC competes for the binding sites in CF that retain water, reducing CF's water-binding properties. As DFC decreases, WBC increases, especially when heat treatment at sufficient temperatures allows for the dissolution of pectin residues, increases fiber mobility, and expands its contact surface with the dispersing phase.

3.3 Particle size

3.3.1 EFH ingredients particle size

To better understand the behavior of the ingredients and their interactions following the WBC and OBC analyses, it was decided to investigate particle size and particle distribution. This distribution can influence solubilization behavior, rheology, and mechanical properties, and more (Jiang et al., 2022). The particle distribution was analyzed for apricot puree, DFC (both hot and cold, at 0 and 24 hours), fiber (cold, at 0 and 24 hours), the three different combinations of CF:DFC, and apricot-based

emulsions. The following figure (Figure 26) and table (Table 36) presents a comparison of the distribution among the puree, DFC, and fiber, both as a graph and as numerical values:

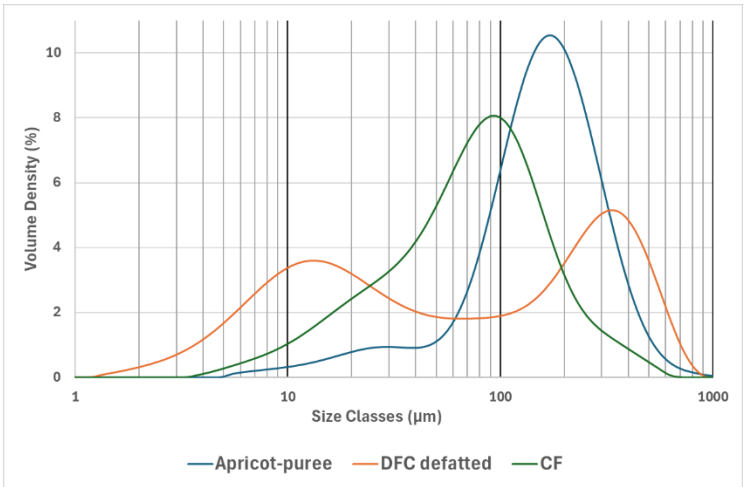

Figure 26. Particle size distribution of EFH ingredients.

Table 36. Particle size analysis results for EFH ingredients. Values in the same column marked with different lowercase letters are significantly different ($p \leq 0.05$).

Samples	Span	SSA (m²/kg)	D [4;3] (µm)	Dv(10) (µm)	Dv(50) (µm)	Dv(90) (µm)
Apricot-puree	1.67±0.02^{a}	64.04±0.26^{a}	180.86±2.49^{b}	57.66±0.27^{b}	160.39±0.57^{b}	324.99±4.56^{b}
Defatted DFC	6.80±0.15^{c}	319.50±2.76^{c}	154.61±1.58^{b}	6.90±0.05^{a}	61.80±1.10^{a}	426.80±4.44^{c}
CF	2.28±0.01^{b}	139.30±0.44^{b}	96.41±0.18^{a}	18.97±0.08^{a}	76.27±0.10^{a}	192.52±1.01^{a}

By comparing the numerical values in Table 36 with Figure 26, it can be observed that the DFC exhibits the highest span, indicating the broadest and most heterogeneous particle distribution. Compared to other samples, it contains both the largest and smallest particles. To ensure accuracy, it was analyzed in a defatted state to prevent oil from clumping particles together, which would otherwise make them appear larger than their actual size.

Due to the high concentration of particles between 1 and 20 µm, DFC also shows the highest Specific Surface Area (SSA), which is inversely proportional to particle size. Since DFC has been used in EFH as an emulsifier with stabilizing effects, its large SSA driven by the fraction of smaller particles (with 10% of total particles under 6.90 µm) enables it to interact with a significant number of particles. This high level of interaction positively influences system stability (Binks & Lumsdon, 2001). The apricot puree demonstrates a narrower distribution with the most uniform particle sizes, as it has the lowest span (1.67 ± 0.02). The fiber sample's homogeneity is not significantly different from that of the apricot sample, but it has the lowest D(4,3) value. Furthermore, when considering particles with the largest dimensions represented by Dv(90) the fiber sample exhibits lower values than the others.

3.3.2 DFC responses to treatment

Given the importance of particle size in influencing emulsion properties, the swelling capacity of DFC was evaluated (Figure 27) under various conditions of water contact. This was done to simulate DFC exposure in water at room temperature and under thermal treatment, using temperatures and times comparable to those required for emulsion and EFH preparation.

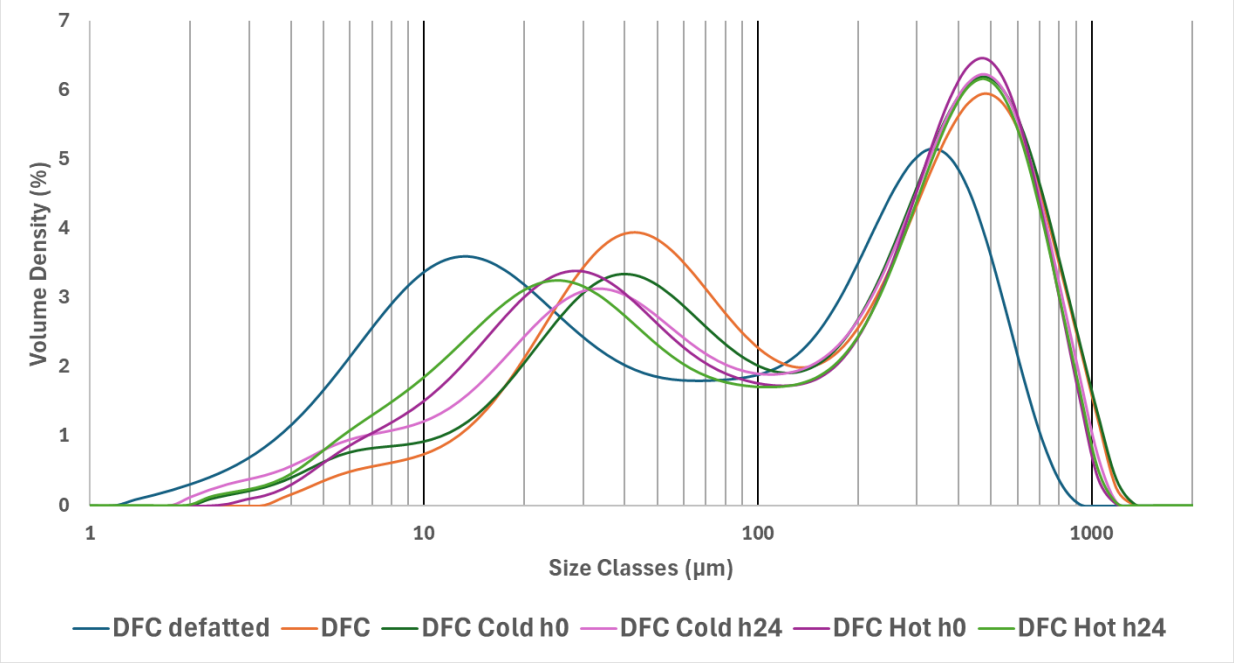

Figure 27. Particle size distribution of DFC with different exposure conditions to water.

Table 37. Particle size analysis of DFC with different water exposure conditions. Values in the same column marked with different lowercase letters are significantly different ($p \leq 0.05$).

Samples	Span	SSA (m^2/kg)	D [4;3] (µm)	Dx (10) (µm)	Dx (50) (µm)	Dx (90) (µm)
DFC	3.84 ± 0.07^{b}	113.27 ± 1.68^{a}	266.03 ± 3.60^{bc}	21.57 ± 0.33^{e}	166.51 ± 3.77^{b}	660.33 ± 9.31^{b}
DFC Cold h_0	3.39 ± 0.14^{a}	140.53 ± 3.44^{b}	274.05 ± 11.54^{c}	17.60 ± 0.44^{d}	192.66 ± 14.47^{c}	668.84 ± 24.75^{b}
DFC Cold h_{24}	3.64 ± 0.24^{b}	174.67 ± 4.67^{d}	256.34 ± 7.35^{a}	13.38 ± 0.40^{b}	171.57 ± 13.93^{b}	635.47 ± 10.67^{ab}
DFC Hot h_0	3.77 ± 0.10^{b}	154.80 ± 3.72^{c}	249.62 ± 8.38^{ab}	14.06 ± 0.31^{c}	160.85 ± 7.17^{ab}	620.22 ± 21.59^{a}
DFC Hot h_{24}	4.18 ± 0.04^{c}	182.27 ± 2.08^{e}	244.70 ± 7.42^{a}	11.75 ± 0.12^{a}	145.91 ± 3.71^{a}	622.16 ± 20.36^{a}

In Figure 27, the particle distribution curve of defatted DFC has been included to provide a benchmark against other particle distribution images. Instead for measuring it has been used the unmodified DFC to accurately represent the realistic swelling behavior that it might undergo under the selected conditions. Table 36 and Table 37 show that the defatted DFC deviates from the DFC as is, due to the presence of oils that increase the average dimension and the stickiness between particles, especially between the smallest ones. It exhibits the highest span and specific surface area (6.80 ± 0.15 and

319.50 ± 2.76, respectively), indicating a more heterogeneous and broader particle distribution, and a bigger presence of smaller particles. The treatments, whether hot or cold, have a low effect on particle heterogeneity (Table 37). However, it reduced the dimensions of smaller particles and larger ones. Probably the main difference is between the two methods used for the particle analysis, when the DFC was analyzed with Malvern's aero attachments using air as a dispersant, to not affect particle dimension with water, the smaller particles remain attached to larger ones, due to electrostatic forces and the presence of oil, which promotes particle aggregation. After exposure to water and mixing, the proportion of large particles decreases in favour of smaller ones (Figure 26). This effect is even more pronounced in samples subjected to heat treatment. Despite particle swelling due to water absorption, heat discourages separation, as evidenced by a substantial decrease in the Dv(10) value in the "Hot h24" sample compared to all other samples considered.

3.3.3 CF:DFC mixture's responses to treatment

Figure 28 displays the particle size volume distribution curves for CF:DFC mixtures to assess the effects of varying ingredient ratios and to better understand the types of interactions occurring between them.

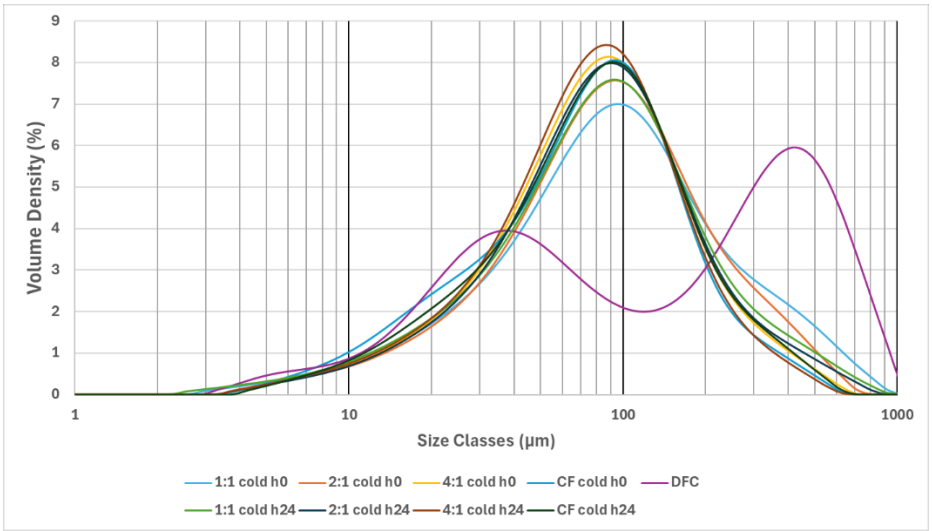

Figure 28. Particle size distribution of CF:DFC mixture with different exposure conditions to water.

Table 38 presents the particle size data for DFC and CF combinations. While span and specific surface area (SSA) values are numerically close, they are statistically distinct, suggesting that the fiber concentration does not lead to significant variations in particle size or distribution. Thus, the contribution of fiber remains stable across different concentrations. The particles in the mixture primarily cluster around 80 µm, representing 6-9% of the volume density. In Figure 28, the large DFC particles seem to disappear with the addition of CF, but this is due to data representation. When small CF particles are mixed with DFC (as Figure 26) and CF is the predominant weight component, the

sample volume primarily reflects CF particles. Consequently, the two DFC peaks visually consolidate into a single peak close to CF's, as shown in Figure 28.

Table 38. Particle size analysis of CF and DFC mixture with different exposure conditions to water. Values in the same column marked with different lowercase letters are significantly different ($p \leq 0.05$).

Samples	Span	SSA (m^2/kg)	D[4;3] (µm)	Dx (10) (µm)	Dx (50) (µm)	Dx (90) (µm)
CF:DFC-1:1 h_0F	3.19±0.05^f	121.93±0.40^c	136.29±0.97^f	23.23±0.06^c	91.61±0.31^h	315.23±5.68^f
CF:DFC-2:1 h_0F	2.69±0.02^e	116.83±0.23^a	120.41±0.63^e	24.74±0.05^f	88.14±0.36^g	261.84±2.10^e
CF:DFC-4:1 h_0F	2.32±0.02^c	123.80±0.26^d	103.81±0.74^b	23.61±0.08^d	79.82±0.20^c	209.09±1.67^b
CF h_0F	2.28±0.01^b	139.30±0.44^g	96.41±0.18^a	18.97±0.08^a	76.27±0.10^a	192.52±1.01^a
CF:DFC-1:1 $h_{24}F$	2.67±0.02^e	132.10±0.36^f	116.59±0.58^d	21.87±0.05^b	83.79±0.21^f	245.87±2.35^d
CF:DFC-2:1 $h_{24}F$	2.48±0.03^d	120.70±0.26^b	111.97±1.00^c	24.17±0.06^e	82.58±0.16^e	228.56±3.02^c
CF:DFC-4:1 $h_{24}F$	2.16±0.00^a	126.30±0.00^e	97.04±0.27^a	23.34±0.02^c	77.34±0.05^b	190.64±0.12^a
CF $h_{24}F$	2.36±0.01^c	125.97±0.81^e	103.86±0.64^b	21.81±0.17^b	80.34±0.45^d	211.43±1.74^b

As shown in Table 38, increasing the concentration of CF relative to DFC results in higher sample homogeneity and an increase in the mean diameter (D[4;3]), Dx(50), and Dx(90) values, given that CF particles are generally smaller than those of DFC. However, the Dx(10) value shows an opposite trend. This is due to the bimodal distribution of the DFC which contains a substantial portion of smaller particles Figure 27. For instance, in Table 38, CF has a Dx(10) of 18.97 ± 0.08 µm, whereas DFC has a Dx(10) of 17.60 ± 0.44 µm. Theoretically, the Dx(10) of the blend should fall between these two values; however, observed values are consistently higher across samples (Table 38), including those exposed for 24 hours (h_{24}) and in all blend ratios tested. This may suggest that the small particles in the DFC, after dispersion, bind with CF, forming complexes that increase the particle size detected by the instrument. For Dx(50) and Dx(90), this effect is less noticeable. because the smaller DFC particles, combined with CF's medium and large particles, produce only minor volume changes that remain below the sensitivity threshold of the measurement. Additionally, these percentiles are strongly influenced by the presence of CF. As the concentration of CF increases, the overall particle size decreases.

3.3.4 CF emulsion

To formulate an EFH, the initial analysis focused on the relationship between varying concentrations of CF and the particle size of the emulsion. The results are presented in Figure 29.

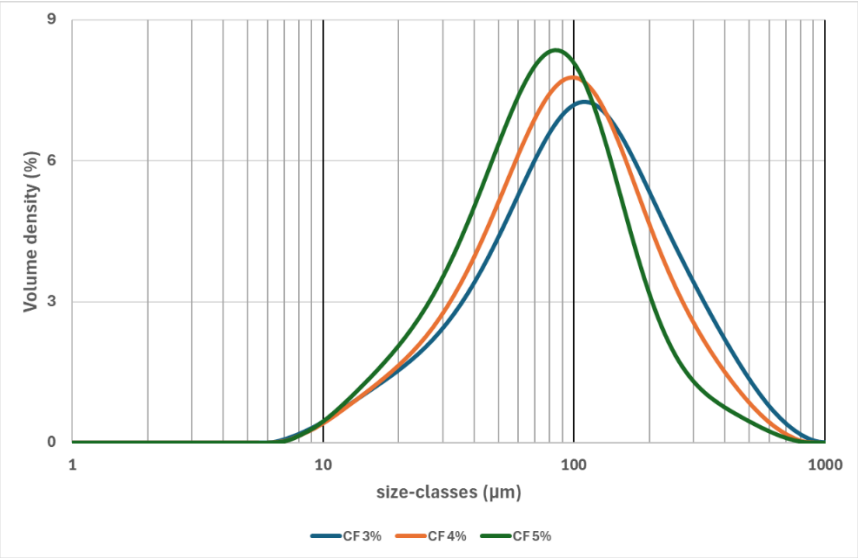

Figure 29. Particle size distribution average curve of CF emulsion with a fixed fiber content and varying oil content.

Table 39. Particle size distribution of emulsions made with different CF content and oil content. Values in the same column marked with different lowercase letters are significantly different ($p \leq 0.05$).

CF% w/w	Oil% W/W	Span	SSA (m²/kg)	D(4:3) µm	Dx(10) µm	Dx(50) µm	Dx(90) µm
3	20	2.54±0.82^{ef}	91.66±0.93^{a}	138.47±3.31^{e}	29.68±0.42^{ef}	104.92±1.20^{e}	295.93±10.07^{e}
	25	2.66±0.11^{g}	91.19±0.72^{a}	143.14±4.68^{f}	29.72±0.43^{ef}	105.05±1.06^{e}	309.46±13.45^{f}
	30	2.59±0.51^{fg}	91.29±1.07^{a}	138.71±2.00^{e}	29.87±0.38^{f}	103.36±1.16^{d}	298.07±6.35^{e}
4	20	2.51±0.41^{de}	96.49±0.21^{b}	124.97±1.72^{d}	27.92±1.19^{c}	91.41±1.68^{c}	266.71±0.59^{d}
	25	2.41±0.02^{c}	97.81±0.49^{c}	120.78±0.89^{c}	28.66±0.18^{d}	92.08±0.36^{c}	250.15±2.49^{c}
	30	2.45±0.05^{cd}	96.18±0.89^{b}	122.76±2.01^{cd}	29.17±0.28^{de}	92.38±0.94^{c}	255.86±6.73^{c}
5	20	2.28±0.03^{b}	111.00±0.16^{e}	101.99±0.70^{b}	26.06±0.04^{b}	76.61±0.21^{ab}	201.04±2.39^{b}
	25	2.08±0.00^{a}	113.50±0.14^{f}	95.63±0.47^{a}	24.93±0.04^{a}	75.37±0.12^{a}	181.54±0.40^{a}
	30	2.12±0.01^{a}	109.65±0.77^{d}	97.94±0.74^{a}	26.18±0.21^{b}	77.07±0.58^{b}	189.80±1.94^{a}

The emulsions were created using increasing CF percentages (3%, 4%, and 5% w/w) and a constant 20% of oil. As clearly highlighted in Figure 29 there is a significative effect of fiber's concentration on the particle size. This indicates that as the concentration of CF increases, the particle size decreases. Smaller particle sizes lead to the formation of more stable emulsions with reduced phase separation and improved consistency (Yang et al., 2023).

3.4 Oil release quantification

In combination with the particle size analysis of the emulsions, the resistance to external physical stresses, such as centrifugation, was quantified to assess the resilience of the network formed by CF and its capacity to retain the oil within. Phase separation measures the tendency of an emulsion to separate into distinct phases. Experiments were conducted to identify the best recipe by utilizing various concentrations of the raw materials. Simple emulsions were prepared based on apricot puree, hazelnut oil, and CF, using three different fiber concentrations (3%, 4%, and 5% w/w) and three

different oil concentrations (20%, 25%, and 30% w/w). Oil release was evaluated for these samples (Figure 30)(Table 40).

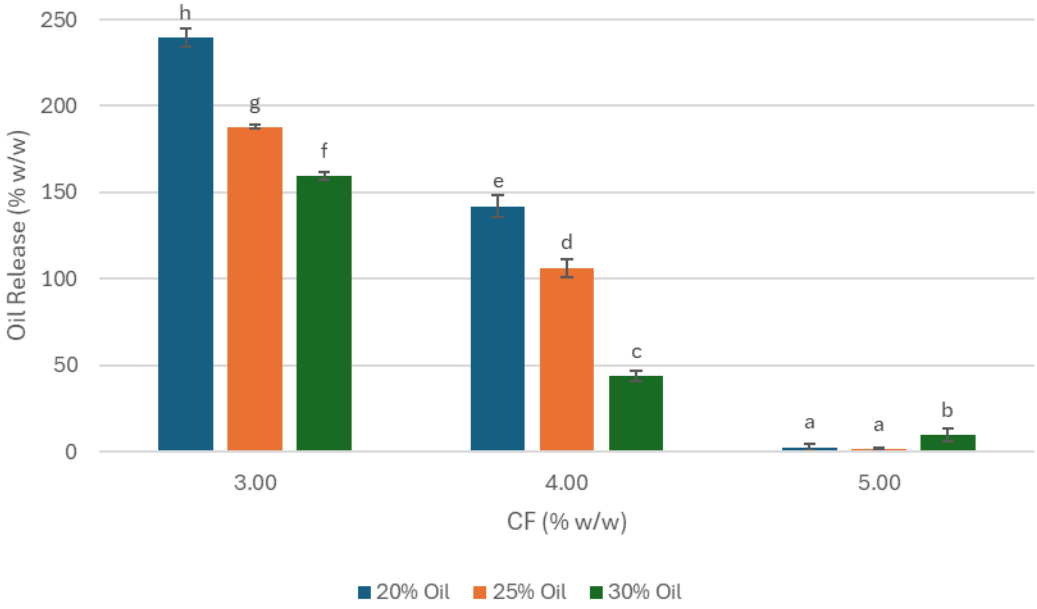

Figure 30. Oil release after centrifugation. Results are reported as a percentage (w/w) of the initial oil weight. Values with different lowercase letters are significantly different ($p \leq 0.05$).

Table 40. Oil release quantification on CF emulsions. Data were represented by means ± SD. Data with different lowercase are significantly different ($p < 0.05$).

		CF w/w		
		3%	**4%**	**5%**
Oil w/w	**20%**	239.68±5.29^{h}	141.93±6.27^{e}	2.58±2.02^{a}
	25%	187.91±1.30^{g}	106.39±5.22^{d}	1.52±1.06^{a}
	30%	159.43±2.10^{f}	43.83±2.66^{c}	9.46±3.86^{b}

From Figure 30 and Table 40 it can be observed that the most significant oil separation occurs at a CF concentration of 3% (w/w), substantially exceeding 100%. Referring to Table 40 it can be noticed that CF's WBC is insufficient to fully absorb the moisture from the apricot sample (Table 34). Consequently, although CF creates a network, it is not dense enough to withstand the centrifugal force. The presence of unbound water within the system enhances mobility within the emulsion, resulting in a noticeable release of oil. The connection between WBC and oil release can also be inferred from analyzing the sample with 4% CF. Normally, an increase in oil concentration at a fixed fiber level would lead to higher oil separation, but the sample containing 30% oil (w/w) shows the least oil release despite having the lowest water content. This suggests that achieving a sufficiently dense network depends not only on the total CF concentration but also on the specific weight ratio

between CF and water content. At a CF concentration of 5%, a notable shift in behavior is observed: oil release is nearly zero regardless of the amount of oil used, except in the sample containing 5% CF and 30% oil. As oil content increases, thereby reducing the water content, oil release increases again. For CF to emulsify and retain oil optimally, a minimum fiber concentration is required to absorb all available water in the sample. However, excessive CF without a proper CF-to-water ratio diminishes its oil affinity, leading to further oil release. Although the 5% CF formulation showed the best results in terms of minimized oil release, the choice was made to continue with the 4% fiber and 20% oil formulation. This decision was driven by several factors related to emulsion stability, consistency, and sensory qualities of the final product. Selecting this second-best formulation (4% fiber rather than 5%) allows for an analysis of the impact of additional ingredients, providing superior quality compared to the 3% (w/w) fiber formulation. If the fiber had fully emulsified the system, the effects of adding DFC would likely be minimal, making 4% CF the preferred choice for continued experimentation. The analyses were repeated by adding DFC in varying proportions to CF before initiating the emulsification process. Keeping CF at a constant 4% and oil at 20%, 1g, 2g, and 4g of DFC were added to create emulsions with ratios of 4:1, 2:1, and 1:1, respectively. Even with the minimum addition of DFC, oil release was eliminated. However, the opposite effect was observed: no oil was released, but apricot juice began to separate at the bottom of the Eppendorf tube, causing noticeable phase separation also noted by Ruan et al. (2019) with increasing emulsion stability due to the addition of corn peptides. Proteins are the second most abundant component in DFC, and their emulsion-stabilizing properties are well known (Wen et al., 2023). They can interact with both soluble (pectin, Neirynck et al., 2004) and insoluble (Genc et al., 2024) components of citrus fiber. As the amount of added DFC increased, the released juice gradually decreased until it completely disappeared at a 1:1 ratio, with 4g of CF and 4g of DFC. Thus, the addition of DFC successfully eliminated both oil and juice release. The low particle size of some DFC fractions, as shown in Table 36, likely allowed it to integrate within the CF network, forming complexes that interact with both the soluble and insoluble fractions. Given the reduction in water retention capacity in the 4:1 formulation, it is possible that groups previously free to bind with water became complexed with the addition of DFC, enhancing the system's emulsification ability but reducing hydrophilicity. This outcome is particularly promising for subsequent EFH formulations that incorporate DFC as a functional ingredient.

3.5 Peroxide values (PV)

The peroxide analysis was used to determine the initial oxidation levels of fats and oils. It was conducted on the hazelnut oil, Water-based EFH, and apricot-based EFH (Table 41). This is a

fundamental parameter for assessing the freshness, quality, and oxidative stability of a food product containing lipids. Lacking in a specific regulation, according to Regulation (EC) No. 1513/2001 on olive oil, the hazelnut oil used can be considered of excellent quality, as the peroxide value (PV) is below 5 meq O_2/kg. A value between 5 and 10 meq O_2/kg indicates slight oxidation; however, the product can still be considered acceptable in many cases. A peroxide value exceeding 10-20 meq O_2/kg is generally regarded as a sign of significant or excessive oxidation. At these levels, the oil or fat is likely to have begun developing unpleasant flavors and odors due to the rancidity process. Peroxide values above 20 meq O_2/kg are typically associated with advanced rancidity (Rabadán et al., 2018).

Table 41. Peroxide values (PV) of Hazelnut oil and EFH. Data with different lowercase letter are significantly different ($p \leq 0.05$)

	Pectins	PV (meq O_2/kg)	Alfa	mg GAE/g
FA	/	/	/	0.05±0.00[a]
Purea di albicocca	/	/	/	0.78±0.02[b]
Hazelnut oil	/	1.22±0.36[a]	472.61±22.51[b]	n.d.
Water-based EFH	**LM12**	1.47±0.85[a]	507.00±17.08[b]	0.80±0.00[b]
	LM18	1.35±0.63[a]	478.32±22.56[b]	0.83±0.00[b]
	LMA10	1.23±0.49[a]	504.08±22.00[b]	0.84±0.00[b]
	LMA20	1.47±0.39[a]	493.02±29.34[b]	0.81±0.00[b]
Apricot-based EFH	**LM12**	0.98±0.40[a]	373.58±11.62[a]	n.d.
	LM18	0.85±0.24[a]	375.46±0.37[a]	n.d.
	LMA10	1.21±0.30[a]	385.57±47.01[a]	n.d.
	LMA20	1.45±0.04[a]	368.74±41.05[a]	n.d.

Regarding the EFH (Table 41), it can be observed that there are no significant differences between the EFH samples and the original hazelnut oil. This indicates that the process, despite mixing, exposure to air, and high temperatures, did not compromise the quality of the oil. Assessing the peroxide number in the context of hydrogels is essential to ensure oxidative stability, safety, and product quality. The oxidation of lipids within hydrogels can lead to the formation of degradation products that may deteriorate the food over time. Measuring peroxides helps identify and prevent early deterioration, ensuring that the hydrogel maintains its functionality during storage and use. Elevated peroxide values may indicate issues in the production process, such as excessive exposure to oxygen or inadequate antioxidant protection. Oxidative stability is directly related to the shelf life of the product and can also affect sensory characteristics adversely (Rangrej et al., 2015).

3.6 Tocopherols

Based on the peroxide analysis results, it was hypothesized that oxidation may have been reduced due to the action of antioxidant molecules, such as tocopherols, which are naturally present in

hazelnut oil (Parcerisa et al., 1998). They play a significant antioxidant role by reducing the formation of peroxides. The quantity and quality of tocopherols in Water-based EFH, and apricot-based EFH was determined and compared with those present in the hazelnut oil used (Table 42). Regarding the ingredients used, the apricot puree was analysed too but it does not contain tocopherols, or its values are below the limit of detection.

Table 42. Tocopherols content (α, β, γ, δ homologues). Values reported within the same column with different lowercase letter are significantly different ($p \leq 0.05$).

Sample (mg/kg oil)	Pectins	Alfa	Gamma+Beta	Delta
Apricot- based	LM12	507,00±17,08^{b}	210,60±7,69^{b}	35,58±1,06^{cd}
	LM18	478,32±22,56^{b}	198,81±10,75^{b}	33,83±3,05^{c}
	LMA10	504,08±22,00^{b}	211,68±4,98^{b}	39,26±1,29^{bde}
	LMA20	493,02±29,34^{b}	206,60±11,36^{b}	33,88±1,60^{c}
Hazelnut oil	/	472,61±22,51^{b}	225,35±6,73^{b}	40,55±2,78^{e}
Water-based	LM12	373,58±11,62^{a}	166,61±6,10^{a}	24,37±0,35^{a}
	LM18	375,46±0,37^{a}	166,90±0,51^{a}	28,64±0,98^{b}
	LMA10	385,57±47,01^{a}	179,74±9,76^{a}	37,25±1,20^{cde}
	LMA20	368,74±41,05^{a}	164,03±17,85^{a}	37,07±3,01^{cde}

As shown in Table 42, the tocopherols in hazelnut oil are predominantly represented by the alpha homolog, followed by the gamma+beta homologs, with delta-tocopherol present in the smallest amount. Noteworthy differences appear when comparing apricot-based EFH to water-based emulsions: the apricot-based formulations display significantly higher levels of alpha and gamma+beta-tocopherols than those in water-based emulsions. Only delta-tocopherol does not show a reduction in concentration between the oil and EFH samples, as it is the most resistant to external stressors compared to the other homologs (Zaunschirm et al., 2018). This indicates that in water-based EFH, tocopherols are more susceptible to thermal treatment and mixing compared to other samples. This increased sensitivity appears to be linked to the type of dispersing phase used, given that the production process was consistent across both formulations. Tocopherols could have faced a reduction in water-based samples because of the lack of protection that in the other samples is offered by apricot puree.

3.7 Total phenolics content

Following the tocopherols' analysis results, the total phenolics content was quantified to determine whether it was affected by the processing methods used to produce the EFH or by differences in the dispersing phases. The results are detailed in Table 43.

Table 43. Total phenolic content of the samples. Values with different lowercase letters are significantly different ($p \leq 0.05$).

		mg GAE/g
Ingredients	**Apricot puree**	0.78±0.02[b]
	Hazelnut oil	n.d.
	CF	0.05±0.00[a]
Apricot-based EFH	**LM12**	0.80±0.00[b]
	LM18	0.83±0.00[b]
	LMA10	0.84±0.00[b]
	LMA20	0.81±0.00[b]
Water-based EFH	**LM12**	n.d.
	LM18	n.d.
	LMA10	n.d.
	LMA20	n.d.

It can be observed Table 43 that polyphenols are predominantly present in the apricot puree. This aligns with findings reported by Bassi & Selli (1990), with minimal or no content in the CF and hazelnut oil. As for the emulsion-filled hydrogels (Table 43), their polyphenol values are very similar to those of the puree. Given the minimal amount of CF in the EFH, its phenolic contribution can be considered negligible, with most phenolic content instead derived from the apricot puree. In the apricot-based EFH, there is no significant difference between the types of pectin used. However, in the water-based emulsion-filled hydrogels, it was not possible to quantify any phenols they contained. In the water-based samples, the phenolic component is absent, which may have contributed to the reduction in tocopherols observed in Table 42. In this situation, tocopherols lack the antioxidant protection typically provided by apricot-derived phenolics, leading to a decrease in their levels. This reduction is attributable to the susceptibility of tocopherols to oxidative degradation, which can be induced by both heat treatment and air exposure, conditions commonly encountered during the EFH production process (Zaunschirm et al., 2018). Regarding the apricot-based EFHs, the synergistic combination of antioxidant effects from both the phenolic compounds and tocopherols plays a crucial role in controlling peroxide formation. This interaction ensures a high level of resilience during the EFH production process. The presence of phenolics enhances the stability of tocopherols, thereby contributing to the overall antioxidant capacity and protecting the emulsions from oxidative degradation. This dual action is essential for maintaining the quality and shelf-life of the final product.

3.8 pH

pH is a key factor influencing the physical, chemical, and microbiological properties of foods. Since the product is gelled with pectins, pH is particularly critical in determining the final structural properties (Wang et al., 2023). Pectins require an optimal pH range to function effectively, depending on their degree of esterification. Table 44 presents the measured pH values for both the water-based and puree-based emulsion-filled hydrogels (EFH), with and without the addition of hazelnut pomace (DFC).

Table 44. EFH's pH is presented as Mean ± Standard Deviation. Values with different letters in the same column are significantly different ($p < 0.05$)

Dispersant	Pectin	EFH	CF+DFC EFH
Apricot	**LM 12**	3.63±0.01^{a}	3.71±0.01^{a}
	LM 18	3.66±0.01^{b}	3.75±0.01^{b}
	LMA 10	3.71±0.01^{c}	3.82±0.01^{c}
	LMA 20	3.63±0.01^{a}	3.82±0.01^{c}
Water	**LM 12**	3.57±0.01^{a}	4.38±0.01^{a}
	LM 18	3.83±0.01^{b}	4.73±0.00^{b}
	LMA 10	3.96±0.00^{c}	5.03±0.01^{c}
	LMA 20	4.77±0.02^{d}	5.05±0.01^{c}

In both formulations, the pH displays moderate acidity, clearly influenced by the specific EFH composition. As seen in Table 34, apricot itself has a naturally low pH, which is slightly raised by the addition of CF and pectins, with significant differences between them. Given that the ingredients remain consistent within samples using the same dispersing phase, the observed differences in pH in EFH samples (Table 44) can be attributed to the type of pectin used. Additionally, the pH values are strongly influenced by the dispersing phase. In water-based samples, it's possible to notice bigger pH variations. Comparing EFH samples with and without DFC reveals that, for the same pectin type, the addition of DFC with a considerably higher pH than apricot and other ingredients (Table 34) increases the overall pH, especially in water-based samples. Cross-referencing the measured pH of the EFH with the optimal pH range for pectin gelation, as shown in Table 33. This comparison suggests that LMA pectins in apricot-based samples have gelled at a pH lower than optimal, which may have led to pre-gelation, compromising the gel's structure both with and without DFC. However, given the pH increase associated with DFC addition, it is possible that pre-gelation effects were partially mitigated. In contrast, the water-based EFH formulations provided favorable conditions for gelation. LM pectins were generally found in an environment with a favourable pH for gelation. LM18 is the only exception (Table 44) in samples containing added DFC, which placed it in a slightly less acidic setting than optimal. However, the values listed in (Table 33) refer to ideal conditions, and it should be noted that pectins can still gel effectively outside this optimal pH range, as long as deviations from the ideal

are not too pronounced (Alba et al., 2015). An excessively high or low pH can compromise the ability of pectins to properly interact with calcium ions, reducing the stability of gels. A higher pH than required by the pectin leads to creating a watery structure, while a lower pH results in forming a stiffer structure that tends toward pre-gelation. Consequently, the product becomes difficult to handle during processing, exhibits poor texture quality, and shows inadequate distribution of ingredients (sedimentation/separation), along with a limited shelf life (Chandel et al., 2022).

3.9 Texture profile analysis (TPA)

3.9.1 EFH

The TPA test was conducted on the water-based and apricot-based EFH with and without DFC. EFHs with added DFC were prepared using a 1:1 ratio with CF. From Table 45, it is evident that firmness and Force B values are higher in the apricot-based EFH compared to the water-based ones, indicating that using apricot puree instead of water significantly increase these forces. In fact, both the force measured during the first compression (Firmness) and the second (Force B) are strongly influenced by pectin's gelling condition, such as pH (Kim et al., 2008) and the presence of solutes. Although LM pectins do not require sugars to gel, there is a positive correlation between their presence and increased gel strength. The values for these two parameters are substantially higher in the apricot-based samples than in the water-based ones. This difference can be attributed to a considerable pH variation between the two samples and a lower dry matter content in the water-based, due to the differing dispersing phase. Additionally, the sample with the highest firmness contains amidated pectin, which, although outside the optimal range, achieves increased resistance thanks to the presence of amide groups especially when coupled with a low degree of esterification (Kim et al., 2020). The values of springiness and cohesiveness, however, did not show any significant differences, regardless of whether water or apricot puree was used as the dispersing phase. Springiness defines elasticity and measures a food's ability to return to its original shape after being compressed or crushed. The range of values is from 0 to 1, with values closer to 1 indicating greater elasticity and, consequently, less rigidity. In this case, the values range from 0.80 to 0.90, suggesting that the food has good elasticity and significantly returns to its original shape after deformation. This may indicate a pleasant and soft consistency, similar to what one might find in products like fresh bread, soft cakes, or soft cheeses, where the food shouldn't undergo permanent deformation when chewed or pressed (Kim et al., 2020).

Table 45. EFH texture profile analysis (TPA) results. Values with different letters in the same column with the same dispersing phase are significantly different ($p<0.05$).

Dispersant	Pectin	Firmness (N)	Force B (N)	Springness (%)	Cohesiveness	Gumminess (N)
Apricot	LM12	218.88±25.20^{a}	195.88±22.13^{a}	0.81±0.10^{a}	0.61±0.04^{a}	132.00±15.17^{a}
	LM18	430.88±36.71^{b}	359.63±28.80^{b}	0.93±0.10^{a}	0.58±0.05^{a}	237.25±14.39^{b}
	LMA10	768.71±102.39^{c}	654.00±88.72^{c}	0.90±0.10^{a}	0.60±0.00^{a}	465.14±67.15^{c}
	LMA20	216.00±30.46^{a}	193.38±27.64^{a}	0.90±0.12^{a}	0.60±0.00^{a}	128.38±18.85^{a}
Water	LM12	94.63±28.15^{a}	84.00±25.01^{a}	0.80±0.17^{a}	0.59±0.08^{a}	54.88±16.73^{a}
	LM18	148.22±34.00^{b}	126.44±26.38^{b}	0.86±0.13^{a}	0.54±0.07^{a}	81.56±16.76^{b}
	LMA10	127.00±16.94^{b}	112.78±14.85^{b}	0.87±0.13^{a}	0.54±0.05^{a}	71.11±10.15^{b}
	LMA20	100.25±11.63^{a}	88.38±10.31^{a}	0.85±0.12^{a}	0.54±0.05^{a}	57.00±9.00^{a}

Cohesiveness defines the resilience of the sample, indicating its ability to maintain structure after being compressed or chewed. The values range from 0 to 1, with values closer to 1 indicating greater resistance and, consequently, less deformability. The product exhibits values between 0.50 and 0.60, suggesting that it maintains its structure well during chewing but still disintegrates relatively easily (Rosenthal & Thompson, 2021). A lower cohesiveness value would indicate a product that tends to disintegrate easily, while a higher value would suggest a food that maintains its integrity and compactness even under pressure or during chewing. Gumminess represents the resistance that a food provides when compressed by the teeth. It is the product of firmness and cohesiveness. For both water-based, the values are very low making the product a light-textured food that does not stick to the teeth and disintegrates easily when chewed, without requiring significant effort to manipulate in the mouth. Products with low gumminess are ideal for people having difficulty with harder foods and for individuals with swallowing or chewing difficulties (Wee et al., 2018).

3.9.2 CF:DFC EFH

Adding DFC, in a 1:1 ratio with CF (Table 46), has positively affected the structure and increased the values of the considered texture parameters:

Table 46. EFH added with DFC texture profile analysis (TPA) results. Values with different letters in the same column with the same dispersing phase are significantly different ($p<0.05$).

Dispersant	Pectins	Firmness (N)	Force B (N)	Springiness (%)	Cohesiveness	Gumminess (N)
Apricot	LM12	196.17±45.08^{a}	175.50±38.77^{a}	0.83±0.19^{a}	0.55±0.05^{a}	108.67±22.84^{a}
	LM18	802.67±259.65^{c}	656.33±210.35^{b}	0.88±0.08^{a}	0.52±0.04^{a}	431.67±153.20^{b}
	LMA10	592.50±144.48^{b}	511.33±118.97^{b}	0.93±0.08^{a}	0.60±0.00^{a}	350.33±84.48^{b}
	LMA20	297.33±32.15^{a}	261.98±24.79^{a}	0.83±0.19^{a}	0.55±0.08^{a}	167.50±4.97^{a}
Water	LM12	104.00±23.28^{a}	94.17±19.90^{a}	0.92±0.10^{a}	0.60±0.09^{a}	62.00±9.08^{a}
	LM18	200.00±47.25^{b}	177.33±39.05^{b}	0.85±0.14^{a}	0.57±0.05^{a}	112.67±25.34^{b}
	LMA10	283.67±93.79^{c}	249.50±79.01^{c}	0.77±0.08^{a}	0.60±0.00^{a}	161.50±53.61^{c}
	LMA20	192.67±41.83^{b}	170.67±34.50^{b}	0.87±0.15^{a}	0.53±0.05^{a}	104.33±18.74^{b}

Adding the DFC has a positive effect because it does not negatively affect the texture of the hydrogel. If the DFC particles were disrupting the gel network, this would have reduced its resistance to compression. Therefore, the incorporation of DFC contributes to maintaining the integrity of the gel while enhancing the other properties. There is a significant increase in compactness and B-force, almost doubled in the water-based samples where the DFC contributes to increasing the firmness. The sample that benefits most is LMA10, now under ideal gelling conditions (Table 33), making it the firmest sample. In general, the samples containing amidated pectins respond better to DFC addition, because the amide groups improve the interactions with the DFC formed by interactions of and amide group with carboxyl-, hydroxyl- groups (Tyapkova et al., 2014) of proteins. Notably, the apricot-based samples also showed an increase in firmness, except LMA10 which showed a slight decrease. However, LM18 benefited significantly from adding DFC and became the firmest ever. Softness and cohesiveness remain unchanged, while gumminess increases slightly, indicating an easy to chew product. Texture analysis is influenced by particle size, phase separation, water binding capacity (WBC), and oil binding capacity (OBC). A good texture is generated by a stable matrix, adequate binding of water and oil, optimal particle size, and low lipid oxidation. The improvement in phase separation due to DFC addition is reflected in EFH samples. DFC's proteins' ability to enhance emulsion stability is linked to its capacity to reinforce the gel's microstructure. This strengthening effect on the gel network enhances both phase stability and structural integrity, improving the overall performance of the EFH in practical applications. Additionally, the particle size of the DFC enables smaller particles to integrate within the CF network (Diao et al., 2024), boosting emulsion stability. Meanwhile, larger particles likely interact with the pectin network (Zhang et al., 2022) outside the emulsion, contributing to the gel's surrounding microstructure. This dual interaction of internal stabilization by smaller particles and external reinforcement by larger ones supports a more robust and resilient hydrogel structure.

3.10 Tribological properties

All EFH samples, with different dispersing phases and with or without DFC addition, were subjected to tribological property analysis. The goal was to study the friction, lubrication, and wear occurring within the microstructure of the sample during relative motion. The resulting curves are presented in Figure 31.

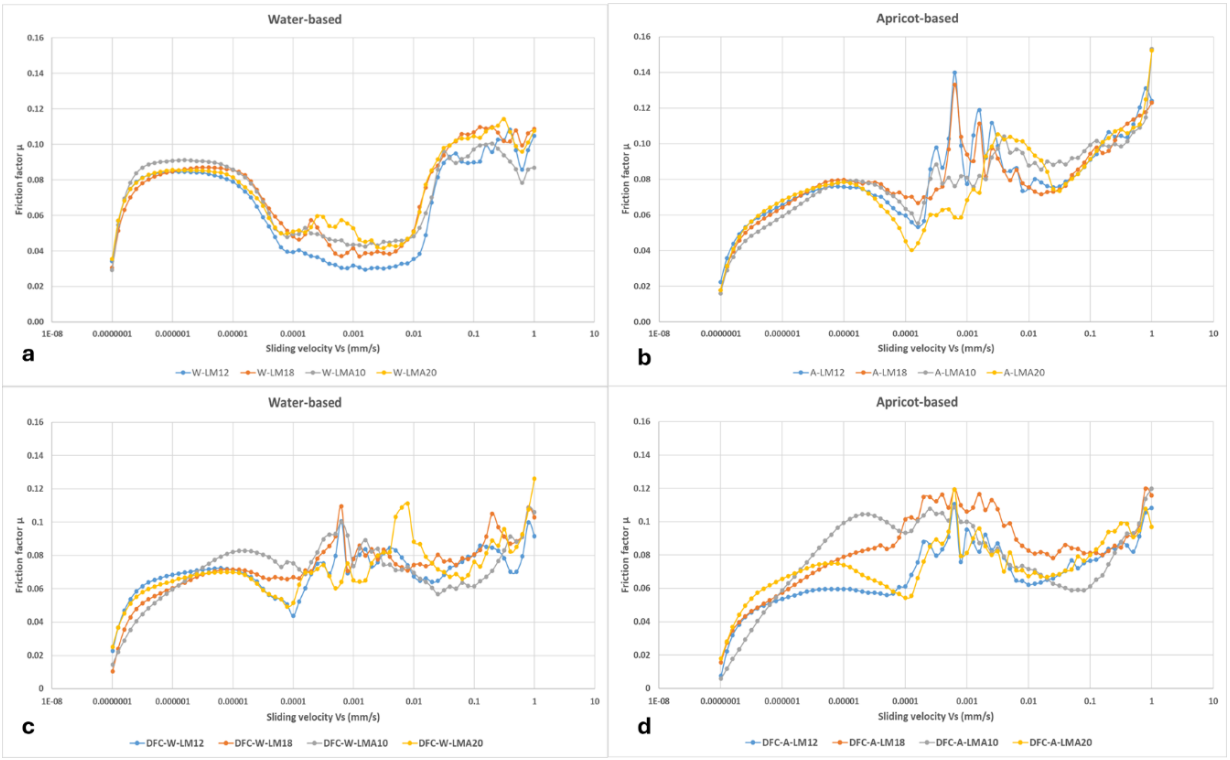

Figure 31. The Stribeck curve for EFH with different dispersant and DFC addition, a-b without DFC, c-d with DFC in 1:1 proportion with CF.

The mouthfeel of emulsions is largely shaped by their flow properties and how well-emulsified oil droplets lubricate during consumption. Initial texture perception is driven by viscosity, principally at the front of the mouth (Ruan et al., 2019). EFH network density rises with dry matter content, type of ingredient, and dispersant phase, increasing the perceived thickness as it takes greater force to deform it between the tongue and palate. This effect intensifies as the oral surfaces draw closer during chewing, engaging tribological interactions that enhance sensations of creaminess and smoothness. These dynamics reflect the emulsion's shear-thinning properties, as shown by changes in viscosity with shear rate (Chapter 5) emphasizing how those elements' concentration in emulsions influences texture. Stribeck curve shows the friction coefficient of an emulsion or fluid across different entrainment speeds, illustrating how it behaves under various lubrication regimes, boundary regime, mixed regime and hydrodynamic regime (Prakash et al., 2013). The curve helps evaluate EFHs' effectiveness in providing lubrication across different usage conditions. As observed in Figure 31a-b, the EFHs' curves exhibit common characteristics but also many differences. In the first segment, which pertains to peripheral lubrication, the water-based hydrogel shows a slightly higher friction coefficient (μ) compared to the apricot-based. The water-based has lower lubrication effectiveness under peripheral conditions compared to the apricot puree, which exhibits better adhesion and lower initial friction. The difference in the curves is attributed to variations in viscosity and chemical composition between the two recipes, as well as the particle size (Kieserling et al., 2019) of the

ingredients and the increase in dry matter. The low friction coefficient observed across all EFH samples is attributed to a physical effect where, upon contact, the tribology probe compresses the sample, releasing a small amount of oil at the contact interface, which acts as a lubricant. Previous studies (Chapter 5) have shown that water-based emulsions are more resistant to phase separation under physical stress compared to apricot-based ones. Apricot interacts with the CF network due to its pH (Table 33), fiber composition and particle size, altering its structural resistance. In the second sector, during mixed lubrication, the roles are reversed, with the water-based hydrogel offering significantly lower friction compared to the apricot puree hydrogel. This suggests that, under mixed lubrication conditions, the water-based hydrogel performs more effectively as a lubricant due to its resilience under stress, delaying oil release. In contrast, the apricot puree hydrogel is less effective in reducing friction, likely due to the larger particle size (Figure 26), which diminishes its ability to sustain a continuous lubricating layer. This particle size difference can compromise lubrication efficacy by reducing the uniformity and stability of the contact layer, especially under conditions where smoother layers are essential for effective lubrication. In hydrodynamic lubrication, the curves for both formulations converge, indicating similar behavior at high sliding velocities. Under these conditions, a thin lubricating layer, due to released oil, remains present in the first and second phases. However, the CF particles, the main common component across both EFH samples, are the main factor influencing tribological properties. These particles contribute to stabilizing the hydrodynamic layer and maintaining consistency. Once the initial structure is lost, the internal friction generated by fiber fragments outweighs the friction contributed by the pectin and oil. The addition of the DFC, in a concentration of 1:1 with the CF, modifies completely the behavior of the water-based EFH and, to a lesser extent, the tribological properties of the puree-based EFH (Figure 31c-d). In contrast to the EFH without DFC, which showed significant differences in the first and second segments, those with DFC have more similar behavior. In particular, the second segment is characterized by an increase in the friction coefficient (μ) in both formulations. The effect becomes even greater when we compare the two water-based EFHs. Here, the impact of hazelnut is very evident, with a substantial reversal of the trend in the first two lubrication regimes. We can say that in a model system like the water-based one, the effect of DFC surpasses that of CF. This effect is caused by the composition of the DFC, which contains larger particles (larger than those of the CF and apricot, Figure 26) and provides protein, overshadowing all other components present in the emulsion. In contrast to the EFH without DFC, which showed significant differences in the first and second segments, those with DFC exhibit more similar behavior. Specifically, the second segment is characterized by an increase in the friction coefficient (μ) in both formulations. The effect becomes more pronounced when comparing the two water-based EFHs, where the impact of the DFC is evident, leading to a substantial reversal of the

trend in the first two lubrication regimes. In a model system like the water-based one, the effect of the DFC overshadows the CF. This effect is caused by the composition of the DFC, which contains larger particles (larger than those of the CF and apricot, as shown in Figure 26) and smaller particles. The larger particles are responsible for the sensation of friction, while the smaller ones penetrate the CF network, stabilizing the emulsion. If CF is responsible for building the network, the DFC has the ability to interact with it and smooth out the differences between the two dispersing phases. The behavior of the pomace particles significantly influences the second segment of the tribological analysis, specifically the mixed lubrication phase. In this scenario, the pomace fails to achieve maximum lubricating effect, increasing the friction coefficient (μ). Comparing Figure 31 (a-c), it can be observed that in the first segment, pertaining to peripheral lubrication, the friction coefficient is immediately higher in the hydrogels without DFC, while it increases more slowly and reaches lower friction coefficient levels in the EFH containing hazelnut. The emulsion is more stable and does not release oil. Consequently, in the second region, lubrication does not occur (as it does in samples without pomace), and the probe perceives the pomace particles and their friction, resulting in a significant increase in the friction coefficient (μ). The third segment is consistent across both formulations, with increased friction coefficient due to the progressive increase in probe speed. For the puree-based EFH (Figure 31 b-d), the same applies as for the water-based samples, with the exception that in both cases, there is a slow and gradual increase in the friction coefficient (μ) in the first segment, attributed to the characteristics of the apricot puree. Tribological analysis shows how particle size, texture, and phase separation impact the frictional behavior of emulsions. When comparing Figure 31 with the TPA results in Table 45 and Table 46, it becomes clear that higher friction coefficients are not always directly linked to elevated firmness values. However, in Figure 31, the samples with the highest firmness also demonstrate the highest friction coefficients. This suggests that firmness may influence tribological performance but is not an absolute indicator of the friction coefficient in all cases.

4. Conclusion

The analyses led to the development of an EFH, composed of CF, apricot puree, hazelnut oil, DFC, and pectin. CF demonstrated a high capacity for water absorption and served as an emulsifying agent, while DFC enriched the EFH with fiber and protein and further contributed to emulsification, enhancing product consistency. Variations in ingredient composition were shown to significantly influence the structural properties of the EFH. CFs' content directly affected emulsion stability: while low concentration was insufficient for maintaining structural integrity, 4% and 5% concentrations provided a stable emulsion, as confirmed by oil release analysis. Adding pectin as a gelling agent enabled the formation of a cohesive hydrogel around the emulsion. This hydrogel features an acidic pH, advantageous for preservation thanks to coupling with the applied thermal treatment (90°C for 1 min). It contains good amounts of phenols and tocopherols, which contribute to the antioxidant properties that protect the system against oxidation. Texture and tribology analyses revealed that, when scooped and chewed, the hydrogel presents a compact structure with a double consistency. However, upon mastication, the structure quickly disintegrates, creating minimal tactile perception, a characteristic particularly beneficial for dysphagia-suffering people. This unique property, largely imparted by the CF, also supports thermal resistance, underscoring its potential as a therapeutic food solution. To conclude, this research highlights the promising application of EFH as nutritionally enriched, stable, and sensorially adaptive products, tailored to meet also the needs of specialized dietary populations.

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Chapter 7

General conclusion

The doctoral project focused on the study of byproducts, with a particular emphasis on depectinized citrus fiber a currently underutilized ingredient within the food industry. Given the growing need to maximize resource use, minimize waste, and address the industry's constant demand for innovative ingredients, citrus fiber could offer a promising avenue for creating novel structures. This allows for the development of unique ingredients, textures, and products. To further illustrate the potential of citrus fiber for industrial applications, the project aimed to develop a nutrient-dense, easy-to-swallow food product tailored for elderly individuals and those requiring texture-modulated foods. This effort followed a structured four-part methodology that included analyzing raw materials, exploring structural interactions, evaluating rheological properties, and assessing the final emulsion-filled hydrogel formulation. The study's first phase focused on a detailed analysis of tree nuts, particularly their tocopherol profiles and protein content, assessing nuts like hazelnuts, pistachios, and apricot kernels for their nutritional potential. Hazelnuts were found to have high levels of α-tocopherol, while pistachios and apricot kernels were richer in γ-tocopherol. The research demonstrated the value of these nuts both as standalone nutritious ingredients and as parts of food formulations. Cold-press oil extraction preserved tocopherol content in both the oils and the remaining press cakes, which retained essential proteins, fibers, and residual fats. These defatted press cakes, often considered byproducts, emerged as nutrient-rich sources with significant potential for further food applications, supporting a sustainable approach to food production by reducing waste and maximizing resource use. Additionally, it was observed that tocopherols do not distribute proportionally with the oil yield after extraction; instead, their distribution depends on the nut type and, in pistachios, even on the specific variety. This variability suggests that certain proteins within the nuts can selectively retain tocopherols. Turkish hazelnuts were selected to be implemented in the next studies, due to their balanced profile, containing all four tocopherol homologs with a particularly high α-tocopherol content. *Tonda Gentile* hazelnuts contain higher levels of α-tocopherol but it is the only tocopherol homolog present, which makes it unsuitable. Using Turkish hazelnuts allowed for a more comprehensive study of the effects of processing on all tocopherol homologs, supporting a nuanced approach to retaining maximum nutritional value in the final product.

In the second phase, the research shifted focus to the interactions within an emulsion-filled hydrogel system, investigating how the oils, fibers, and mixing parameters within these matrices influenced

the final product's stability and texture. This approach allowed us to leverage the unique functional properties of each component to optimize the texture of the product. The study focused on total citrus fiber, a fibrous by-product of citrus juice extraction, which was divided into its soluble (pectin) and insoluble (de-pectinized citrus fiber) fractions. This separation process, commonly used in the industry to isolate pectin as a high-demand ingredient, enables selective utilization of both components for maximum functional benefit. The de-pectinized citrus fiber proved to be particularly effective at stabilizing increasing amounts of oil as its concentration and mixing duration increased. The fiber's emulsifying mechanism is a hybrid between Pickering emulsion stabilization and network based. With its fibrous structure, citrus fiber swells in solution, forming an interconnected fiber mesh that fills its volume. As the fiber concentration increases, the density of this mesh also increases, reducing the size of gaps within the network. These gaps hold the dispersed oil, and as the gaps narrow, they reduce the size of the oil droplets, creating a stable emulsion. The fiber essentially forms "compartments" that encapsulate oil, with more fiber resulting in smaller compartments and thus smaller, more stable oil droplets. These droplets are further stabilized by proteins on the microfibril surfaces of the citrus fiber, which anchor them in place. Pectin, identified as an effective structuring agent, interacts with citrus fiber, especially when oil is present, to modify the texture of the emulsion-filled hydrogel. If only water-soluble compounds are present (without oil), citrus fiber dominates the structuring effect, reducing pectin's impact. This interaction proved essential for forming a heat-stable emulsion matrix capable of withstanding various processing conditions, offering a resilient structure that is ideal for oil encapsulation and targeted nutrient delivery. Given the remarkable properties of citrus fiber, the study further analyzed the mechanisms behind its emulsifying capabilities and its interactions within the emulsion-filled hydrogel, aiming to enhance the structural robustness and stability of these formulations.

The third phase focused on assessing the rheological properties of citrus fiber-based emulsions in both water and apricot puree as dispersing phases. This phase revealed that the network-forming ability of citrus fiber varied significantly depending on the dispersing medium. In apricot puree, the presence of the apricot's fiber content created a "matrix effect" that influenced stability and network formation. When dispersed in water at increasing concentrations (4-5%), citrus fiber absorbed more water, enhancing emulsion stability. However, in the apricot puree system, an opposite effect was observed; as citrus fiber concentration increased, centrifugation tests showed a higher rate of oil release, likely due to the interactions between the different fiber types. The difference in particle sizes between citrus and apricot fibers also contributed to phase separation behaviors. Optimal stability occurred at moderate citrus fiber concentrations, particularly when the oil content remained below

25% w/w. Rheological analysis indicated that all emulsions displayed viscoelastic properties, with the storage modulus (G') consistently exceeding the loss modulus (G''), and a shear-thinning behavior was observed, where viscosity decreased as the angular frequency increased. The primary factor affecting viscosity and resilience to physical stress was the concentration of citrus fiber, with oil concentration having a noticeable impact only at 5% fiber levels. As the citrus fiber concentration increased, so did the viscosity and linear viscoelastic region (LVER) values, indicating enhanced rigidity within the emulsion's structure. The stabilization mechanism was network-based: as citrus fiber concentration increased, it formed a tighter mesh with finer pores, which stabilized the oil more effectively. Larger fiber particles, while increasing viscosity and rigidity, created pathways that allowed for easier oil release under stress, resulting in a lubricating effect. This balance of fiber concentration and dispersion medium underscores the critical role of citrus fiber in enhancing the stability and textural properties of emulsions, depending on the formulation's specific requirements.

In the fourth and final phase, the study consolidated prior findings and ingredient selection into the creation of an emulsion-filled hydrogel, incorporating citrus fiber, apricot puree, cold-pressed hazelnut oil, hazelnut press cake, and pectin. This hydrogel demonstrated high thermal stability due to the water binding properties of citrus fiber and the oil phase stabilizing effects of hazelnut press cake. Detailed analysis showed that increased citrus fiber concentration in both water- and apricot-based systems enhanced emulsifying capacity, indicating a primarily physical stabilization rather than a Pickering-type emulsion. After centrifugation, any separated oil was unbound, suggesting that citrus fiber's three-dimensional microstructure remained intact under stress. Otherwise, we would have seen a phase separation and not a release of free oil. In this matrix, the hydrogel effectively encapsulated oil, reducing oil release even when the citrus fiber network was relatively loose. A concentration of 4% citrus fiber was chosen, as lower concentrations led to complete oil release. The addition of pectin created an extra network layer that held oil while also allowing it to gradually release, providing a lubricating effect during mastication. Despite pectin's high-temperature solubility requirements and the need for sequencing carefully ingredients and continuous mixing, no peroxide formation was detected, preserving the nutritional integrity of cold-pressed hazelnut oil. Tocopherol homologs responded differently depending on their type and the dispersing phase. In the water-based, α- and γ-tocopherol levels decreased, while these homologs in apricot puree-based samples remained stable, suggesting apricot offered oxidative protection. In both phases, δ-tocopherol, known for lower oxidative resistance, showed a decrease. Apricot also contributed unique phenolic compounds, supplying hydrophilic antioxidants unaffected by oxidation, accentuating the prospects of incorporating fruit as an effective dispersing phase for products exposed to high temperatures and air.

The interaction between pectin and citrus fiber network was crucial for forming a uniform, easily swallowable hydrogel, a key property for individuals with dysphagia. Texture analysis showed that the sugars and increased total solids in apricot promoted pectin gelation, while its pH provided ideal conditions for pectin functionality. The emulsion-filled hydrogel exhibited a firm texture initially but softened with chewing, ensuring ease of swallowing, a critical feature for dysphagia patients who benefit from a texture that is satisfying yet safe. This product represents a promising approach for delivering tailored nutrition in texture-modulated foods while preserving taste, mouthfeel, and health benefits. Texture improvement and modulation are essential for satisfying mastication needs in elderly consumers accustomed to foods with limited texture. Pectin proved highly effective in modulating texture, with different pectin types yielding varied consistencies depending on whether the hydrogel was dispersed in water or apricot puree. Apricot-based samples showed higher firmness, benefiting from the additional sugars and solids, which facilitated pectin gelation. Hazelnut press cake also positively impacted pH across samples, particularly in water-based ones, enhancing gelation within the optimal pH range and almost doubling firmness values. The tribological analysis confirmed the product's suitability for dysphagic individuals. Upon compression, the hydrogel released oil like a sponge, providing lubrication. Apricot-based samples released oil almost immediately, lowering the friction coefficient early in the curve. Water-based samples were more stable, releasing oil and reducing friction only in the mixed region. Samples with added press cake showed a consistently low initial friction coefficient, with gradual increases; none exceeded a 0.14 friction coefficient, demonstrating the product's adaptability under stress.

In conclusion, utilizing agro-industrial byproducts in food formulation is a promising route to reduce waste while maintaining nutritional and technological quality. Citrus fiber's water-absorption capacity and network-forming ability allow it to trap a fat phase that is released easily upon structural modification, such as chewing, ensuring ease of swallowing and targeted nutrient delivery. This study underscores the potential for developing innovative, nutrient-dense food products that cater to specialized dietary needs through sustainable practices.

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List of contributions

Publications on international peer-reviewed journals

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Oral presentation: Panzanini, M., Dordoni, R. "Structural Interaction between citrus fibre and fruit-based system for emulsion formulation" Pt.1, 38th EFFoST International Conference (12nd – 14th November 2024) Bruges, Belgium.

Oral presentation: Panzanini, M., Dordoni, R. "Structural Interaction between citrus fibre and fruit-based system for emulsion formulation" Pt.2, 22nd IUFOST World congress of Food Science and Technology (8th – 12nd September 2024), Rimini, Italy.

Oral presentation: Panzanini, M., Spigno, G., Pastrana Castro, L. M., Dordoni, R. "Formulation of High-value-oil-rich Ingredients by Citrus Pectin and Insoluble Fiber", 37th EFFoST International Conference (6th – 8th November 2023), Valencia, Spain.

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EFF2023 - 4th International conference on engineering future food (20th - 22nd September 2023) Firenze, Italy.

Contributed paper: Panzanini, M., Spigno, G., Pastrana Castro, L. M., Dordoni, R., “Sviluppo di sistemi lipidici innovativi per il miglioramento nutrizionale e/o funzionale di alimenti per anziani” in Healthy Aging Week 2023. Across and Beyond Disciplines (Alba, Cuneo, 06th -11th November 2023), Fondazione Ferrero, Alba (CN), Italy.

Abstract poster: Panzanini, M., Dordoni, R., “Development of high-value-oil-based systems through innovative structuring agents and different homogenization techniques for the nutritional and/or functional enhancement of food and non-food matrices”, 28th Workshop on the Developments in the Italian PhD Research on Food Science Technology and Biotechnology, Department of Agricultural Science, University of Naples - Federico II (13rd -15th September 2023), Portici (NA), Italy.

Abstract poster: Panzanini, M., Alberici, N., Dadi, F., Dordoni, R., Spigno, G., “Proteins extraction from whole soybean flour: influence of mixing rate on yield and quality”, NIZO plant protein functionality conference (11th -13rd October 2022) Papendal, Netherland.