



Article

# Impact of Hair Damage on the Penetration Profile of Coconut, Avocado, and Argan Oils into Caucasian Hair Fibers

Carolina Botelho Lourenço <sup>1,2,\*</sup>, Rebeca Mantuan Gasparin <sup>1,2</sup>, Fernanda Malanconi Thomaz <sup>1</sup>, Gustavo Carlos da Silva <sup>3</sup>, Airton Abrahao Martin <sup>3</sup>, Ana Cláudia Paiva-Santos <sup>4,5</sup> and Priscila Gava Mazzola <sup>2</sup>

- Symrise Global Hair Care Center, Cotia 06715-725, SP, Brazil; rebeca.gasparin@symrise.com (R.M.G.); fernanda.malanconi@gmail.com (F.M.T.)
- Faculty of Pharmaceutical Sciences, University of Campinas, Campinas 13083-871, SP, Brazil; pmazzola@fcf.unicamp.br
- DermoProbes Efficacy Test, Sao Jose dos Campos 12246-870, SP, Brazil; gustavo@probes.com.br (G.C.d.S.); airton.martin@probes.com.br (A.A.M.)
- Department of Pharmaceutical Technology, Faculty of Pharmacy of the University of Coimbra, Azinhaga Sta. Comba, 3000-548 Coimbra, Portugal; acsantos@ff.uc.pt
- LAQV, REQUIMTE, Department of Pharmaceutical Technology, Faculty of Pharmacy of the University of Coimbra, Azinhaga Sta. Comba, 3000-548 Coimbra, Portugal
- \* Correspondence: carolina.lourenco@symrise.com

Abstract: The mitigation of damaged hair conditions involves the application and penetration of substances to stabilize broken bond sites, restore lipids and proteins, reinstate hydrophobicity, and recover hair mechanical properties. Vegetable oils, in general, exhibit a list of advantageous characteristics much desired by consumers, given the associated benefits for hair fibers. While coconut oil is highly popular in the hair care market and extensively studied for its ability to diffuse through the hair cortex, the effects of avocado and argan oil on the internal structure of hair and their potential benefits remain underexplored. Tensile and fatigue tests, as well as Raman spectroscopy, were carried out to investigate the interaction of these three oils with virgin and bleached Caucasian hair. The oils were applied in sufficient amounts directly to hair tresses and maintained for 24 h at 25 °C. Our results show that the three oils successfully diffused and interacted with the cortical region of the hairs. Their impact on hair mechanical properties depends on the level of damage and humidity conditions. In virgin hair, coconut and avocado oil reinforce the hydrophobic barrier of the cellular membrane complex, preventing water from causing intense perturbation of the mechanical properties, leading to increased stiffness and break stress. Meanwhile, due to the high degree of unsaturation of its fatty acid chains, argan oil increases water absorption, resulting in losses in hair resistance. When bleached, the hydrophilicity of the hair fiber increases, determining more affinity for argan oil. Consequently, the affinity with water is also elevated, causing increased fragility to mechanical stress. The analyzed vegetable oils are not always beneficial for hair care. Their specific chemical characteristics and hair conditions will influence the final results and should be taken into consideration in hair care product development.

**Keywords:** argan oil; avocado oil; coconut oil; hair treatment; penetration of oils; Caucasian hair; Raman; mechanical measurements



Citation: Lourenço, C.B.; Gasparin, R.M.; Thomaz, F.M.; da Silva, G.C.; Martin, A.A.; Paiva-Santos, A.C.; Mazzola, P.G. Impact of Hair Damage on the Penetration Profile of Coconut, Avocado, and Argan Oils into Caucasian Hair Fibers. Cosmetics 2024, 11, 64. https://doi.org/10.3390/cosmetics11020064

Academic Editor: Elisabetta Esposito

Received: 21 February 2024 Revised: 26 March 2024 Accepted: 9 April 2024 Published: 21 April 2024



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

#### 1. Introduction

The diffusion capacity of materials into the hair shaft is crucial for the effectiveness of cosmetic treatments. Commonly used chemical treatments, such as bleaching, straightening, and coloring, profoundly alter the cortex's structure upon reaching it by breaking covalent bonds, oxidizing lipids, and degrading keratin and other associated proteins [1–5]. The entry of external molecules is essential to mitigate the damage caused to the structure by neutralizing the generated charged species, restoring hydrophobicity, and partially rescuing mechanical properties [6–8].

Cosmetics **2024**, 11, 64 2 of 13

The use of vegetable oils for hair care has increased considerably over the years. This trend may be linked to consumers' search for plant-based and renewable sources of ingredients, prompting the cosmetic industry to offer alternatives to meet this demand. Additionally, vegetable oils have been associated with hair benefits that extend beyond the traditional combination of lubrication and shine. Potential advantages related to the use of vegetable oils in hair care include the reduction of dryness, moisturization, nourishment, strengthening, sebum balance, enhancement of treatment masks, pre-wash protection, frizz control, split end repair, and protection against salt and chloride [9].

Extensive investigation by the scientific community has revealed that the interaction between different oils and hair is primarily influenced by the affinity of molecules with the cellular membrane complex (CMC), which functions as the intercellular cement that binds the cuticle cells and cortex together, and by molecular structure and size [10–17]. In addition, the condition of the hair may drastically alter its affinities with materials in general. Therefore, it is speculative to theoretically determine the behavior of a molecule when applied to hair.

The study of the effects of vegetable oils on hair, particularly their penetration capabilities, holds practical significance for the cosmetic industry. Numerous studies have al-ready been conducted, most of which focus on oils such as sunflower, olive, rice bran, sesame, mustard, coconut, jojoba, and almond [13–16]. However, some of the most popular oils in hair care, including avocado and argan oil, lack sufficient studies exploring their impact on the internal structure of hair and potential benefits.

Several techniques have been adopted to assess the penetration properties of molecules in hair [18]. More sophisticated methods of analysis are often required to investigate the molecular interactions that drive the diffusion of materials into the hair structures, such as spectroscopy, spectrometry, and tomography, among others [18–26]. However, these techniques frequently involve laborious sample manipulation and/or high operational costs, limiting their widespread application in an industrial context.

Considering the aforementioned data, the objective of the present study was to evaluate the penetration of argan and avocado oil, in comparison with the better-known coconut oil, into hair fibers using a combination of traditional and modern techniques commonly employed in hair science, particularly Raman spectroscopy and tensile and fatigue tests [19–22,27–30].

## 2. Materials and Methods

# 2.1. Vegetable Oils

Three commonly used vegetable oils in hair care, namely argan, avocado, and coconut oil (Symrise AG, Holzminden, DE), were selected for the experiments.

#### 2.2. Triacylglycerols Compositions of Vegetable Oils

The oil samples were analyzed through chromatography (Agilent 6850 Series GC System, Santa Clara, CA, USA) using a DB-17 HT Agilent Catalog: 122–1811 (50% phenylethylpolysiloxane) capillary column measuring 10 m in length, with an internal diameter of 0.25 mm and a film thickness of 0.15  $\mu m$ . The flow rate was 1.0 mL/min, with a linear speed of 40 cm/s. The temperatures of the detector and injector were set to 375 °C and 360 °C, respectively. The oven temperature was programmed from 250 °C to 350 °C, with a heating rate of 5 °C/min, and the final temperature was maintained for 20 min. The injected volume of the carrier gas (He) was 1.0  $\mu L$ , with a split ratio of 1:100. The sample concentrations were 10 mg/mL of tetrahydrofuran [31].

#### 2.3. Hair

Natural white hair swatches (25 g, 10 cm wide, and 25 cm long) were purchased from International Hair Importers & Products (New York, NY, USA). The hair strands, initially received from the supplier in strips measuring 10 cm wide, were further cut into smaller pieces (2.0 cm wide), each weighing approximately 2.0 g. The hair was submitted to a

Cosmetics **2024**, 11, 64 3 of 13

cleaning process using a 10% solution of sodium lauryl ether sulfate (SLES), applied at a proportion of 1.0 mL for each 10 g of hair. The solution was massaged into the hair for 1 min between fingers and rinsed for 1 min with tap water at 32  $\pm$  2 °C, at a flow rate of 4.0 L/min. Subsequently, the hair was left to dry overnight under controlled conditions (22  $\pm$  2 °C and 50  $\pm$  5% relative humidity, RH). Four hair tresses were separated for each vegetable oil treatment group, and another four for the untreated groups.

## 2.4. Bleaching Process

Half of the tresses from each group were subjected to a bleaching process (30 min at 25 °C) using a 1:2 (w/w) mixture of a commercially available 12% hydrogen peroxide emulsion (Yamá, Cotia, Brazil) and bleaching powder (Yamá, Cotia, Brazil), at a ratio of 2.5 g of product per gram of hair. Following the bleaching procedure, the tresses were rinsed under running water (33  $\pm$  3 °C and 4.0 L/min), washed with 10% SLES solution, and left to dry overnight under controlled conditions (22  $\pm$  2 °C and 50  $\pm$  5% RH).

## 2.5. Vegetable Oil Application

The oils were applied immediately after the strands had dried under the controlled conditions mentioned above. Each vegetable oil was applied directly to the tresses at a ratio of 1.0 g per gram of hair in each treatment group, which were then individually wrapped in aluminum foil and allowed to rest for 24 h at 25 °C before being cleaned once with 10% SLES solution to remove excess oil from the fibers' surface. After washing, the tresses were dried under controlled conditions (22  $\pm$  2 °C and 50  $\pm$  5% RH).

#### 2.6. Tensile Test

Forty-five fibers were randomly collected from each treatment group. Their cross-sectional dimensions were measured using an FDAS-770—Fiber Dimensional Analysis System (Dia-Stron, Andover, UK) and an LSM-6200—laser scan micrometer (Mitutoyo, Kawasaki, Japan). The obtained areas were used to calculate the stress to which the fibers were subjected during the tensile test, performed with an MTT-680—Miniature Tensile Tester (Dia-Stron, Andover, UK) at a constant stretch rate of 15 mm/min and under controlled temperature conditions (22  $\pm$  2 °C). Subsequently, the fibers were soaked in water for 1 h in the equipment's carousel to assess wet tensile strength. Elastic modulus and break stress parameters were determined using UvWin software version 2.35 build 3 (Dia-Stron, Andover, UK). Data analysis was conducted through one-way ANOVA, followed by Tukey's post hoc HSD test, with a 95% confidence interval ( $p \leq 0.05$ ). The analyses were performed using Microsoft Office Excel with XL STAT.

## 2.7. Fatigue Test

The cross-sectional dimensions of 50 fibers randomly collected from each group were determined using an FDAS-770—Fiber Dimensional Analysis System (Dia-Stron, Andover, UK) and an LSM-6200—laser scan micrometer (Mitutoyo, Kawasaki, Japan). The obtained areas were then used to calculate the stress to which the fibers were subjected during the fatigue test, performed using a CYC-801—Cyclic Tester (Dia-Stron, Andover, UK) at a constant stress of 130 MPa and a stretch rate of 40 mm/min. Data analysis was carried out using UvWin software version 2.35 build 3 (Dia-Stron, Andover, UK).

## 2.8. Raman Spectroscopy Analysis

Six fibers from each group were randomly collected and individually positioned over a Raman system lens at  $40\times$  magnification. Three points on each fiber were analyzed using a Confocal Raman—Model 3510 Skin Composition Analyzer (Rivers Diagnostics, Rotterdam, NLD) coupled to a solid-state excitation laser operating at 785 nm, with a power of  $20\pm2$  mW, and a Charge-Coupled Device (CCD) detector. Spectra acquisition was performed over a spectral range of 1800 to  $400~{\rm cm}^{-1}$ . The final spectrum consists of a combination of those obtained for each treatment.

Cosmetics **2024**, 11, 64 4 of 13

#### 3. Results

## 3.1. Triacylglycerols Compositions of Vegetable Oils

The vegetable oils' triacylglycerol composition was analyzed using the official methods and recommended practices of the American Oil Chemists' Society [31]. Table 1 shows the results of the triacylglycerol distribution analysis for argan, avocado, and coconut oil.

**Table 1.** Triacylglycerol distribution of the vegetable oils, determined by gas chromatography (GC), evidencing the percentage of normalized area and indicating the relative distribution of compounds in the samples. The symbolic letters correspond to the fatty acids present in the structure of these triacylglycerols, namely: Cy (caprylic acid, 8:0); C (capric acid, 10:0); La (lauric acid, 12:0); M (myristic acid, 14:0); P (palmitic acid, 16:0); Po (palmitoleic acid, 16:1); S (stearic acid, 18:0); O (oleic acid, 18:1); L (linoleic acid, 18:2).

N. 1. (C.1	m21.1	%			
Number of Carbons	Triacylglycerol -	Coconut Oil	Argan Oil	Avocado Oil	
C28	Cy-La-Cy	0.50	-	-	
C30	Cy-La-C	2.71	-	-	
C32	Cy-La-La	10.66	-	-	
C32	Cy-M-C	1.05	-	-	
C34	Cy-La-M/C-La-La	15.92	-	-	
626	La-La-La	18.85	-	-	
C36	C-La-M	0.50	-	-	
C29	M-La-La	14.12	-	-	
C38	Cy-O-La	6.11	-	-	
	P-La-La/M-La-M	9.92	-	-	
C40	C-M-P	1.21	-	-	
	P-La-M	5.34	-	-	
C42	La-O-La	2.09	-	-	
	La-L-La	0.89	-	-	
C44	S-La-M/P-La-P/P- M-M	1.98	-	-	
	M-O-La	1.76	-	-	
	M-L-La	0.54	-	-	
	S-M-M/S-La-P	0.64	-	-	
C46	P-O-La/M-O-M	1.52	-	-	
	P-L-La	0.53	-	-	
	S-M-P	0.22	-	-	
C48	S-O-La/P-O-M	1.49	-	-	
	La-O-O	0.31	-	-	
C50	S-O-M/P-O-P/M-O- O	0.72	-	-	
	P-O-P	3.31	3.31	3.04	
	P-L-P	1.72	1.72	-	
	P-O-Po/P-L-P	=	-	2.34	
	P-L-Po/Po-O-Po	-	-	0.26	
C52	P-O-S	0.25	2.73	0.73	
	P-O-O	0.18	14.75	22.51	
	P-L-S	-	1.46	-	
	P-O-L	-	11.98	-	
	P-L-L	=	5.27	<del>-</del>	
	P-L-O/Po-O-O	-	-	8.81	
	P-L-L/Po-L-O	-	-	3.08	

Cosmetics **2024**, *11*, 64 5 of 13

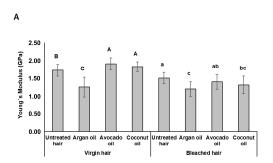
Table 1. Cont.

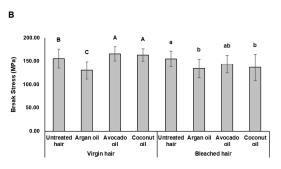
Number of Carbons	Triacylglycerol	%		
		Coconut Oil	Argan Oil	Avocado Oil
	S-O-S/S-L-S	-	0.71	
	S-O-O	-	5.42	3.18
	O-O-O	-	14.83	38.10
C54	S-O-L	-	4.27	
	O-L-O	-	16.70	15.60
	O-L-L	-	11.27	2.35
	L-L-L	-	5.58	

Argan oil is composed of triacylglycerols with long-chain fatty acids containing between 16 and 18 carbons. Its molecular composition typically includes at least one unsaturated fatty acid. The presence of double bonds, compared to saturated chains, increases polarity and adds spatial volume to the molecules. Meanwhile, avocado oil exhibits a similar triacylglycerol distribution to that of argan oil, with structures composed of long-chain fatty acids (16 to 18 carbons). Although avocado oil contains predominantly unsaturated molecular components, their presence is much smaller than in argan oil. In contrast, coconut oil is characterized by saturated molecules, which make up more than 85% of its fatty acid composition, with most chains containing 12 to 16 carbons. The absence of unsaturation in these molecules makes them a hydrophobic mixture of components. However, the higher concentration of shorter chains reduces the hydrophobicity of coconut oil compared to other oils.

#### 3.2. Tensile Test

Figure 1 shows the impact of the oil treatments on (1A) Young's modulus and (1B) break stress for both the virgin and bleached hair fibers. In the virgin condition, the hair became more flexible, as evidenced by a 27.40% decrease in Young's modulus with the use of argan oil. Conversely, the hair showed reduced flexibility, with an increase in Young's modulus of 10.37% and 5.85% with the use of avocado and coconut oil, respectively. Similar trends were observed for break stress, with the argan oil treatment reducing it by 16.28%, while the avocado and coconut oil treatments increased it by 6.59% and 5.04%, respectively. Meanwhile, in the bleached state, the oil treatments resulted in a reduction of the evaluated mechanical parameters. Argan oil had the most significant impact, causing a reduction in Young's modulus by 20.38% and break stress by 13.30%. The avocado and coconut oils also led to a reduction in Young's modulus by 7.05% and 12.67%, respectively, and in break stress by 7.31% and 11.87%, respectively.





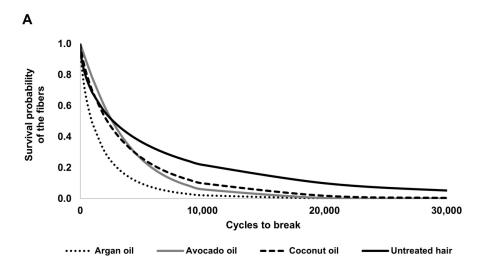
**Figure 1.** Mechanical properties of the hair obtained from the tensile test for both virgin and bleached hair, with and without the application of the oils. **(A)**—Young's modulus, representing the elastic behavior of the fibers. Mean  $\pm$  SD. **(B)**—break stress, representing the maximum stress at the moment of rupture. Mean  $\pm$  SD. Uppercase and lowercase letters represent Tukey's analysis of the differences among treatments, with a 95% confidence interval, for the virgin and bleached hair, respectively. Identical letters indicate p > 0.05, and different letters indicate p < 0.05.

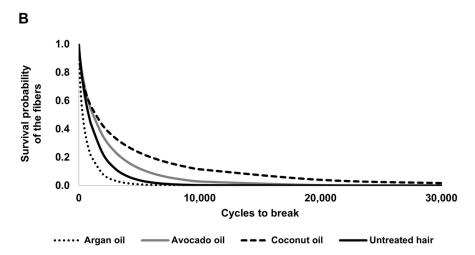
Cosmetics **2024**, 11, 64 6 of 13

## 3.3. Fatigue Test

The fatigue test assesses the propensity for failure in hair fibers subjected to repeated mechanical stresses (cycles) within their elastic behavior zone. The generated data do not adhere to normal distribution; instead, they conform to Weibull distribution, characterized by alpha ( $\alpha$ ) and beta ( $\beta$ ) parameters. Alpha represents the cycle at which 63.2% of the fibers have already ruptured, indicating the fibers' resistance to fracture. Beta, on the other hand, represents the shape of the data distribution and, in the context of the fatigue test, is associated with the premature rupture of fibers, which is related to the accumulation of cracks on their surface [27].

Figure 2 and Table 2 present the survival probability curves over the cycles of mechanical stress obtained for each group, along with their corresponding  $\alpha$  and  $\beta$  values. In the bleached condition, the hair treatments with avocado and coconut oil resulted in an increase in  $\alpha$  and a decrease in  $\beta$ . Meanwhile, argan oil treatment led to a reduction in both  $\alpha$  and  $\beta$  values compared to untreated hair. As for the virgin state, the obtained results took a different direction, demonstrating a reduction in  $\alpha$  with the avocado and coconut oil treatments and an increase in  $\beta$  for all tested oils compared to untreated hair. The decrease in the alpha parameter for the argan oil-treated hair was more pronounced than that observed for bleached hair treated with argan oil.





**Figure 2.** Survival probability curves from the fatigue test for virgin (**A**) and bleached (**B**) hair with and without oil treatments.

Cosmetics **2024**, 11, 64 7 of 13

<b>Table 2.</b> Characteristic life ( $\alpha$ ) and shape parameter ( $\beta$ ) obtained from the fatigue test for virgin $\alpha$	and
bleached hair with and without oil treatments.	

Sample —	Characteristic Life (α)		Shape Parameter (β)	
	Virgin	Bleached	Virgin	Bleached
Untreated hair	4974	1235	0.60	0.85
Argan oil	1569	526	0.73	0.70
Avocado oil	3720	1858	1.05	0.76
Coconut oil	3503	2585	0.80	0.57

#### 3.4. Raman Spectroscopy

Raman spectroscopy is a technique in which the vibrational energy of molecules is altered by the collision of photons through the inelastic scattering of light, resulting in a modification of their frequency [32]. Each functional group within the biomolecules vibrates and scatters light at specific frequencies, enabling their identification in a matrix.

Confocal Raman spectroscopy can be used to study the permeation profile of an oil into a hair fiber by analyzing the molecular composition of the hair at different depths. By focusing a laser beam onto the hair surface, Raman scattering from the molecules within the hair can be measured. As the oil penetrates the hair fiber, changes in the Raman spectra will indicate alterations in the molecular composition and distribution within the hair. Depth profiling can be achieved by adjusting the focal point of the laser beam, allowing for the examination of different layers within the hair. This technique provides valuable insights into the penetration kinetics and depth of oil permeation into the hair fiber.

Considering that hair fibers may have an average cross-sectional measurement of 80 to 100  $\mu m$ , the characteristic spectra of each isolated oil in the untreated and treated virgin hair were obtained every 4.0  $\mu m$  in depth, starting from the cuticles and reaching a depth of approximately 50  $\mu m$  to cover the depth from the surface to the central zone of the fibers. The acquired spectra were superimposed to identify bands of interest, defined as those present in the spectra of the treated hair and oils but absent in the spectrum of un-treated hair.

Figure 3A–C shows the spectra of the argan, avocado, and coconut oils, respectively, highlighting the identified bands of interest. The band at 1064 cm<sup>-1</sup> exhibits significant intensity in all three oils and, consequently, in the hair treated with these oils, albeit with less intensity in untreated hair. Therefore, in this study, this particular band was used as a reference for the penetration analyses.

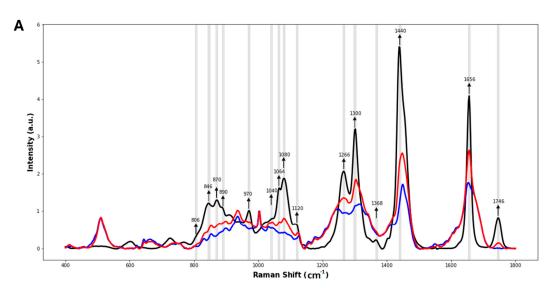
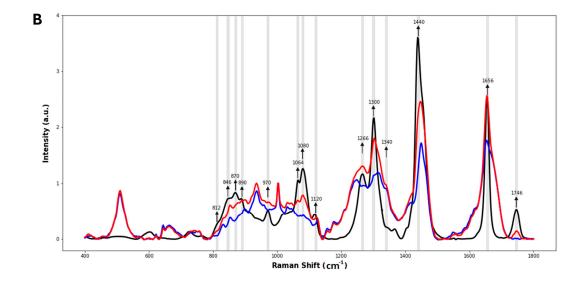
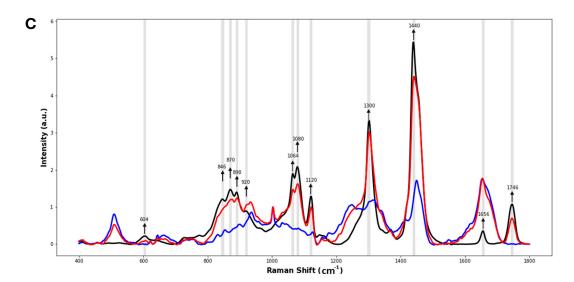


Figure 3. Cont.

Cosmetics **2024**, 11, 64 8 of 13

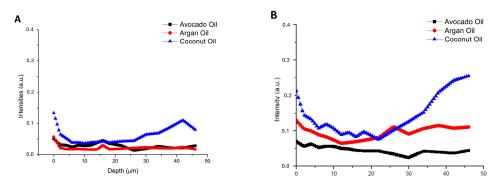




**Figure 3.** Spectra of the isolated oils in treated hair and untreated virgin hair for (**A**) argan oil, (**B**) avocado oil, and (**C**) coconut oil for the determination of the bands of interest, defined as those present in the oils and treated hairs but absent in the untreated hair. In each spectrum, the black line represents the isolated oil, the red line represents the respective oil-treated hair, and the blue line represents the untreated hair. The grey vertical lines highlight the bands of interest for each oil.

Once the penetration profiles were determined for each measurement, averages were obtained (Figure 4) for both the virgin and bleached hair. In both hair conditions, coconut oil was identified at a higher intensity in depths beyond 30  $\mu m$ . The argan and avocado oils were present at lower intensities compared to coconut oil. The penetration profile of the virgin hair featured high intensities of avocado oil up to depths of approximately 25  $\mu m$  and of coconut oil up to 50  $\mu m$ . Argan oil exhibited high intensities at depths between 0 and 5.0  $\mu m$ , but its presence was limited. In general, the oils showed higher penetration intensities in bleached hair than in virgin hair, most likely due to facilitated routes resulting from the oxidation process to which the hair was subjected. Coconut oil diffused at higher intensities in this hair type, indicating accumulation at depths between 30 and 50  $\mu m$ . Argan oil could diffuse in higher amounts than in virgin hair, while avocado oil exhibited limited presence at greater depths.

Cosmetics **2024**, 11, 64 9 of 13



**Figure 4.** Penetration profiles of the argan, avocado, and coconut oils in virgin (**A**) and bleached hair (**B**) as a function of depth in the cortical region, measured from the hair surface to the central area of the cross-section of the fibers.

#### 4. Discussion

Vegetable oils are composed of triglycerides, which consist of one molecule of esterified glycerol and three molecules of fatty acids. The hydrophobic nature of these species is determined by the length of their carbon-saturated chains. Unsaturation can occur in the middle of the carbon chain, creating negative poles due to the concentration of electrons in this molecular zone, providing the molecule with hydrophilic sites. Moreover, unsaturation is responsible for expanding the spatial volume of structures, as it generates folding points in the molecule, thereby increasing the three-dimensional occupied area.

The differences in the triglyceride composition of oils result in varying affinities with the hair structure. Since the structure of hair varies depending on its damage condition, it is anticipated that the affinity with these oils will be influenced by the extent of damage to the hair.

Robbins and Crawford [33,34] concluded from their experiments that variations in the mechanical properties of hair result from alterations in the cortex, independent of the influence of the cuticles. In this context, changes in the tensile test parameters in virgin and bleached hair treated with oils may indicate that the oils were capable of interacting with the hair cortex, suggesting their ability to penetrate the hair fibers.

In the fatigue test, the alpha parameter expresses the fibers' resistance to fracture. In other words, the higher the alpha values within a given group of fibers, the more they will resist applied stresses. The beta parameter, in turn, is associated with the prematurity of fiber rupture, which correlates with the number of accumulated cracks on the fiber's sur-face. Consequently, lower beta values suggest more premature ruptures, indicating a greater presence of cracks on the surface of this given group of fibers [27].

It is a known fact that humidity conditions play a vital role in the mechanical properties of hair. However, it has been observed that the wet state in the tensile test appears to increase the sensitivity of the method, as reported by Evans [30]. In both the tensile test (100%) and the fatigue test (50%), hair was initially exposed to oils and subsequently to humidity. Therefore, the discussion on the penetration of the oils into the hair will take into account the influence of water on the mechanical properties.

Virgin hair presents an intact CMC, which facilitates the diffusion of nonpolar and compact molecules, such as coconut triglycerides. Avocado and argan oil exhibit longer carbon chains and unsaturation as a major part of their composition, hindering the diffusion of these molecules into the hair, with a minor but non-negligible portion composed of shorter carbon chain structures (14.98% and 14.20%, respectively). Young's modulus increased in hair treated with avocado and coconut oil but decreased in hair treated with argan oil, with a similar trend observed in variations of break stress. The  $\alpha$  parameter obtained in the fatigue test is expected to follow Young's modulus, increasing as the hair becomes stiffer and more resistant to stress, thereby elevating the survival probability. The results of the fatigue test indicated that the three oils led to a reduction in the  $\alpha$  parameter and survival probability while increasing  $\beta$  values. Considering these findings for  $\alpha$  and

survival probability, it is reasonable to conclude that the difference in humidity conditions between the two tests influenced the results.

Avocado and coconut oil exhibit less unsaturation in their composition, resulting in smaller molecular volumes, a characteristic that favors deeper diffusion into the cortex of virgin hair. Argan oil was also able to diffuse into the hair, as evidenced by the results, but remained located between the cuticle layers and in the outer zones of the cortical region thanks to its larger molecular volume. The penetration profile of this oil indicated a greater presence from 0 to 5.0 µm towards the fiber interior. Due to its higher degree of unsaturation and limited penetration into the cortex, the argan oil-treated hair cortex remained less hydrophobic compared to that of hair treated with avocado and coconut oil. In the tensile test, these differences in the hydrophobicity of the cortices penetrated by the oils determined their relationship with the added water. The presence of argan oil, rich in unsaturation, led to an increased affinity to water, resulting in an increase in the plasticizing effect in this sample. Consequently, Young's modulus and break stress reduced. On the other hand, the avocado- and coconut oil-treated hair fibers repelled water more intensely, as their cortices were more hydrophobic, leading to an increase in Young's modulus and, consequently, in break stress.

At a relative humidity of 50%, in the fatigue test, the hair's interaction with water is less pronounced. We posit that the observed results more clearly demonstrate the effects of the oils on the structural molecules of the hair, as water is not as relevant for result interpretation. Marsh et al. [35] pointed out that the presence of external materials within the fiber can interfere with molecular interactions in the cortex. Having penetrated through the intact CMC of virgin hair, the avocado and coconut oils likely established hydrophobic interactions with the keratin chains and matrix proteins. These interactions generate competition for both inter- and intramolecular interactions of the matrix and keratin chains [29]. The mechanical stress resistance, supported in part by these interactions, is decreased, leading to a lower breaking force and, consequently, reduced survival probability. The beta ( $\beta$ ) values increased with the oil treatments, indicating a reduction in the propagation of flaws on the hair surface in the presence of the oils.

In bleached hair, the oxidation induced by the bleaching process cleaves bonds and alters the chemical properties of the structural molecules of the hair. The cuticular barrier can be partially reduced, with the loss of scales, or cracked, making the path shorter and facilitating molecule transportation. As a result, bleached hair exhibits a greater affinity with polar substances. The parameters from the tensile test revealed that the effects of treatment with avocado oil differed from those using argan and coconut oil. The latter treatments reduced Young's modulus and break stress, while the treatment with avocado did not.

In this hair condition, the CMC has undergone partial degradation, and there is the presence of charged species in the cortical area. The affinity of the cortex for non-polar materials is reduced. The penetration profiles of these oils in bleached hair indicates that coconut and argan oil were able to diffuse in higher amounts through the cortex than avocado oil. The triglycerides in argan oil, which are richer in unsaturation than those in the other two oils, had an advantage for diffusion due to their polarity. Coconut oil, whose composition presents triglycerides with more polarity compared to avocado oil, also showed greater affinity with bleached hair than avocado oil, indicating that the latter had a disadvantage for diffusion in bleached hair. Although coconut and argan oil were able to diffuse more, the highly hydrophilic condition of the hair was not significantly altered by the presence of the oils. Moreover, the results suggest that the presence of argan oil intensified the hair's affinity with water when compared to coconut and avocado oil, resulting in a more pronounced plasticizing effect, which led to a reduction in the mechanical parameters. The higher number of nonpolar triglycerides and the lower level of un-saturation in avocado oil compared to argan oil may have caused it to concentrate more on the hair surface, being more intensely removed during pre-test washing.

Evans [28] observed that lubrication at the hair surface impacts the reduction in grooming forces, with a consequent decrease in fatiguing forces. This implies that the  $\alpha$ and  $\beta$  values should increase with the surface lubrication effect. In the dry-state fatigue test, avocado and coconut oil promoted an increase in  $\alpha$ , indicating that they contributed to enhancing hair resistance to breakage. Due to the predominantly hydrophobic nature of their molecular structures, the hair's affinity with these oils was reduced. It is likely that they were retained in the outer zones of the cortical region and within the cuticular layers, forming a hydrophobic barrier and slowing the absorption of humidity from the environment. These findings align with those described by Keis et al. [36] in their vapor adsorption experiments, where a similar effect was observed due to a clogging effect caused by the oil treatments, decelerating water dissipation in the hair. Argan oil, on the other hand, lowers the value of  $\alpha$ , increasing hair fragility to mechanical stress. We speculate that the presence of argan oil in the cortex, as observed in the tensile test, contributed to the in-crease in the absorption of humidity from the environment. The  $\beta$  parameter indicated that the treatments led to an increase in the propagation of cracks on the hair surface, suggesting that the oils could not fully protect the hair from premature breakage, an after-effect of the aggressive bleaching process.

The pathway through which materials diffuse into the hair cortex has been a topic of interest in many studies [37–39]. Research suggests that the intercellular pathway is the most preferred route, where materials surround the cells of the cuticle and cortex via the CMC and non-crystalline regions. Hornby et al. [11] noted that low-sulfur, non-keratinous environs swell more easily than highly cross-linked regions, better accommodating the presence of diffusing molecules. In addition, Malinauskyte at al. [8] pointed out that low-molecular-weight species tend to allocate to these regions, where they establish ionic interactions with matrix proteins.

## 5. Conclusions

The penetration of cosmetic agents into hair fibers is a strategy aimed at restoring some of the properties lost during chemical treatments. Vegetable oils, in general, possess a list of relevant and highly convenient characteristics for the cosmetic industry, including relative ease of obtainment, environmentally friendly processes, sustainable labels, safety, efficiency, and numerous benefits for consumers, such as enhanced sensory experience, lubrication, strength, and resistance, among many others. Among the oils commonly used in hair care, avocado and argan oil have not yet been studied in depth. In contrast, coconut oil is well-known for its penetration ability and interactions with the hair cortex, making it a suitable reference for our study. We concluded that all three oils are composed of tri-glycerides capable of penetrating and interacting with the hair cortex.

The chemical nature of hair, whether intact or damaged, will determine its interactions with different materials, either increasing or decreasing their affinity with the internal structure and leading to varying effects. Once these materials penetrate the hair, they modify how the hair interacts with water and, consequently, how water affects the mechanical properties of the hair structure. Avocado and coconut oil, when interacting with hair, emphasize the CMC lipid pathway, intensifying the hydrophobic nature of virgin hair and preventing water from diffusing through the structure. However, in bleached hair, their effects may be insufficient to protect the hair fiber from humidity and restore its mechanical properties. Argan oil, on the other hand, despite having penetrated the hair, acted by increasing its affinity with water rather than reducing it, leading to the expansion of the hair's affinity with water, making it more susceptible to rupture.

**Author Contributions:** Conceptualization, C.B.L., R.M.G., F.M.T. and P.G.M.; data curation, C.B.L., R.M.G. and F.M.T.; formal analysis, C.B.L., R.M.G., F.M.T., G.C.d.S. and A.A.M.; investigation, C.B.L., R.M.G., F.M.T., G.C.d.S. and A.A.M.; resources, C.B.L.; writing—original draft preparation, C.B.L., R.M.G., F.M.T., G.C.d.S. and A.A.M.; writing—review and editing, C.B.L., R.M.G., F.M.T., G.C.d.S., A.A.M., A.C.P.-S. and P.G.M.; visualization, C.B.L.; supervision, C.B.L., A.C.P.-S. and P.G.M.; project

administration, C.B.L.; funding acquisition, C.B.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** The authors declare that this study received funding from Symrise. The funder had the following involvement with the study: study design, collection, analysis, interpretation of data, the writing of this article, and the decision to submit it for publication.

Institutional Review Board Statement: Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author/s.

**Conflicts of Interest:** Authors Carolina Botelho Lourenço, Rebeca Mantuan Gasparin, and Fer-nanda Malanconi Thomaz were employed by the company Symrise. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as potential conflicts of interest.

#### References

- 1. Tate, M.L.; Kamath, Y.K.; Ruetsch, S.B. Quantification and prevention of hair damage. J. Soc. Cosmet. Chem. 1993, 44, 347–371.
- 2. Wortmann, F.-J.; Springob, C.; Sendelbach, G. Investigations of Cosmetically Treated Human Hair by Differential Scanning Calorimetry in Water. *J. Cosmet. Sci* **2002**, *53*, 219–228. [PubMed]
- 3. Wortmann, F.-J.; Sendelbach, G.; Popescu, C. Fundamental DSC Investigations of A-Keratinous Materials as Basis for the Interpretation of Specific Effects of Chemical, Cosmetic Treatments on Human Hair. J. Cosmet. Sci. 2007, 58, 311–317. [PubMed]
- 4. Fujii, T.; Ito, Y.; Watanabe, T.; Kawasoe, T. Effects of Oxidative Treatments on Human Hair Keratin Films. *J. Cosmet. Sci.* **2012**, *63*, 15–25. [PubMed]
- 5. Grosvenor, A.J.; Deb-Choudhury, S.; Middlewood, P.G.; Thomas, A.; Lee, E.; Vernon, J.A.; Woods, J.L.; Taylor, C.; Bell, F.I.; Clerens, S. The physical and chemical disruption of human hair after bleaching—Studies by transmission electron microscopy and redox proteomics. *Int. J. Cosmet. Sci.* 2018, 40, 536–548. [CrossRef] [PubMed]
- 6. Ruetsch, S.B.; Kamath, Y.K. Penetration of cationic conditioning compounds into hair fibers: A TOF-SIMS approach. *J. Cosmet. Sci.* **2005**, *56*, 323–330. [CrossRef] [PubMed]
- 7. Marsh, J.M.; Huangb, S.; Whitakera, S.; Guagliardob, P.; Lucasa, R.L.; Arcaa, H.C.; Jiangb, H. High-resolution visualization of cosmetic active compounds in hair using nanoscale secondary ion mass spectrometry. *Colloids Surf. B Biointerfaces* **2019**, 174, 563–568. [CrossRef] [PubMed]
- 8. Malinauskyte, E.; Shrestha, R.; Cornwell, P.A.; Gourion-Arsiquaud, S.; Hindley, M. Penetration of different molecular weight hydrolysed keratins into hair fibres and their effects on the physical properties of textured hair. *Int. J. Cosmet. Sci.* **2021**, 43, 26–37. [CrossRef]
- 9. Manoel, I. Manual dos Cabelos: O Poder dos Óleos; Laços: Sao Paulo, Brazil, 2003.
- 10. Gode, V.; Bhalla, N.; Shirhatti, V.; Mhaskar, S.; Kamath, Y. Quantitative measurement of the penetration of coconut oil into human hair using radiolabeled coconut oil. *J. Cosmet. Sci.* **2005**, *63*, 27–31.
- 11. Hornby, S.B.; Appa, Y.; Ruetsch, S.; Kamath, Y. Mapping penetration of cosmetic compounds into hair fibers using time-of-flight secondary ion mass spectroscopy (TOF-SIMS). *IFSCC Mag.* **2005**, *8*, 99–104.
- 12. Rele, A.S.; Mohile, R. Effect of coconut oil on prevention of hair damage. Part I. J. Cosmet. Sci. 1999, 50, 327–339.
- 13. Ruetsch, S.B.; Kamath, Y.; Rele, A.S.; Mohile, R.B. Secondary ion mass spectrometric investigation of penetration of coconut and mineral oils into human hair fibers: Relevance to hair damage. *J. Cosmet. Sci.* **2001**, *52*, 169–184. [PubMed]
- 14. Srivastav, A.; Dandekar, P.; Jain, R. Penetration study of oils and its formulations into the human hair using confocal microscopy. *J. Cosmet. Dermatol.* **2019**, *18*, 1947–1954. [CrossRef]
- 15. Leite, M.G.A.; Campos, P.M.B.G.M. Development and efficacy evaluation of hair care formulations containing vegetable oils and silicone. *Int. J. Phytocosmet. Nat. Ingred.* **2018**, *5*, 9. [CrossRef]
- 16. Keis, K.; Persaud, D.; Kamath, Y.K.; Rele, A.S. Investigation of penetration abilities of various oils into human hair fibers. *J. Cosmet. Sci.* **2005**, *56*, 283–295. [CrossRef] [PubMed]
- 17. Fregonesi, A.; Scanavez, C.; Santos, L.; Oliveira, A.; Roesler, R.; Escudeiro, C.; Moncayo, P.; Sanctis, D.; Gesztesi, J.L. Brazilian oils and butters: The effect of different fatty acid chain composition on human hair physiochemical properties. *J. Cosmet. Sci.* 2009, 60, 273–280. [CrossRef]
- 18. Lourenco, C.B.; Fava, A.L.M.; Santos, E.M.; Macedo, L.M.; Tundisi, L.L.; Ataide, J.A.; Mazzola, P.G. Brief descriptions of the principles of prominent methods used to study the penetration of materials into human hair and a review of examples of their use. *Int. J. Cosmet. Sci.* **2021**, *43*, 113–122. [CrossRef]
- 19. Zimmerley, M.; Lin, C.-Y.; Oertel, D.C.; Marsh, J.M.; Ward, J.L.; Potma, E.O. Quantitative detection of chemical compounds in human hair with coherent anti-Stokes Raman scattering microscopy. *J. Biomed. Opt.* **2009**, *14*, 044019. [CrossRef]

 Colthup, N.B.; Daly, L.H.; Wiberley, S.E. Introduction to Infrared and Raman Spectroscopy, 3rd ed.; Academic Press: San Diego, CA, USA, 1990.

- 21. Kuzuhara, A. Raman Spectroscopic Analysis of L-Phenylalanine and Hydrolyzed Eggwhite Protein Penetration into Keratin Fibers. *J. Appl. Polym. Sci.* **2011**, *122*, 2680–2689. [CrossRef]
- 22. Kuzuhara, A. A Raman spectroscopic investigation of the mechanism of the reduction in hair with thioglycerol and the accompanying disulphide conformational changes. *Int. J. Cosmet. Sci.* **2018**, *40*, 34–43. [CrossRef]
- 23. Kojima, T.; Tsuji, S.; Niwa, M.; Saito, K.; Matsushita, Y.; Fukushima, K. Distribution Analysis of Triglyceride Having Repair Effect on Damaged Human Hair by TOF-SIMS. Int. *J. Polym. Anal.* **2012**, *17*, 21–28. [CrossRef]
- 24. Brunelle, A.; Touboul, D.; Laprévote, O. Biological tissue imaging with time-of-flight secondary ion mass spectrometry and cluster ion sources. *J. Mass Spectrom.* **2005**, *40*, 985–999. [CrossRef] [PubMed]
- 25. Saleem, M.; Galla, H.-J. Surface view of the lateral organization of lipids and proteins in lung surfactant model systems—A ToF-SIMS approach. *BBA-Biomembr.* **2010**, *1798*, 730–740. [CrossRef] [PubMed]
- 26. Tsugita, T.; Iwai, T. Optical coherence tomography using images of hair structure and dyes penetrating into the hair. *Skin Res. Technol.* **2014**, *20*, 389–398. [CrossRef] [PubMed]
- 27. Evans, T. Fatigue testing of hair—A statistical approach to hair breakage. J. Cosmet. Sci. 2009, 60, 599–616. [CrossRef] [PubMed]
- 28. Evans, T. A unifying theory for visualizing the causes of hair breakage and subsequent strategies for mitigation. *J. Cosmet. Sci.* **2017**, *68*, 137–140. [PubMed]
- 29. Wortmann, F.-J.; Zahnt, H. The Stress Strain Curve of alpha-Keratin Fibers and the Structure of Intermediate Filaments. *Text. Res. J.* **1994**, *64*, 737–743. [CrossRef]
- 30. Evans, T. Measuring hair strength—Part 1: Stress-Strain Curves. Cosmet. Toilet. 2013, 128, 591-594.
- 31. American Oil Chemists' Society. Official Methods and Recommended Practices of the American Oil Chemists' Society, 5th ed.; AOCS: Champaign, IL, USA, 2009.
- 32. Raman, C.V.; Krishnan, K.S. A new type of Secondary Radiation. Nature 1928, 21, 501. [CrossRef]
- 33. Robbins, C.R.; Crawford, R. Cuticle damage and the tensile properties of human hair. J. Soc. Cosmet. Chem. 1991, 42, 59-67.
- 34. Robbins, C.R. Chemical and Physical Behavior of Human Hair, 5th ed.; Springer: New York, NY, USA; Berlin/Heidelberg, Germany, 2012.
- 35. Marsh, J.M.; Clarke, C.J.; Meinert, M.; Dahlgren, R.M. Investigations of cosmetic treatments on high-pressure differential scanning calorimetry. *J. Cosmet. Sci.* **2007**, *58*, 319–327. [PubMed]
- 36. Keis, K.; Huemmer, C.L.; Kamath, Y. Effect of oil films on moisture vapor absorption on human hair. *J. Cosmet. Sci.* **2007**, *58*, 135–145. [CrossRef] [PubMed]
- 37. Potsch, L.; Moeller, M.R. On Pathways for Small Molecules into and Out of Human Hair Fibers. *J. Forensic Sci.* **1996**, *41*, 121–125. [CrossRef] [PubMed]
- 38. Kelch, A.; Wessel, S.; Will, T.; Hintze, U.; Wepf, R.; Wiesendanger, R. Penetration Pathways of Fluorescent Dyes in Human Hair Fibres Investigated by Scanning Near-Field Optical Microscopy. *J. Microsc.* **2000**, 200, 179–186. [CrossRef]
- Gummer, C.L. Elucidating penetration pathways into the hair fiber using novel microscopic techniques. J. Cosmet. Sci. 2007, 52, 265–280.

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