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Preliminary study of the potential photoprotective effect of organogel-based lipstick formulations: texture analysis, rheological, thermal and sensory properties

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Abstract

With the increase in occupation-specific risks of lip cancer associated with solar radiation, there is a need for developing photoprotective lipsticks to protect skin against harmful effects of UV radiation. Considering the unique chemical and physical properties of low-molecular-weight organogelators (LMOGs), the present study intended to assess the UV protective properties of LMOGs-based lipstick formulations. In this study, dibenzylidene-D-sorbitol (DBS) and 12-hydroxystearic acid (12-HSA) were used to formulate lipsticks : L1 (1% DBS), L2 (10% 12-HSA), L3 (1.5% DBS) and L4 (control, no LMOGs). The lipstick formulations were tested for *in vitro* sun protection factors (SPF), UVA protection factor (UVA-PF), thermal, mechanical and texture analyses. Lipsticks with LMOGs exhibited higher UVA-PF and SPF, and more particularly 12-HSA-based lipstick. Results showed also the viscoelastic and heat-resistant properties of LMOGs and their effect of increasing pay-off values. In general, texture analysis indicating that 12-HSA-based lipstick was significantly harder to bend compared to control, while other formulations became softer and easier to bend throughout the stability study. Finally, sensorial and instrumental analyses permitted to classify lipsticks into two groups. This work suggests the potential use of LMOGs as a structuring agent for lipsticks paving the way towards more photoprotective and sustainable-derived alternatives.

Keywords : LMOGs, organogels, lipsticks, formulation, photoprotection, mechanical properties

Introduction

As the incidence of lip cancer has been rising over the past few decades, ultraviolet radiation (UVR) is considered as the main risk factor [1-3]. Despite growing concerns about lip cancer in some geographical areas (Australia, Israel, Canada, Spain, Denmark) [3,4], research studies on the development of photoprotective lipsticks are still missing. From an anatomical point of view, the lower lips are more permeable to UV radiation than the skin because its epithelium is thinner, has thinner keratin layers and low melanin content [5]. Although multiple factors have been related to lip cancer, outdoors workers are at high risk of developing lip cancer due to their excessive exposure to UVR [6]. Also, the incidence rate of lip cancer is higher in men than in women, which can be explained in part by the use of lipstick [6-8].

Lipsticks are commonly composed of many different ingredients, such as oils, pigments, waxes which are not only for aesthetic purposes but also can act as bioactive agents for environment extreme weather or UV protection [9,10]. Consequently, acceptable lipstick formulations should meet the following criteria : (1) thermal stability with a melting point generally within 55-75 °C and humidity variation to extreme maxima [11]; (2) dermatologically safe; (4) pleasant smell and taste; (5) softening at the lip temperature (32 °C); sufficient mechanical and physical properties with strength maintaining its structural integrity [12] and (7) improved appearance without any defaults (air bubbles, crakes, sweating occurring during preparation steps). Furthermore, special attention should be paid on different physical parameters of lipstick that contribute to adequate photoprotection such as a firm consistency and pay-off in terms of amount of lipsticks (thickness of lipstick layer) transferred into the skin [13].

Waxes are widely used in cosmetic product due to their viscoelastic, thermal and mechanical properties offering broad range of industrial applications (cosmetic, pharmaceutical and agri-food) [14]. Since a wide variety of waxes derived from animal or plant-based affected by environmental concerns, customers are switching to vegan-friendly and nature renewable cosmetics. Therefore, vegetable-based low molecular organogelators (LMOGs) and natural waxes have become an important alternative strategy to replace trans and saturated fats as structuring agents of edible oils [15,16]. 12-Hydroxystearic acid (12-HSA) is derived from naturally occuring ricinoleic, a hydroxylated fatty acid, present as 90% in castor oil and listed as a renewable source [17]. 12-HSA can form self-assembled fibrillar network (SAFiN) upon interaction of fibrillar crystals via non-covalent bonds such as van der Waals interactions, π-π stacking bonds and hydrogen bonds, as well as, firm gels at a low concentration of 1% w/w [18]. Given their high melting point of 76 °C, viscoelastic properties offering better spreadability and their ability to stabilize active molecules such as UVB blockers in sunscreen [19], 12-HSA has been used in cosmetic applications but relatively as-yet unexplored for lipsticks. 1,3:2,4-Dibenzylidene-D-sorbitol (DBS) is a well-known organogelator for over 100 years, employed in personal care products, owing a high melting point at 225 °C and can be a suitable thickener agent in organic phase [20]. DBS esters have been developed for lipstick sticks and compared to waxes and pasty compounds, which exhibited less transparency, glossy effects, stability and strength among others than DBS derivatives [21]. These LMOGs systems permit (1) thermoreversibility and thermostability to offer many advantages in drug delivery and long-term shelf-life systems [22], (2) particular mechanical strength and flexibility due to their viscoelastic properties [18] and (3) low-cost and simple preparation allowing large-scale production [22]. Moreover, the viscosity of the lipsticks has to be tunable to be high enough to maintain the stability of its structure network, while possessing shear-thinning effect under mechanical stress during applications onto the lips [23]. Various studies have characterized the rheological, mechanical, stability and thermal behavior of these LMOGs from diverse formulations [20,24,25]. For instance, Toro-Vasquez et al. studied the influence of organogelator derived from stearic and (R)-12-hydroxystearic acid on the crystalline microstructure organization and its rheological properties at two cooling rates (1 and 20 °C/min) [25]. They noted that the gelator structure influenced the melting/crystallization kinetics, the gelator self-assembly and microstructural organization of the gels through weak intermolecular interactions, which on large-scale impacted rheological properties (elasticity and thixotropy). Lai et al. investigated the viscoelastic properties, network microstructure and morphology of DBS-based organogels using scanning electron microscopy, polarized optical microscopy, and rheology [24]. The results showed that both temperature and organogelator concentration influenced the self-assembly of DBS organogels network. Finally, the stability was related to the thermodynamic equilibrium and was higher with high storage modulus, G′. However, investigation of different LMOGs physicochemical properties on mechanical and thermal properties of lipsticks has not yet been performed. Descriptive sensory analysis is an extremely useful tool in sensory science to obtain both qualitative and quantitative perception of a group of people called panelists according to their senses [26]. Although sensory analysis is well established in cosmetics as single methodology to compare different formulations according to their sensory attributes, there are few articles combining texture analysis and sensory analysis [27,28]. The purpose of this study was to evaluate the use LMOGs to provide a higher degree of protection from UVR compared to non-LMOGs lipsticks containing waxes commonly used in lipsticks. The research was extended to analyse the effect of LMOGs as a substitute structuring agent to replace part of large amount of waxes in lipsticks. First, the sun protection factor (SPF) and UVA protection factor (UVA-PF) of LMOGs-based formulations were determined *in vitro*. Then, the formulations properties including rheological and thermal stability behavior were investigated. Finally, a comparative study between descriptive sensory (spreadability, hardness, greasiness, opacity and glossiness) and texture analyses (hardness, stiffness, firmness and pay-off) was conducted.

Materials and methods

2.1. Materials

12-HSA and DBS organogelators with a purity of 99 % were obtained from Casid® Vertellus (Greensboro, NC, USA) and Sigma-Aldrich (Saint-Louis, MO, U.S.A.), respectively. Vegetable and vaseline oils were bought from, respectively, BASF (Coptis, Lavallois-Perret, France), and Gattefossé (Saint-Priest, France). White petrolatum and beeswax were bought from Sigma-Aldrich. Nesatol and pigments were a gift from our industrial partners. Demineralized water was used for the lipstick preparations.

2.2. Preparation of organogel lipsticks

Lipsticks were formulated by the moulding method using a mixture of natural ingredients reported in Table 1. Firstly, LMOGs (Figure S1) and/or waxes were added into the oily phase homogenized using a high-speed homogenizer) at a speed of 500 rpm.[11] The phase A was then heated up to 125°C and 200°C with the presence of DBS organogelator. Phase B was composed of beeswax and pigments and heated at 100°C to ensure the dispersion of pigments prediluted in Nesatol. Phase B components were added to phase A at the same temperature and homogenized together. Then, the mixture, still hot, was poured into lipstick mold, kept at room temperature and away from direct sunlight. The resulting formulations are represented in Figure S1.

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Table 1. *The set of component mixtures formulations and melting point of the lipsticks used in this study.*

Ingredients	Quantity (% w/w)				
	L1	L2	L3	L4	L5
Phase A					
Vaseline oil	0	40	48.5	0	L'Oréal Nude,TD023, Color Riche 235
Castor oil	14	20	20	15	
Almond oil	45	20	20	45	
White petrolatum	30	-	-	30	
DBS	1	-	1.5	-	
12-HSA	-	10	-	-	
Phase B					
Beeswax	5	5	5	5	
Pigments	5	5	5	5	

2.3. In vitro sun protection factor (SPF) test method

SPF was measured with a spectrophotometer (UV 2000S, Labsphere, Bures sur Yvette, France) to analyse UV transmittance of samples. The lipsticks in the amount of 1.3 mg/cm^2 were spread on polymethyl methacrylate plates (5 x 5 x 0.3 cm, Helioscience, Marseille) uniformly on their roughened surface, following the procedures present in ISO 24443:2012[29]. Glycerin (15 µL) was used for the blank scan to calibrate the spectrophotometer before UV transmittance measurements. PMMA plates (n=3 per sample) were then kept in a dark room for 15 minutes at 25°C. Six different locations were measured for each sample and transmittance spectrum was measured in the range from UVB (290–320) to UVA (320–400 nm) at 1 nm intervals to determine the SPF value of each sample. *In vitro* evaluation of SPF and UVA-PF were calculated using the following equations [29] :

$$SPF_{\ in\ vitro} = \frac{\int_{290}^{400} E_{(\lambda)}\ I_{(\lambda)}\ d_{(\lambda)}}{\int_{290}^{400} E_{(\lambda)}\ I_{(\lambda)}\ 10^{-A_0(\lambda)}\ d_{(\lambda)}} \quad (1)$$

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where E_λ is the erythema action spectrum at wavelength λ, I_λ is the spectral irradiance of the UV source at wavelength λ, $A_0(\lambda)$ is the mean monochromatic absorbance measurements per plate of the test product layer after UV exposure at wavelength λ and d_λ is the wavelength step (1 nm).

Each sample was exposed to the UV exposure dose, which is the initial UVA-PF ($UVA\text{-}PF_0$) [29] value multiplied by a factor 1.2 (J/cm^2).

$$UVA - PF = \frac{\int_{320}^{400} P_{(\lambda)}\, I_{(\lambda)}\, d_{(\lambda)}}{\int_{320}^{400} P_{(\lambda)}\, I_{(\lambda)}\, 10^{-A_e(\lambda)C}\, d_{(\lambda)}} \quad (2)$$

where P_λ is the PPD action spectrum, A_e is the mean monochromatic absorbance measurements plate of the test product after UV exposure and C is the coefficient adjustment determined using the SPF label (SPF *in vitro* adj [29]) generated by the UV-2000's software.

2.4. Mechanical properties

The mechanical properties of samples were evaluated by compression testing (bending and needle probe penetration tests) or tension–compression tests (cycle count test). Samples were kept at 25 and 45°C for 24h before testing. Visual inspection and measurements were taken at day 1, 2 weeks, 4 weeks, and 8 weeks using a texture analyser (Ta.XT+; Texture Technologies Corp., Hamilton, MA / Stable Microsystems, Godalming, Surrey, UK). All samples had an inner diameter of 9 mm and a height of 35 mm. All measurements were carried out with six lipsticks of each type. The data (force, distance) were recorded using Exponent Stable Micro Systems software (version 8). The maximum force value, which provides the hardness of the sample, is the force required to bend the sample until it broke off at the base and for a defined distance and give an indication of the brittleness of the sample. The stiffness of the sample was evaluated with the gradient of the slope during the bending action (Figure S2).

Bending test. Measurements to determine the bending force and stiffness were made using a hemispherical blade coming down at its approximately at 3 mm away from the tip of the horizontally clamped sample (rolled out to its maximum length). The test and target type was set to "compression" mode and "distance", respectively. All measurements were carried out at a trigger

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force of 20 g, pre-test, test and post-test speeds of 1.0, 1.0 and 10.0 mm s^{-1} and a target value of 10 mm.

Needle probe penetration tests. This method for testing lipstick hardness and firmness is adopted from the ASTM Standard Method of test D1321-10 using a 2mm Needle Probe (TA39). Measurements were performed in the following conditions : (1) the test and target type were also set on “compression” mode and ‘distance”, respectively; (2) a penetration depth of 10 mm; (3) a trigger force of 5g; (4) a pre-test, test and post-test speeds of 1.0, 2.0 and 10.0 mm s -1, respectively. Before the test, each lipstick was centered under the needle probe to facilitate their penetration.

Cycle count test. Pay-off test aims to determine the mass released while applying a lipstick. Briefly, 1 cm portion of lipstick was removed and the tip was rubbed on a piece of paper to obtain a homogeneous flat lipstick tip. The experimental setup consisted of a slot arrangement having a TTC vertical friction rig for holding the lipstick perpendicular to the paper strip (~7 cm wide) fixed at a stationary vertical plate to create a flat surface and separated with a 5 mm distance. The cycle count test was performed for 3 cycles with a speed of 5 mm/s and a deformation distance of 60 mm. Each lipstick was preweighed and reweighed after the test, in order to calculate the pay-off value.

2.5. Thermal properties

Melting point. The melting points of the lipsticks were determined by the drop-ball method (ASTM D127). Lipstick samples (2g) were poured into a thin-walled capillary of hard glass, about 20 cm long, with an internal diameter of 0.6 mm and sealed at both ends. Each tube was dipped into a glass beaker containing water, a thermometer and heated of 1 °C/min until the temperature reach 95 °C. A stainless steel ball having a diameter of 0.5 mm (1g) was put on the surface of lipstick. The transition temperature at which the material forms a liquid and the ball reaches the bottom is considered as the melting point (*Tm*).

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2.6. Rheological studies

For the rheological characterization of the lipsticks, temperature ramp test was conducted in a stress-controlled rheometer (AR 1000, TA Instruments) with parallel plate geometry (8 mm diameter and 0.7 mm gap). In order to prevent slippage of samples, both lower and upper plates were covered with sandpaper (the viscoelastic response of the sample was not affected by this layer). The rheometer was equipped with a Peltier plate regulating the temperature within ± 0.1 °C of the set value. The sample preparation steps were conducted as reported by Pan *et al.* [12]. Briefly, each uniform lipstick slices were disposed between the two plates. To prevent dehydration and to maintain humidity of the sample, a thin layer of paraffin oil was placed at its surface and moist pieces of cotton have been disposed around each slice. The linear viscoelastic region (LVR) was determined thanks to an isothermal strain sweep ($0.001\%<\gamma<100\%$) at a fixed angular frequency ($\omega = 1$ rad.s^{-1}) to identify linear and non-linear regions. Within the LVR, the dynamic storage or elastic modulus (G') and loss or viscous modulus (G'') are independent of the strain amplitude. The temperature ramp test was performed in the LVR and the temperature range of 20–150 °C for all lipsticks , according to melting point study at a heating rate of 1 °C.min^{-1} and at a frequency of 1 Hz. This test aimed at evaluating the dynamic storage or elastic modulus (G'), loss or viscous modulus (G'') and the loss tangent tanδ during temperature variation.

2.7. Sensory analysis

Sixteen female participants aged between 18–25 years who frequently used lipstick products were recruited for sensory evaluation. The overall sensory analysis was performed at room temperature (25 ± 2∘ C/ 60% RH ± 5%). The samples were evaluated in randomized order and lipstick identified anonymously. Sensory analysis consisted of a nine-point hedonic scale (1-9) whereby sensory attributes : spreadability, hardness, opacity, glossy and greasy effects were evaluated. Five designed lipsticks formulations (Table 1) were evaluated by the panel of female participants. A commercial lipstick (REF, L'Oréal Nude,TD023, Color Riche 235) was also included to test the sensitivity of the recruited panels. Each panellist filled out questionnaires with parameters scored between 1 and 9, where 9 represented the highest intensity of the parameter.

2.8. Statistical analysis

Analysis of variance was performed on the *in vitro* SPF, mechanical properties and pay-off using Graphpad Prism 7.0 and for sensory data using PanelCheck V1.4.2 software. The difference of SPF among lipstick formulations was analysed for significance using Kruskal-Wallis and Dunn's Multiple Comparison post hoc test. Regarding mechanical profiles and pay-off test, statistical tests were performed by paired t-test and one-way analysis of variance (ANOVA) followed by Tuckey's test, respectively. For sensory analysis, Friedman's two-way ANOVA followed by Fisher's LSD test was used with panelist and product effect interactions as variation factors. Principal component analysis (PCA) was applied to establish the relationship between attributes and lipsticks along with mean ratings of attributes from the sensory panel vs those from the texturometer. A value of $p < 0.05$ was regarded as significant, and data were represented as average value ± SD.

Results and discussion

Effect of organogelators on in vitro SPF and UVA-PF

In vitro SPF and UVA-PF were evaluated in all lipstick formulations. Since some organogels have "self-healing" or thixotropic properties, the formulations were able to easily spread and form a protective film layer over the skin rapidly when the pressure was withdrawn. In Figure 1A, the photoprotection efficiency of lipsticks is depicted through UV-absorbing profile of L1, L2, L3, L4 and L5 formulations in the UVB (290–320 nm), UVA II (320–340 nm) and UVA I (340–400 nm). L2 formulation containing 10% 12-HSA as organogelator showed higher UV-absorbing ability in comparison with the other formulations containing DBS as organogelator (L1 and L3) or no organogelator (L4, L5). In addition, within the absorbance range from 0.2 to 0.6, the UV-absorbing capacity of formulations containing DBS was greater than lipsticks without organogelator. Many studies emphasized that the level of protection provided by a formulation may not depend only on SPF but also on its absorption spectrum and UVA-PF [30]. Indeed, UVA is involved among others in the UV-induced immunosuppression, in the generation of DNA damage and in cellular signaling pathways that regulate responses to DNA damage in melanocytes [31]. Regulatory guidelines in the European Union recommend a minimum UVA-PF/SPF ratio of at least 1:3 and an *in vitro* critical wavelength (CW) ≥ 370 nm [32]. All formulations were in agreement with these regulations except for L4 and L5 formulations, which failed to provide a broad-spectrum filter. *In vitro* SPF and UVA-

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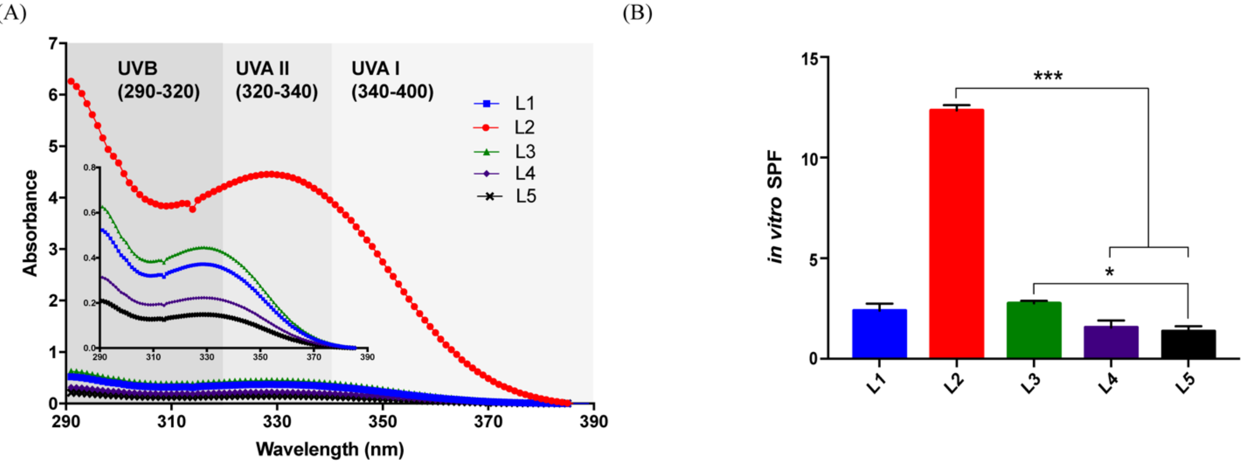
PF calculated respectively in the range 290-400 nm (Figure 1B) and 320–400 nm (Figure 1C) indicated that formulations with LMOGs, and more particularly, 12-HSA formulation had the highest SPF compared with the others. On the other hand, SPF and UVA-PF of L3 was higher than L1 with an improvement of SPF value (15.0%) due to its higher DBS content. In light of these results, organogelators can offer photoprotective effects like UV filters based on their physical structure through non-covalent interactions. However, SPF-15 or higher is the recommended blocking strength to prevent risk of cancer or skin ageing [33]. To some extent, the combining use of natural broad-spectrum sunscreens should be considered for further investigations. Nevertheless, these findings provide an additional evidence on the photoprotective effect of 12-HSA that appeared to increase the UVB radiation absorption of a sunscreen formulation of gelled particles containing an immobilized organic filter (2-ethylhexyl-p-dimethylaminobenzoate) due to the formulation diffusing capacity related to their viscous consistency [19].

(A) (B)



(C)

Ingredient	λcr (mn)	UVA-PF
L1	371.8 ± 0.8	3.52 ± 0.09
L2	377.2 ± 0.8	39.33 ± 0.87
L3	377.1 ± 0.7	4.13 ± 0.08
L4	362.8 ± 0.6	1.99 ± 0.09
L5	356.4 ± 0.6	1.44 ± 0.07

Figure 1. *Ultraviolet photoprotective performance of lipsticks. UV absorbance spectra profile (A), in vitro SPF (B) and UVA protection factor (UVA-PF), critical wavelength (λcr) (C). SPF, λcr and UVA-PF values are expressed as mean ± SD of six experimental measurements per*

*lipsticks. * $p < 0.05$, *** $p < 0.001$, Kruskal-Wallis test followed by Dunn's Multiple Comparison post hoc test for (B).*

Instrumental texture analysis (hardness, stiffness, firmness and pay-off) and stability studies

Lipstick instrumental attributes (hardness, stiffness and firmness) obtained by texture profile analysis (TPA) were reported based on the measure of the maximum force to compress the lipstick. Lipstick ingredients, storage temperature and storage time had a significant effect ($p < 0.05$) on hardness, stiffness and firmness (Figure 2). Hardness depends generally on the type and amount of waxes in the formulation [27], the oil polarity [34] and the oil:wax ratio [35]. In all lipstick formulations, the oil:wax ratio was constant for L1 and L4 formulations but lower than L2 < L3 due to the addition of white petrolatum. Hardness of L2 formulations did not change significantly at 25 and 45 °C over 12 weeks, however, L1 and L4 formulations became softer after 12 weeks at 25 and 45 °C ($P<0.05$) (Figure 2A). Furthermore, the difference in hardness between L1 at 25 and 45 °C at weeks 4 and 8, L3 at 25 and 45 °C at weeks 4 and 12, as well as for L4 at 25 and 45 °C during all the study was statistically significant and attributable to softer lipsticks at 45 °C ($P<0.05$). L4 was statistically significantly weakened and easier to bend than the other formulations and especially L2 ($p < 0.05$). A commercial formulation (L5) was also tested in a single time point on day 1 and both temperatures, as reference formulation. Hardness of L5 was similar to L3 at 25°C and L4 at 45°C. Acceptable solid lipsticks for the consumers should achieve at least 30 gf at 20°C for 8.1 and 12.7 mm diameter stick, as reported for current patented lipsticks [36-38]. Consequently, hardness values of all lipsticks were considered acceptable since values were above those of the commercial formulation or above 30 gf at RT. The material properties of DBS organogels (L1 and L3) and especially the formulation without organogelator (L4) were also affected by higher temperatures. Indeed, at higher temperatures waxes became softer and are responsible for weak network strength [39]. Interestingly, the presence of LMOG as well as higher organogelator concentration increased thermal stability of the global network. These results were previously confirmed in different studies reported by Esposito *et al.*, wherein organogels heated up above Tgel temperature undergo a molecular reorganization due to disruption of physical interactions between organogelator molecules [22].

Stiffness or resilience of the sample refers to its ability to resist deformation during the bending action and is dependent on the elastic modulus (Young's modulus). At 25 and 45°C, L4 was the

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less stiffer lipstick throughout the study (Figure 2B). At 25°C, the stiffness of L1-L2 was generally higher compared to the others, meaning they were less flexible, whereas L3 values was closest to the control. At 45°C, L2 and L4 became less stiff over the weeks and indicate for 12-HSA-based organogel a disruption of the network structure at this higher temperature [22], whereas lipstick containing no DBS was consistent with greasier and lubricant properties of wax/oils [40]. Lastly, firmness of the lipsticks was also affected by the presence of LMOG molecules and especially their weak physical interactions with the oily phase in the gel network structure, as reported [41]. This mechanical property is an important parameter that can play a role in tuning pay-off, friction and softness [35]. L3 exhibited the highest firmness and values remained constant compared to all other lipsticks over 12 weeks at 25°C (Figure 2C). L4 values at 25 and 45°C were close to the control suggesting they were softer than L1-L3 lipsticks. This finding could be explained as the temperature increases near their melting point temperature. At 45°C, L1-L4 formulations as well as control exhibited significantly softer texture throughout the weeks ($p < 0.05$). As expected, the presence and higher concentration of LMOGs enhance firmness; however as temperature increased, the viscoelastic modulus (G′) of the material decrease (organogel liquefaction) [42] which accelerate oil losses from the network and thus reducing the firmness of LMOG-based formulations.

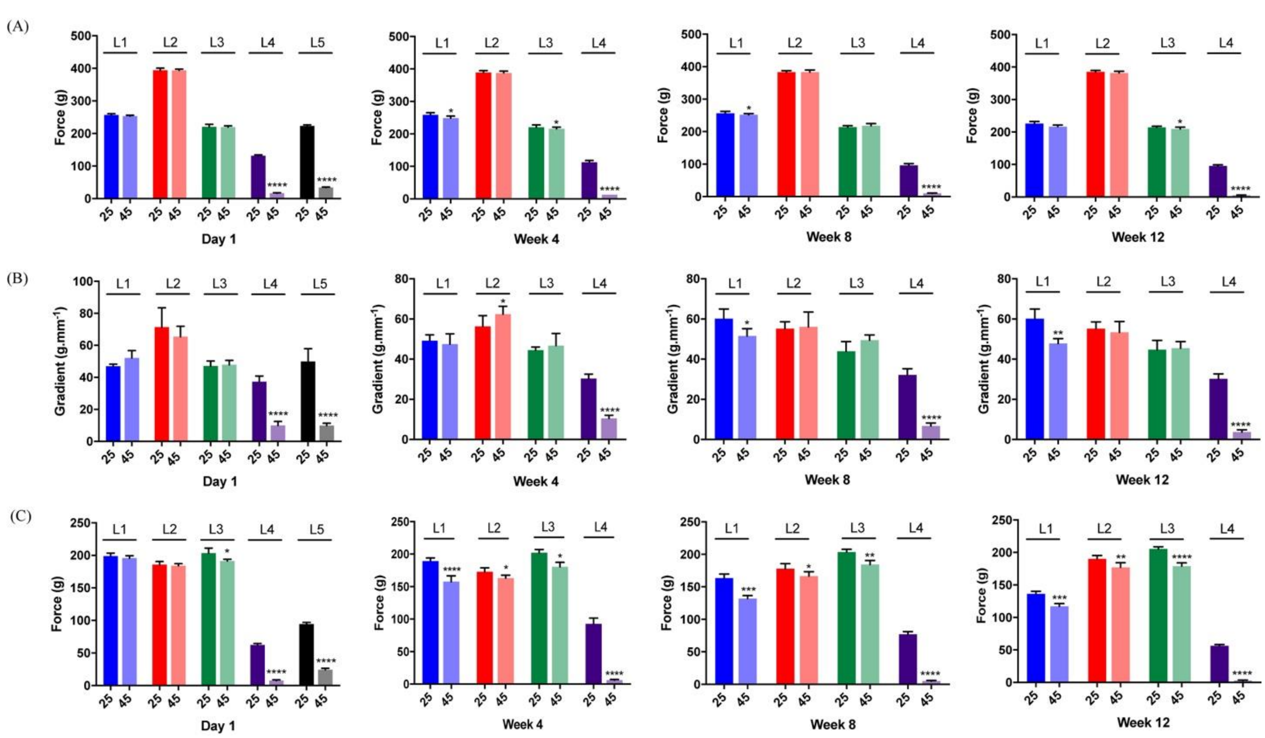

Figure 2. *Mechanical profiles of lipsticks. Hardness (A), stiffness (B) and firmness (C) during stability studies carried out for 1, 28, 56, 84 and 365 days, at 25 and 45 ° C. Force values are expressed as mean ± SD of n=6 lipsticks per group.* p < 0.05, **** p < 0.0001, Paired t-test.*

From a consumer point of view, a lipstick product must comply with desired mechanical strength and pay off characteristics to withstand the quality standard and requirement for an easy-glide application. Regarding requirements, the lipstick should have at least a pay-off of 0.0001gm/cm [43]. Although a lower pay-off results in low amount of product attributes (color, long-lasting, coverage) transferred, a balanced low/high pay-off needs to be considered to reduce product consumption and undesired sensation (waxy buildup). In addition, photoprotective formulations have to fulfil various requirements such as a high pay-off and a firm consistency with respect to their efficient photoprotective capacity [13]. L2 > L3 > L1 showed the higher pay-off to fabric results, whereas L4 < L5 had lower amounts transferred on paper during the experiments (p < 0.001) (Figure 3). However, it should be noted that all pay-off lipsticks had passed the minimum requirement. The higher pay-off values between LMOG-based and "classical" lipstick formulations can be explained by an higher frictional force change attributed to gels with roughest surface [44].

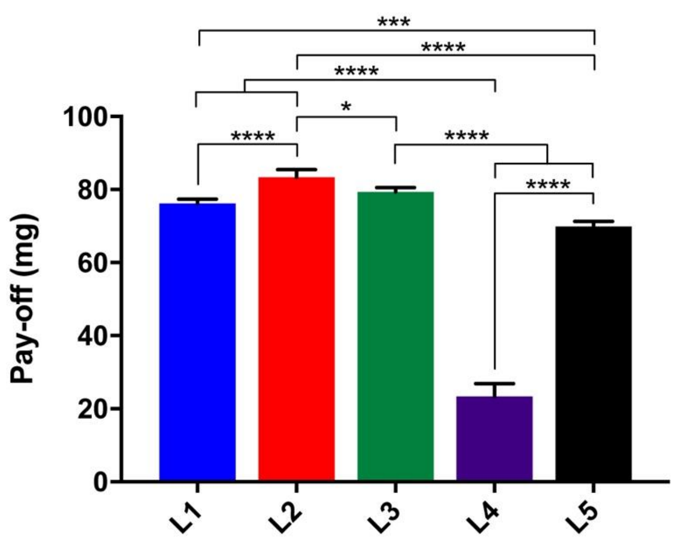

Figure 3. *Pay-off to fabric of lipsticks (expressed in mg, mean ± SD, n=6).* p < 0.05, *** < 0.001, **** p < 0.0001, One-way anova followed by Tukey's multiple comparison.*

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Considering the overall mechanical attributes, LMOGs have a great potential to replace part of waxes in lipstick formulations and to contribute in attaining the desired textural properties for photoprotective cosmetics.

The combined use of thermal and rheological analysis on the dynamic structure network of lipsticks

The temperature sweeps are displayed in Figure 4 and were performed in LVE regime to assess the effect of organogels-based lipsticks between 15 and 150 °C on the dynamic elastic behavior (G′) and the dynamic viscous behavior (G″). The organogel-based lipsticks exhibited thermoreversibility and viscoelastic properties. According to the classical viscoelasticity theory, the initial rise in G′ is due to 3D network formation while onset sol-gel phase transition (Tgel) of each lipstick can be estimated from the abrupt increase in G′. Indeed, Tgel is determined by the G′/ G″ crossover point from G′ < G″ to G′ > G″ of each cooling curve. Initially, we noticed two plateaus, a decrease in G′ with increasing temperature in the region 45-140 °C and a crossover point of G′ and G″, identified as the gel melting point (Tm). Upon cooling, the resulting disordered fluid-like state of the gel undergoes a sol-gel transition generating a viscoelastic solid-like structure of crystalline organogelator molecules [18]. L1 and L3 showed a crossover point at high temperatures underlying a more stable network with highest melting stability [12,45], while L2 and especially L4 and L5 were more heat amenable and prone to soften at low temperature.

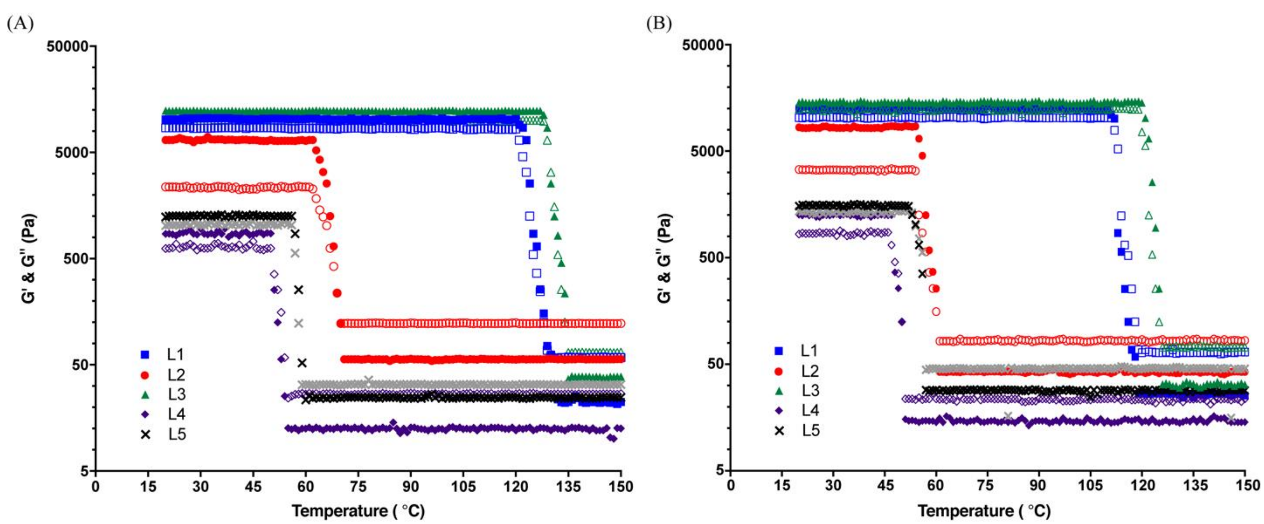

Figure 4. *Temperature sweep experiments. Heating (A) and cooling (B) cycles for lipsticks L1 (blue squares, ν), L2 (red circles, λ), L3 (green triangles, σ), L4 (purple diamonds, ♦) and L5 (black cross, ×). Linear elastic (G') and viscous (G") moduli are shown as plain and open symbols, respectively. Each temperature ramp was performed with a heating rate of 1 °C.min^{-1}, at a fixed angular frequency of 1 rad.s^{-1} and a 1% strain within the LVE regime.*

Tgel and Tmelt values determined in the rheological study were compared to Tm values obtained from melting point and are displayed in Table 2. The Tm values determined by melting point and rheology were in close agreement and were related to the breakage of particle interactions holding up the 3D structure. It was also noted a small but significant (p value < 0.05), increase in the Tgel value and in a maximal G′ of 12.9 times, with the addition of DBS organogelator at 1.5% (w/w) in the lipstick network (L3), compared with the control (L4). As the gel strength correlates with viscoelastic parameters, this indicates an increase in intermolecular interactions and the formation of a reticulated 3D network structure [46].

Table 2. *Gelling (Tgel), melting (Tm) temperatures obtained with rheology (determined as reported)* [22,47]*, melting point technique and maximum* G′ *recordings of lipstick formulations.*

Formulations	Tgel (°C)	Tm rheology (°C)	Tm melting point (°C)	Maximum G′ value (Pa)	Temperature at which max. G′ value was recorded (°C)
L1	119.6 ± 0.5	120.3 ± 0.6	> 95	10,502	32
L2	61.8 ± 0.7	62.1 ± 0.4	62	6,985	32
L3	127.2 ± 1.1	127.5 ± 0.5	> 95	12,398	63
L4	50.7 ± 0.4	50.6 ± 0.7	49	963	37
L5	56.6 ± 0.4	55.7 ± 0.6	54	1,295	36

The gelation point can also be observed with the tan δ (i.e., G″/G′, damping coefficient) at tan(δ) = 1, as a simple indicator. Figure S3 show the loss tangent curves of the lipstick formulations (L1 to L5). At temperatures lower than 50 °C for L2, L4 and L5 or 129°C for DBS-based lipsticks respectively, tan(δ) < 1, indicating that the sample behaves more like a solid with elastic properties, while at tan(δ) > 1 the organogels are viscous liquid. When comparing gelation points obtained during heating and cooling ramp test, there was a significant decrease (p < 0.05) in gelation points

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for L1, L2, L3, L4 and L5 formulations (14.5, 13.04, 3.47, 0.99 and 12.5%, respectively) for cooling compared to heating sweep. This difference between gelation point values during melting and crystallization processes highlighting the hysteresis effect [46] and may be due to the heat dissolution of waxes and LMOGs clusters during the heating process [48], delayed kinetically by hydrogen-bond breaking.

Nevertheless, all lipsticks showed acceptable thermal stability and consumer choice according to this criterion will be guided according to the climate and the temperature exposure of the heat-resistant lipstick.

Relationships between descriptive sensory and instrumental analysis of organogel-based lipsticks

All organogel-based formulations (L1-L3), as well as control (L4) and a commercial formulation (L5), have been evaluated for sensorial attributes as response with a panel of consumers. This quantitative description analysis (QDA) aimed to (i) characterize the sensory properties profile of the produced lipsticks and (ii) perform a principal component analysis (PCA) for mapping the main similarities and differences between samples and their sensory attributes. All tested attributes: spreadability, hardness, opacity, glossiness and greasiness were tested by assessors through an objective evaluation and scored following the intensity of each attribute for each product (corresponding to a numerical variable between 0 and 9). The performance of the panel was evaluated through different criteria: consensus (agreement between panelists) and discrimination between product and attributes. F-values and P-values, according to two-way ANOVA followed by Fishier LSD post-hoc test, were appropriate to measure discrimination power and are reported in Table 3. Regarding panelist effect and attribute discrimination, panelists were able to significantly discriminate attributes reaching a consensus (p-values < 0.001), while all attributes were considered discriminating (p-values < 0.001) among the formulations. From mean ± standard deviation values (Table 3) and spider-plot of the evaluated attributes for each formulation (Figure 5A), greasiness and glossiness sensory attributes are the most discriminative ones varying from 1.0-7.5 and 1.0-7.8, respectively. The lipstick showed low glossiness effect consists of 10% of 12-HSA organogelator compared to the other L1 and L3 DBS-based formulations. L3 lipstick containing the highest amount of vaseline oil (48.5% w/w) compared to other ingredients such as white petroleum (L1) and organogelator (L2) was assessed as the least greasy formulation. Medium desired greasiness was achieved for LMOGs-based formulations (L1-L2) with an average of 5.6

points. All lipsticks expressed a good spreadability with non-significantly different values ranged from 6.7 to 8.1 points. The hardest and softest lipsticks were L2 and L1/L4, respectively, which was in agreement with texture analysis, except for L1 at day 1. This exception may have been caused by the lack of ingredients to provide a soft touch despite a consensus reached between panelists with low values variability.

Table 3. *Results of two-way ANOVA and Fisher's LSD test examining the influence of product effects according to panel responses.*

Formulations	Effects	Statistics	Attributes				
			Spreadability	Hardness	Opacity	Glossiness	Greasiness
L1		Means	7.1	4.3	4.2	7.1	5.6
		SD	0.64	0.92	1.43	0.87	1.64
L2		Means	8.1	8.1	3.3	1.0	5.5
		SD	0.82	0.82	1.01	0.0	1.77
L3		Means	8.1	6.1	4.3	7.5	1.0
		SD	0.82	1.33	0.92	1.09	0.0
L4		Means	6.7	4.3	6.3	7.0	7.8
		SD	1.01	1.24	1.13	1.09	1.24
L5		Means	7.9	6.8	7.1	4.0	7.5
		SD	0.96	1.15	0.64	1.53	1.37
	Panellist	F value	11.22	13.89	10.24	7.35	9.77
	Product		27.11	125.87	103.04	257.85	176.16
	Panellist	P value	<0.001	<0.001	<0.001	<0.001	<0.001
	Product		<0.001	<0.001	<0.001	<0.001	<0.001

The PCA was also performed on both sensory and instrumental of pick-up sensory properties (hardness, firmness, stiffness) data [49] to facilitating raw materials choice to formulate desired lipsticks (Figures 5B-C and S4). The two principal components (PC1 and PC2) accounted for 93.1% of the total variance between samples. The plot used to read PCA scores of each sample (represented as dots) allows identifying the positioning of the sensory attributes and the identification of the more relevant sensory descriptors close to +1 and -1 and thus contributing mostly to PC (Figure 5B). As observed in Figure 5B, the glossy aspect (-0.969) contributed negatively to PC1, while hardness (0.750) contributed positively. Moreover, spreadability (0.791) contributed positively to PC2 whereas greasy effects (-0.859) contributed negatively. According to Buehler *et al.*, correlation between two variables and two component analysis is shown as a vector, which indicates the strength of the relationships following the vector length and whether if the correlation is positive or negative according to its direction. Since the main attributes are identified, the loadings plot (Figure 5C) displays more information about the relationships between sensory descriptors and lipstick formulations. It seems there is a covariance between different sensory attributes. Indeed, a higher hardness is generally associated with a lower glossy effect, as it is observed for L2. It is also interesting to notice that all formulations are different from each other's and do not form a cluster. L2 and L3 formulations are less related to greasy effect, while L3, L1 and L4 are related to glossiness.

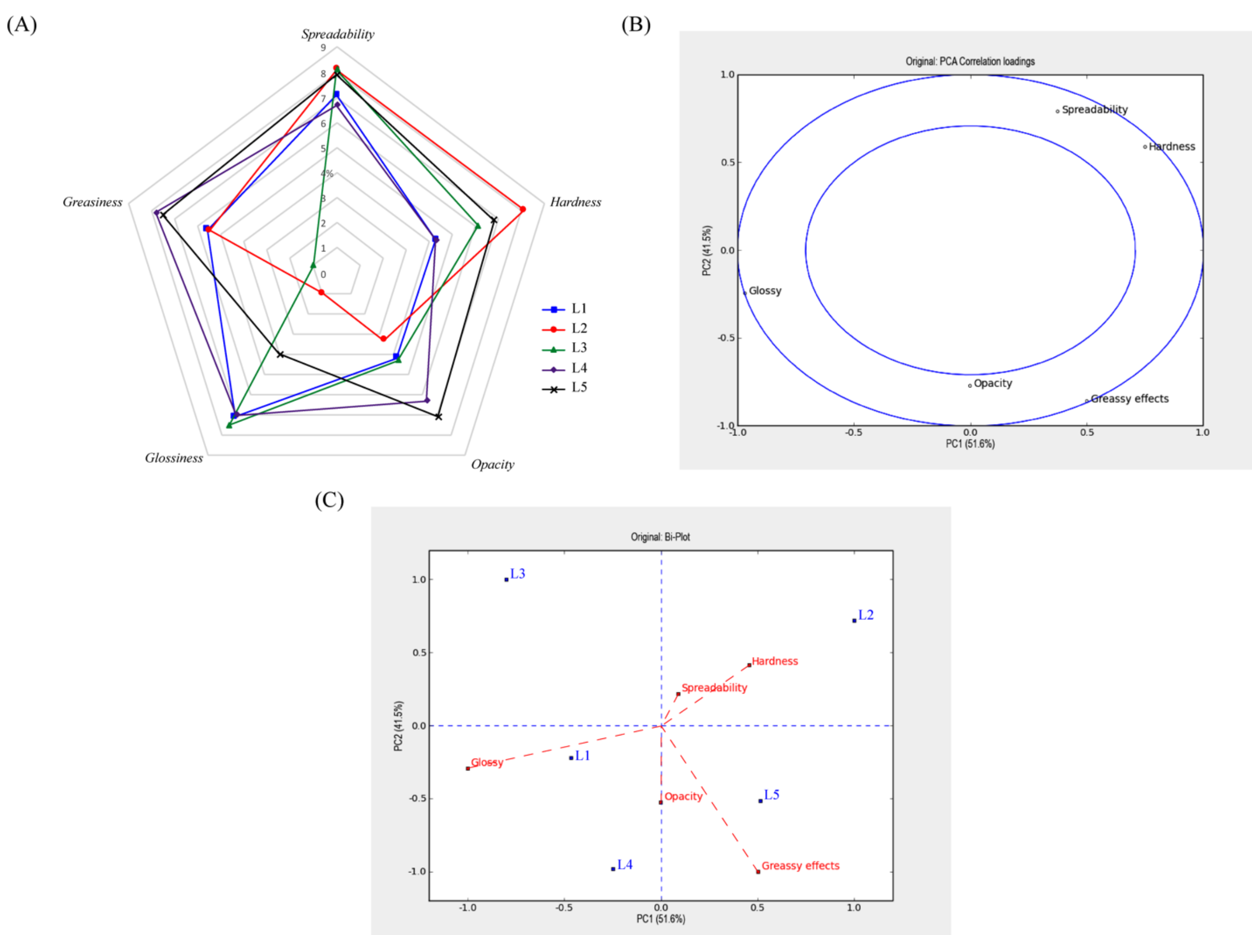

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Figure 5. *Sensory evaluation results of the produced and commercial lipsticks after application. Spider-plot (A), correlation loadings of the principal component analysis (PCA) for all the sensory attributes (B) and biplot representation of PCA illustrating relationship between attributes and formulations (C).*

Another loadings plot (Figure S4) was performed combining both texture characteristics and sensory descriptors with numerical variables represented as lines and dotted lines, respectively. All instrumental analysis: hardness (0.973), firmness (0.792), stiffness (0.907) and hardness form sensory analysis (0.657) contributed positively to PC1, while opacity (-0.831) and the glossy effect (-0.630) contributed negatively (Figure S4A). Furthermore, instrumental hardness is essentially correlated positively with firmness. According to the representation in Figure S4B, formulations can be split into 2 different clusters of sensory and instrumental attributes: (1) L2 is essential characterized by instrumental measures and essentially hardness and firmness, while L4 is negatively correlated to these parameters, (2) L1 and L3 are much more related to firmness, and to some extent glossiness.

Conclusion

Despite growing concerns about lip cancer and the importance of photoprotection, there is still a need for novel strategy to design photoprotective lipsticks. Indeed, *in vitro* sunscreen testing methods showed that LMOGs and especially 12-HSA lipstick formulation significantly increase both SPF and UVA-PF compared to lipsticks based on waxes. The thermal properties of lipstick showed that DBS-based organogels were more heat stable, which was directly correlated to the resistance of the organogel structure to deformation. Furthermore, all organogels exhibited a typical viscoelastic and hysteresis behavior of these non-newtonian systems that may be explained by the difference in the dynamic structure organization and disorganization through hydrogen bonding of the gel network. Regarding texture characteristics, 12-HSA-based lipstick was significantly harder to bend than the control formulation (without organogelator) and stable at 25 and 45 °C, while others lipsticks generally became softer for both temperatures throughout the long-term study (8 weeks). We further explained that LMOGs-based lipsticks higher pay-off values may be explained by higher frictional force of organogel surfaces. By combining sensory attributes (glossy) and instrumental parameters (hardness, firmness), we were able to cluster the formulations.

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Considering the overall mechanical, thermal and photoprotection attributes, LMOGs-based formulations have a great potential to replace part of waxes in lipsticks, while offering higher photoprotective capacity to target a large number of customers.

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