“Innovative application of freeze-drying in the production of make-up compacts”

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1. Introduction

An increasing trend towards the “zero waste”, and thereby a huge demand for solid cosmetics including powders, is taking place in the cosmetic market. In the same time, consumers are looking for multifunctional products being both make-up and skincare products. In this context, the global face compact market size was valued at $1.3 billion in 2021 and is projected to reach $2.2 billion by 2031 [1]. Compacts are mainly produced by uniaxial die compaction and must result with a smooth surface without delamination and traces of residual grains, and a uniform color. It must also be strong enough to resist to transport and falls while keeping their end-use properties [2,3]. However, the process remains artisanal since the final product quality depends on the formulator who adapts the process to the formulation on a caseby-case basis. The formulation, usually anhydrous, does not allow incorporating easily hydrophilic active substances in the final product. One alternative to this technique could be the freeze-drying process. Freeze-drying is a one-step process: the product suspension is poured in a mold, placed in a freeze-dryer and successively submitted to a freezing and drying steps. Freeze-drying allows obtaining a porous matrix from a colloid system by preserving the integrity of the product and potentially offers new sensory feeling. The aim of this project is to produce freeze-dried make-up powders by evaluating their pickup, hardness and sensory properties [4,5]. The originality of the research is to use a nano-emulsion as a binder, able to encapsulate lipophilic and hydrophilic substances. Various nano-emulsions were formulated to study the impact of the nature and proportion of the oily phase, the pigment mixture and the cryoprotectants. First results proved that freeze-drying seems to be a promising technology to produce compacted powders since they have good organoleptic properties. The addition of cryoprotectants in the nanoemulsion also enhanced the freeze-dried powders physical properties.

2. Materials and Methods

2.1. Materials

Octydodecanol was obtained from BASF (France) and Isononyl isononanoate was supplied by Seppic (Castres, France). Polyglyceryl-4 laurate was obtained from Evonik (France). Talc, magnesium stearate and sorbitol were purchased from Cooper (Melun, France). Silica (and) titanium dioxide (CI 77891), sodium potassium aluminium silicate (and) titanium dioxide (and) silica, boron nitride and pigments were a kind gift from Merck. Mannitol was obtained from Roquette. Deionized water was used for the preparation of the dispersions.

2.2. Formulation of the make-up compacts

2.2.1. Formulation of nanoemulsions

Two nanoemulsions were formulated differing by their oil phase (octydodecanol and isononyl isononanoate) (14.4%w/w), but both stabilized by polyglycerol laurate at 5.6% (w/w) as the emulsifier. The surfactant was added to the water. The oil was poured into the dispersion and the mixture was mixed using an Ultra-Turrax at 4000 rpm for 5 minutes using a cold process. Dilutions of the dispersions were conducted in order to study the influence of the proportion of oil on the compacts with the following dilution factors: 0 (undiluted), 2, 5, and 10. Two cryoprotectants were added to the several diluted dispersions with a concentration of 1%, 2% and 5% for the mannitol and with a concentration of 2% and 5% for the sorbitol.

2.2.2. Formulation of the pigment mixture

The composition of the pigment powder is presented in Table 1. The powders were pre-homogenized in a mortar and then subsequently transferred to a blade mixer, where they were vigorously mixed for 10 seconds, three times. Then, the binder was added to the powder mixture and blended for 20 seconds. The pigment mixture consists of the composition mentioned in Table 1 ranging from talc to pigments.Then, the pigment paste was obtained by wetting the pigmented powder with the nanoemulsion with a ratio of 1:1.6. Finally, an antioxidant was incorporated, followed by the agitation of the mixture for 20 seconds, three times.

Table 1. Composition of the pigment powder for the compacted powders

INCI names	Proportion in the formulation
Talc	70.1 %
Silica (and) Titanium Dioxide (CI 77891) (and) Iron Oxides (CI 77491)	15.2 %
Boron Nitride	10.2 %
Magnesium stearate	2.0 %
Pigments	1.5 %
Bis-Ethylhexyl Hydroxydimethoxy Benzylmalonate	1.0 %

2.2.3. Freeze-drying process

The pigment paste was freeze-dried by using a Cryotec freeze-dryer (Cryonext). The products are frozen with a freezing rate of 1°C.min^{-1} and maintained at -20°C for 3 hours. The primary drying phase consists of a gradual temperature increase to 0°C (0.03°C/min) at 0.3 mbar followed by a plateau phase at 0°C for 23 hours. Finally the temperature was increased to 20°C during the secondary drying over a period of 23 hours at 0.1mbar.

2.3. Measurement of the droplet size of the dispersion

The particle size in terms of the z-average diameter (z-ave) and polydispersity index (PDI) of both nanoemulsions were assessed by photon correlation spectroscopy (PCS) using a Malvern Zetasizer Nano Series ZS (Malvern Instruments, UK). PCS yields the z-ave and the PDI which is defined as a measure of the width of the particle size distribution. Prior to the measurement, the samples were diluted with purified water to obtain a suitable scattering intensity. Measurements were performed at a scattering angle of 173°, and the z-average and PDI values were calculated as the mean of three evaluations.

2.4. Characterization of the make-up compacts

The make-up compacts were evaluated according to four criteria : the visual aspect, the pick-up, the strength and stability, the sensory feeling during the application. The visual aspect control was performed by inspecting the surface of the compact in order to ensure that its surface is uniform and does not present drawbacks (holes or crusts). The pickup is assessed firstly through the ease of moving the product while it is being gently rubbed into a circular movement between the thumb (cushion effect) and the forefinger, and secondly through the movement attenuation induced by the product (slipperiness) [3]. The final strength and stability was assessed by the measurement of the drop test. In this test compact powders are allowed to fall from a height of about 30 cm. This test allowed evaluating the friability of the compact, which is namely its ability to break down into powder. Finally, the sensoriality during application describes the sensation that procures the powder when being applied on the skin. Table 2 reports the description of the different levels for each criterion.

Table 2. Description of the levels of each criterion

	Visual aspect	**Pickup**	**Friability**	**Sensoriality during application**
Level -1	Non-uniform	No pickup	Too friable	Dry touch
Level 0	-	Moderate pickup	(Quite) Friable	Greasy touch
Level 1	Uniform	Good pickup	Not friable	Soft touch

The objective is to obtain freeze-dried uniform and stable compacts which have a soft touch and a good pickup.

3. Results

3.1. Impact of the oily phase on the dispersion

Dispersions with octyldodecanol and isononyl isononanoate have a mean droplet size of respectively 812 nm and 446 nm with a z-average of 0.5. Thus, both emollients allowed obtaining stable nanoemulsions which could be used as a binder for the compacts.

3.2. Impact of the oily phase on the compact properties

Table 3 reports the aspect and the sensoriality of the freeze-dried compacts according to the nature and the proportion of oil in the nanoemulsions.

Table 3. Evaluation of the freeze-dried compacts

Evaluation	**Dilution**	**Octyldodecanol**	**Isononyl isononanoate**
Visual aspect	0	Non-uniform	Non-uniform
	2	Uniform	Uniform
	5	Non-uniform	Non-uniform
	10	Non-uniform	Non-uniform
Sensoriality	0	Greasy touch	Greasy touch
	2	Soft touch	Soft touch
	5	Soft touch	Soft touch
	10	Non evaluable*	Non evaluable*
Pickup	0	No pickup	No pickup
	2	Moderate pickup	Moderate pickup
	5	Good pickup	Non evaluable*
	10	Non evaluable*	Non evaluable*
Friability	0	Friable	Friable
	2	Friable	Friable

5	Too friable	Too friable
10	Too friable	Too friable

*Non evaluable = impossible to do the test because the compacts were too fiable.

For both emollients, the wetting of the pigmentary paste by the nanoemulsions allows producing compacts. However, these compacts were friable, greasy and had a bad pickup (Table 3). Even though both emollients have different sensoriality (rich touch for the octyldodecanol and dry touch for the isononyl isononanoate), a greasy touch was perceived for the compacts. Regarding the compact appareance, their surface was globally covered by small holes.

In order to overcome the greasiness and the pickup of the previous compacts, which is certainly attributed to the high amount of emollient in the compact, dilution of the nanoemulsions were performed before the wetting phase. As depicted in Table 3, dilution of the nanoemulsions led to a greater friability of the compacts. At the highest dilution, the compacts broke almost immediately upon handling. Dilutions of the dispersion 2 or 5-fold resulted in a smoother, more pleasant texture. When considering the octyldodecanol, the most promising result was obtained with a dilution factor of 2, which provided a soft touch but poor pickup of the product. The dilution by 5 also offered a soft touch, an improved pickup but was too friable. For isononyl isononanoate, the dilution by 2 resulted in moderate pickup, but the compact remained fragile. At higher dilution levels, the compact became too weak and broke easily. They were discarded from testing the sensoriality and the pickup assays. The results showed the better binding properties of octyldodecanol comparatively to isononyl isononanoate for dilutions 2 and 5. For these dilutions, the compacts are less friable with octyldodecanol. Higher dilutions (10-fold) leads to poor stability because of the lack of binder but the sensory feeling was inversely correlated leading to better sensory feeling at high dilution ratio (10-fold).

3.3. Impact of cryoprotectants on the compact properties

The aim of adding cryoprotectants in the nanoemulsions is to improve the stability of the compacts. An initial attempt involved the incorporation of 5% sorbitol into the nanoemulsion, used with both octyldodecanol and isononyl isononanoate (Table 4). This corresponded to a final concentration of 2.8% sorbitol in the formulation after wetting the powders at 160%, with emulsions diluted by 0, 2, 5, and 10. For compacts containing octyldodecanol, only the 1:10 dilution yielded promising results, with good pickup, effective transfer, and a soft touch as seen in Table 4. The other dilutions showed no meaningful pickup of the product since the sorbitol had plastified the compact matrix structure. In the case of isononyl isononanoate, again, only the 1:10 dilution showed acceptable characteristics, including good pickup and satisfactory application. However, the texture remained dry to the touch, and the other dilutions failed to provide sufficient pickup. Based on these results, the formulation of the compacts with 2% of sorbitol in the nanoemulsion were realized with octydodecanol only. The freeze-dried compacts containing 2% sorbitol in the nanoemulsion, which corresponded to 1.2% sorbitol in the final formulation after wetting the powders at 160% resulted in compacts with a dry feel and poor pickup for the dilution by 2. The dilutions by 5 and 10, by contrast, exhibited a good pickup. The dilution by 5 provided a velvety, non-friable texture, whereas the dilution by 10 produced a soft but friable compact. Therefore, by diminishing the sorbitol concentration the compact appareance, friability and touch were globally improved.

Table 4. Evaluation of the freeze-dried compacts containing octyldodecanol with 2 and 5% of sorbitol

Evaluation		**2% of sorbitol**	**5% of sorbitol**	
	Dilution	***Octyldodecanol***	***Octyldodecanol***	***Isononyl isononanoate***
Visual aspect	2	Uniform	Non-uniform	Non-uniform
	5	Uniform	Non-uniform	Non-uniform
	10	Uniform	Uniform	Uniform
Sensoriality	2	Dry touch	Dry touch	Dry touch
	5	Soft touch	Dry touch	Dry touch
	10	Soft touch	Soft touch	Dry touch
Pickup	2	No pickup	No pickup	No pickup
	5	Good pickup	No pickup	No pickup
	10	Good pickup	Good pickup	Good pickup
Friability	2	Not friable	Not friable	Not friable
	5	Not friable	Not friable	Not friable
	10	Friable	Not friable	Not friable

The Table 5 describes the freeze-dried compacts formulated with octyldodecanol only and obtained with 1, 2 and 5% of mannitol.

Table 5. Evaluation of the freeze-dried compacts containing octyldodecanol with 1, 2 and 5% of mannitol

Evaluation	**Dilution**	**1% of mannitol**	**2% of mannitol**	**5% of mannitol**
Visual aspect	2	Non-uniform	Non-uniform	Non-uniform
	5	Non-uniform	Non-uniform	Non-uniform
	10	Non-uniform	Non-uniform	Non-uniform
Sensoriality	2	Greasy touch	Greasy touch	Dry touch
	5	Dry touch	Soft touch	Dry touch
	10	Dry touch	Dry touch	Dry touch
Pickup	2	No pickup	Moderate pickup	No pickup
	5	Moderate pickup	Good pickup	Moderate pickup
	10	Good pickup	Moderate pickup	Good pickup
Friability	2	Not friable	Quite Friable	Not friable
	5	Friable	Friable	Not friable
	10	Friable	Friable	Not friable

As a confirmation of the previous results, a concentration of 5% of mannitol led to plasticized compact while a concentration of 2% mannitol with a dilution by 5 resulted in a soft touch and good pickup even though the compact was too friable for practical use. However having only 1% of mannitol in the nanoemulsion did not provide positive outcomes for the compacts since they were too friable and had an unpleasant sensory. Finally, unlike sorbitol, the use of mannitol did not enhance the compact appareance. Thus, finding a balance between oil and cryoprotectant proportion is required to obtain soft touch, good pickup, and adequate mechanical integrity of the compacts.

4. Discussion

The dispersions obtained with both emollients, octylododecanol and isononyl isononanoate, resulted in stable nanoemulsions having comparable droplet size. However, freeze-dried compacts wetting by nanoemulsions containing octyldodecanol, which is well-known for being a good dispersant and binder, has shown better outcomes than those containing isononyl isononanoate. As a consequence, the freeze-dried make-up compacts were globally less friable and have a smooth and pleasant touch with this emollient. Therefore, the nature of emollient in the nanoemulsion has a considerable influence on the physical properties compacts as for conventional compacts.

Depending on both proportion of emollient and cryoprotectants in the nanoemulsions, various compacts, from too friable to plasticized, were obtained. Having a high proportion of emollient in the nanoemulsion led to greasy freeze-dried make-up powder which is not appreaciable. By decreasing the amount of emollient, the sensory touch could be dry but also smooth.

The presence of cryoprotectants within the nanoemulsion considerably modify the structure of the freeze-dried compacts. In high proportion in the final formulation, the compacts are too hard and picking up some powder is impossible. Conversely, low quantities led to freeze-dried compacts stable and with a good pickup and interesting sensory characteristics. Sorbitol and mannitol were both able to enhance the sensory effect of the compacts. The oil-to-cryoprotectant ratio is an important parameter that requires to be explored for further studies.

Finally, most freeze-dried compacts had a non-uniform surface mostly due to the presence of holes. This could be promoted by the presence of big ice crystals formed during the freezing step. Modifying the freezing rate could be an option to tackle the presence of holes on the surface of the compacts.

5. Conclusion

The freeze-dried of make-up compacts turns out to be a promising method since it was possible to produce compacts with a correct integrity and interesting sensory proporties. The octyldodecanol yields compacts with a smooth touch and its proportion in the nanoemulsion has to be sufficient enough for giving stable compacts with good stability and soft touch. Isononyl isononanoate was less efficient for providing compacts with smooth touch and good hardness. The use of sorbitol and mannitol were useful to improve the stability of the compacts depending on their concentration and oil-to-cryoprotectant ratio. However, this work demands to continue the optimization of both the formulation and the process parameters to obtain better compacts.

References

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