

# Preparation and Synthesis of Aluminum Starch Octenylsuccinate (ASO) and It's Use in Sunscreen Cream Formulation

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**Abstract:** In order to synthesized Aluminum Starch Octenylsuccinate (ASO), which is a natural polymer, aluminum salt and octenylsuccinic anhydride were used as additives to modify the starch. The synthesis process was undertaken in two steps. The synthesized ASO was subsequently incorporated into the formulation of a sunscreen crème where it served as an organic filter against UV radiations from the sun. Finally, a comparison was made between the results of the modified crème with those of the formulation without ASO. Corn starch ASO was synthesized using 2-octenylsuccinic anhydride and aluminum sulfate; the synthesized product was then identified by FT-IR, H-NMR and <sup>27</sup>AL-NMR. In the next stages, it was formulated into a sunscreen cream. Sensory analyses were performed on formulations with a SPF of 15 without ASO and those containing ASO at 2.0%. The tests were performed in silico at a critical wavelength of 353 nm using BASF® Sunscreen Simulator. The obtained results made it clear that the polymer could create a great feel of softness and velvetiness on skin when incorporated into a sunscreen formulation, while considerably attenuating the associated oiliness feel on the skin. 45 (75%) out of the 60 volunteers participated in the study perceived the change in the brightness of skin following the application of the polymer formulation as either little or insignificant. Being natural and highly safe for human health, ASO is a good candidate for improving skin care products.

**Keywords:** Aluminum Starch Octenylsuccinate, Octenylsuccinic Anhydride, Aluminum Sulfate, Corn Starch, Skin Care, Sun Screen, Natural Polymer, Cosmetics Industry

## 1. Introduction

Starch comprises a major portion of food supply from plants and serves as the main food supply for human [1]. Starch is cheap and widely available everywhere. It can be extracted from different plants such as cereals grains (corn, wheat, and rice), roots (potatoes, tapioca), fruits (bananas, green) and seeds (beans, peas, lentils) [2].

In cosmetic products, a type of modified starch called Aluminum Starch Octenylsuccinate (ASO) is used. ASO is an aluminum salt which is obtained as corn starch reacts with 2-octenylsuccinic anhydride [3]. It is a white powdered material which exhibits hydrophobicity and has found applications as moisture absorbent, anti-wrinkle agent,

viscosity enhancing agent, non-aqueous agent, fast spreading of cream, and sun protection factor in cosmetics and hygiene products. Sunscreen cream attenuate UV radiations in the wavelength ranges of 320-400 nm (UVA) and 280-320 nm (UVB) using physical and/or chemical filters [4]. UV is an adverse radiation which results in burning or, in more severe cases, damaging collagen and elastin, ending up with wrinkles on the skin (accelerating the process of aging). Protective effect of sunscreens is identified by their Sun Protection Factor (SPF). In physical sunscreen cream, mineral filters made of titanium dioxide and zinc dioxide are used. These filters protect the skin against sunlight by reflecting, diffracting, and propagating the incident light [5], [6]. In chemical sunscreen creams, organic filters such as ASO are used; these protect the skin against sunlight by

absorbing UV radiations, so that, even at concentrations as low as 2%, this valuable compound can enhance the resultant SPF by as much as 40%, making it to levels comparable to those obtained with titanium dioxide and zinc dioxide [7]. ASO is a material of unique properties – a modified, harmless natural polymer; and this can explain its wide application in skin care products. It has been used in such products as hair conditioners, shampoos, creams and lotions, lipsticks, face masks, etc [8].

ASO is of no harm for eyes. It has been observed to generate no skin reactions in the experiments on animals [9]. This compound has shown no skin irritation when tested on rats, neither showing any adverse effect via inhalation. Application of ASO in cosmetics and hygiene products has been observed to enhance the effects of anti-cracking and non-aqueous thickening agents by up to 30%.

In the present research, as a natural polymer, ASO was synthesized in two steps. It was then formulated as an organic filter for UV radiations of the sun in a sunscreen cream, with the results compared to those of the ASO-free cream.

## 2. Materials and Method

### 2.1. ASO Synthesis

Firstly, corn starch and deionized water were used to prepare a 35%(w/w) suspension. The suspension was subjected to stirring at appropriate rate. pH of the suspension was adjusted to 7 using 3%(w/w) sodium hydroxide. Afterwards, different amounts (1%, 2%, 3%, 4%, 5%, 6%, DSB, respectively) of 2-octenylsuccinate anhydrate was introduced into the suspension in a dropwise fashion while the system was being stirred within 2 hours. Twelve hours after start of the reaction, suspension stirring was stopped and the suspension was washed with deionized water three times and then filtered and placed in an oven at 40 degree centigrade for 36 hours. Subsequently, the powder obtained in this stage and deionized water were used to prepare a 35%(w/w) suspension which was then placed on a stirrer. pH of the suspension was adjusted to 7 using 3%(w/w) sodium hydroxide and different amounts (1%, 2%, 3%, 4%, 5%, 6%, DSB, respectively) of  $Al_2SO_4$  solution was gradually added to the suspension in 2 hours. Twelve hours after start of the reaction, suspension stirring was stopped and the suspension was washed with deionized water three times and then filtered and placed in an oven at 40 degree centigrade for 36 hours. The obtained powder was then sieved through 300 mesh.

### 2.2. Formulation of ASO in Sunscreen Crème

Table 1. Sunscreen cream formulation.

Compound	FormulF	Formul G
A Deionized Water	QS	QS
A Disodium EDTA	0.04	0.04

Compound	FormulF	Formul G
A Glycerin	1.50	1.50
A Aluminum Starch Octenyl Succinate (ASO)	2.00	-----
B Stearic Acid	3.00	3.00
B Glyceryl Monostearate	2.00	2.00
B Cetostearyl Alcohol	0.50	0.50
B Coconut Oil	0.50	0.50
B Isopropyl palmitate	0.50	0.50
B Isopropyl Myristate	0.50	0.50
B Argania Oil	0.75	0.75
B Propylparaben	0.15	0.15
B Methylparaben	0.20	0.20
C Essential Oil	QS	QS

For the Formula F, firstly, Tanks A and B were separately prepared. Tank A was fed by all of the mentioned material in aqueous phase, where those were stirred and heated at 75-80 degree of centigrade. Tank B was rather introduced by all of the mentioned material in oil phase, where those were stirred and heated at 75-80 degree of centigrade. Afterwards, contents of Tank A were gradually added to Tank B where those were thoroughly mixed. Once a uniform emulsion was achieved, the mixture temperature was lowered down to 35 degree of centigrade, so that the essence could be added to the emulsion. The heating source was then removed to let the emulsion cool down for 24 hours in room temperature. These steps were repeated for Formula G, but in absence of ASO.

### 2.3. FT-IR Spectroscopy

A Vector 33 FT-IR spectrophotometer (Bruker, Ettlingen, Germany) was used to undertake FT-IR spectrometry on samples formed into KBr pellets. The device was capable of achieving a spectral resolution of  $4\text{ cm}^{-1}$ . For each spectrum, a total of 64 scans were recorded.

### 2.4. $^{27}Al$ -NMR Spectroscopy

$^{27}Al$ -NMR spectrometry was performed on Bruker AVANCE spectrometer (Bruker Biospin Co., Karlsruhe, Germany) which was configured for NS = 2048, P1 = 14.00 uses, and SOF1 = 130 MHz. For the sake of the tests, ASO in DMSO solutions were used as sample.

### 2.5. $^1H$ -NMR Spectroscopy

H-NMR studies were conducted on a Bruker DRX-500 NMR (Bruker Biospin Co., Karlsruhe, Germany) spectrometer at 500 MHz, using ASO in DMSO solution samples.

### 2.6. Evaluating SPF of the Formulations Tested

The considered formulations had their SPF evaluated using silico tests utilizing BASF® Sunscreen Simulator. This software provides a tool to assess SPF on the basis of UV absorption properties of sunscreens of considered formulation, rather than undertaking experimental investigations [17].

Reliability of this software comes from reproducibility of experimental SPF values of three sunscreens patterns, provided in-vivo values of SPF are unknown (determined as per corresponding European protocol) [17].

### 3. Results and Discussion

#### 3.1. FT-IR Spectroscopy

Figure 1 shows FT-IR spectra of original and OS-starches-Al. The peaks at  $3381\text{ cm}^{-1}$  and  $2929\text{ cm}^{-1}$  were attributable to hydroxyl groups (O-H) and stretching vibration of the C-H

on glucose, respectively. The significant absorption peak at  $1644\text{ cm}^{-1}$  corresponded to residual bound water [16]. The obtained curves for OS-starch samples contained a pair of new absorption bands at  $1726\text{ cm}^{-1}$  and  $1572\text{ cm}^{-1}$ , in comparison to the curve for wheat starch (Figure 1A). The peak at  $1726\text{ cm}^{-1}$  was related to stretching vibration of C=O on ester group [17], while the one observed at  $1572\text{ cm}^{-1}$  was associated with the asymmetric stretching vibration of carboxyl group [18]. The absorption bands at  $1726\text{ cm}^{-1}$  and  $1572\text{ cm}^{-1}$  had their intensities enhanced once DS content of the starch samples was increased (Figure 1B).

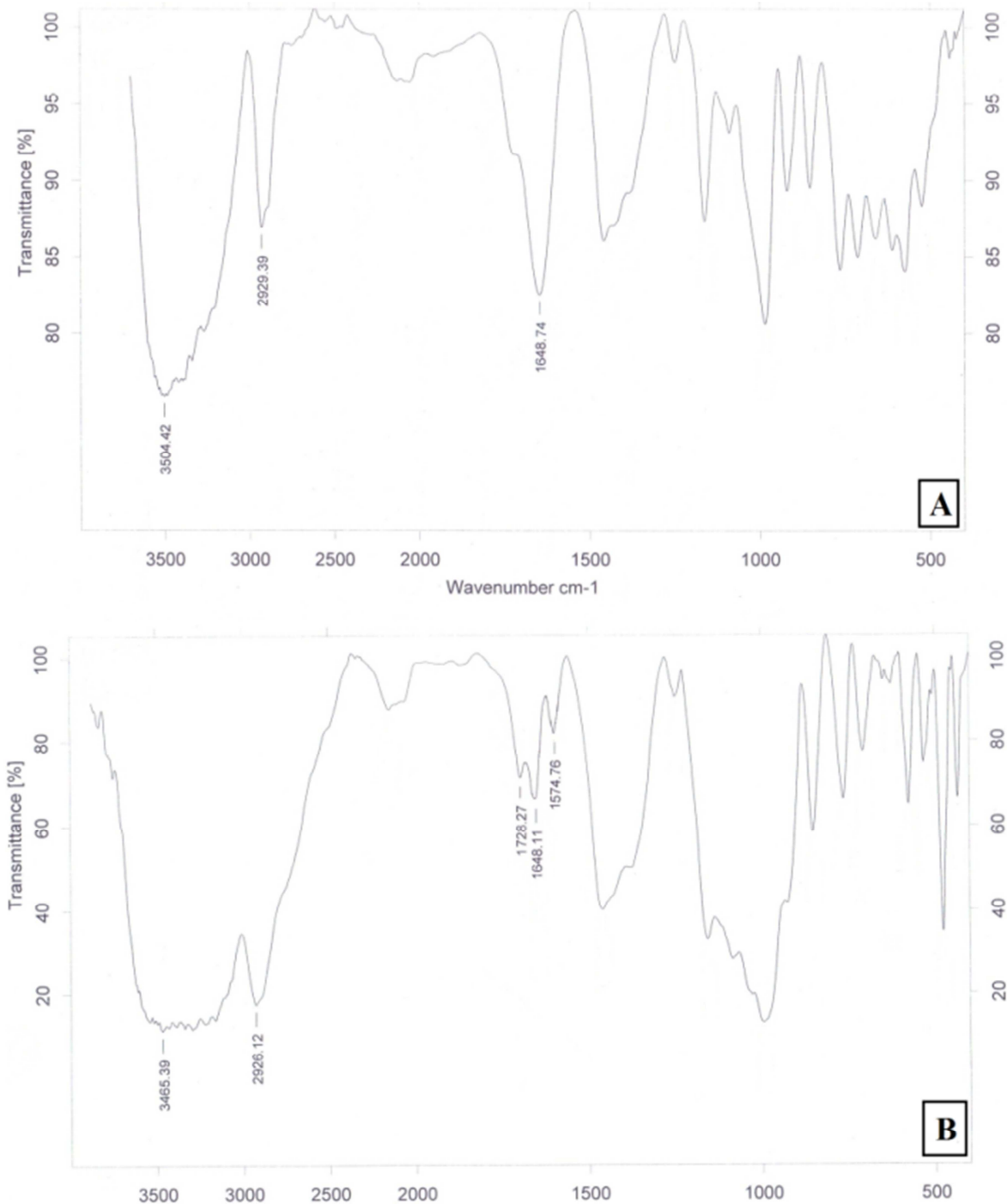


Figure 1. A: FT-IR spectra for original starch, B: FT-IR for aluminum starch octenyl succinate.

### 3.2. $^{27}\text{Al}$ -NMR Spectroscopy

Figure 2 demonstrates  $^{27}\text{Al}$ -NMR spectra for 2% OS-starch and 2% OS-starch-Al, where 2% OS-starch-Al is characterized with an extra peak at around 4.747 ppm, indicating the presence of  $\text{Al}^{3+}$ . Previous studies have (Huang *et al.*, 2010; Shogren *et al.*, 2000; Sui *et al.*, 2013; Zhang *et al.*, 2011) have shown that, OS group tends to be distributed over starch granules surface. This is an indication of the fact that, esterification and cross-linking with  $\text{Al}^{3+}$  are performed

mainly on the starch granules surfaces. Deionized water could be used to wash off free or uncross-linked the  $\text{Al}^{3+}$ . In addition,  $\text{Al}^{3+}$  content of OS-starch was observed to abruptly rise upon adding to the concentration of  $\text{Al}^{3+}$  from 0 to 5%, indicating that, cross-linking between  $\text{Al}^{3+}$  ions OS-starch was performed mainly on the starch granules surface. Deionized water could be used to wash off free or uncross-linked the  $\text{Al}^{3+}$ .

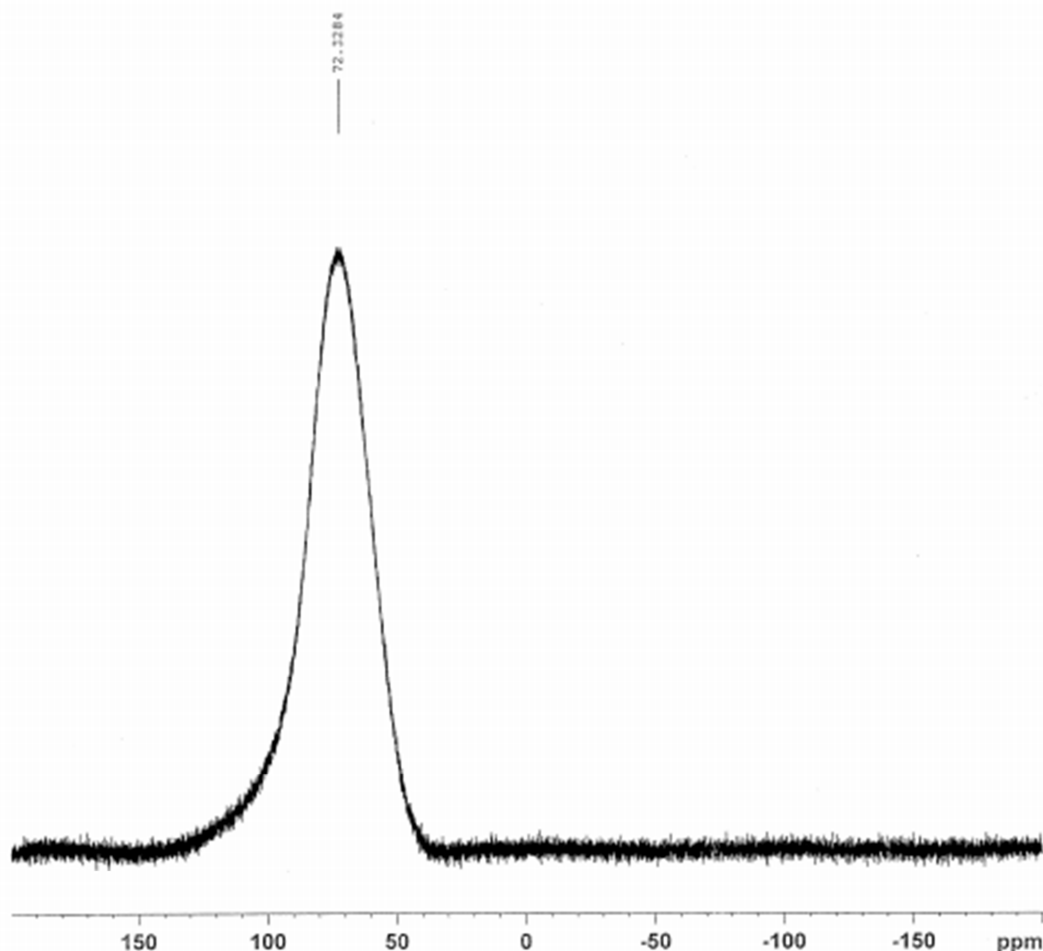


Figure 2. Demonstrates  $^{27}\text{Al}$ -NMR spectra.

### 3.3. $^1\text{H}$ -NMR Spectroscopy

Figure 3 shows not only the structure of ASO, but also  $^1\text{H}$ -NMR spectrum of the considered ASO derivative. The signals in the range 4.54-5.09 ppm were related to anomeric proton, with the only exception being the water peak at 4.86 ppm. Further, the signals at 4.64 and 5.23 ppm were corresponded to H-1 of  $\beta$ -form and  $\alpha$ -form reducing ends, respectively. The minor peak at 4.96 ppm and the one at 5.37 ppm were attributed to H-1 at  $\alpha$ -1,6 branching point and  $\alpha$ -1,4 internal linkage, respectively. Investigations showed overlapped signals for the protons H-2, H-3, and H-5 in the range 3.19 to 4.09 ppm. Consistent with literature [20], the

signals at 3.95 ppm and 3.84 ppm were attributed to H-3 and the overlapping region between H-3 and H-5, respectively. Meanwhile, the signal at 3.64 ppm was explained by the combination of H-2 and H-4. The signal resolved at 3.43 ppm was related to H-4, and the multiplet at 3.27 ppm was attributed to H-2 of  $\beta$ -form reducing end. Following OSA modification, more signals were seen in the range of 0.80-3.00 ppm, with a shoulder attached to  $\alpha$ -1,4 internal linkage signal. The shoulder at 5.45 ppm was related to the proton attached to the C=C bond on OS side chain. Methyl group on OSA was responsible for the doublet at 0.85 ppm.

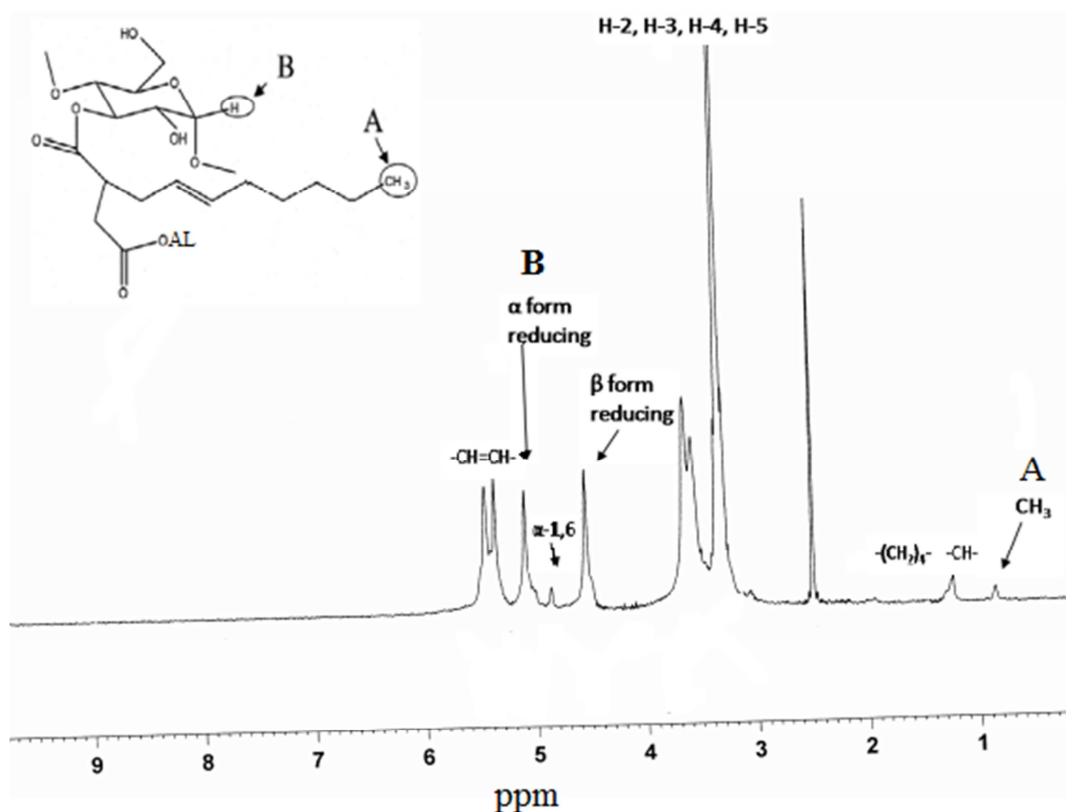


Figure 3. <sup>1</sup>H-NMR spectroscopy.

### 3.4. Evaluating SPF of the Formulations

According to the results of silico tests in BASF® Sunscreen Simulator [17], the tested formulations were found to end up with a SPF of 15 and critical wavelength of 353 nm.

### 3.5. Clinical in Vitro Studies on ASO

Comparative Investigation of Effects of the Formulations F and G in Sunscreen Cream. Responses to the questionnaire were used to assess different sensory aspects of the considered formulations. Mean and standard deviation of the sensory attributes are reported in Table 2, as evaluated by the respondents.

Table 2. Shows the mean score and standard deviations related to the sensory attributes evaluated by the volunteers on each formulation.

Sensory Attributes	Formulation	Formulation
Brightness	3.82±1.19	2.78±1.19
Greasiness	3.53±1.10	2.62±1.29
Absorption	3.90±0.84	3.20±1.15
Texture	4.30±0.60	3.70±1.19
Global Assessment	4.00±0.80	3.60±1.17
Softness	4.00±0.74	3.00±1.07
Tackiness	4.00±1.41	3.10±1.16
Spreadability	4.70±0.56	3.80±1.36

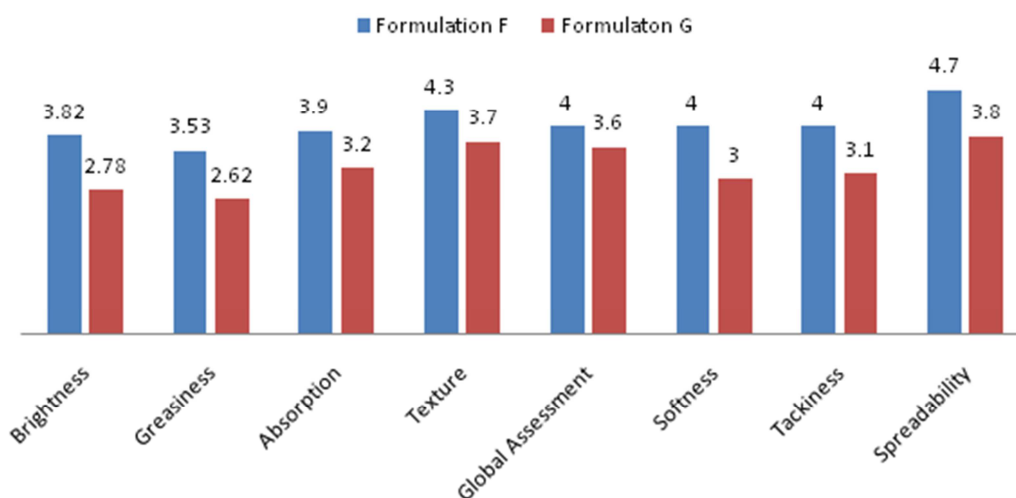


Figure 4. The chart shows the mean score and standard deviations related to the sensory attributes evaluated by the volunteers on each formulations.

In order to produce a sunscreen crème to be welcomed by consumers, it is necessary to formulate the sunscreen by respecting some criteria including affordable and reasonable price, adequate resistance to water, and non-sticky feel [20]. Figure 1 shows that Formulation G exhibits lower spreadability and tackiness than those of Formulation F which is based on a natural polymer; this is against the findings of Parente, Gámbaro and Ares [21] who found a direct proportionality between solid content, in one hand, and difficulty to spread and stickiness of a formulation, on the other hand. The difficulty to spread might be attributed to skin-product interaction-dependent properties raised when the product was mechanically applied to the skin [21]. According to [22], the difficulty to spread and skin adhesion could be explained also by a physicochemical property of the formulation, namely viscosity which gives resistance of a material to flow. Moreover, Formulation F was superior when it came to spreadability probably because of physical properties of the base polymer in terms of fine and uniform particles. Spreadability represents a profoundly important property of a sunscreen, as it is closely related to the application mode of the product. Indeed, a good sunscreen should form a uniform layer on the skin to ensure the expected SPF. One can attenuate the original oily feeling of the formulation by introducing some raw materials (at 1.5-2.5%, or say 3%) to absorb the oil content, such as ASO [23]. This was well observed as Formulation F (containing ASO at 2%) was of significantly lower oily feeling than Formulation G.

### 3.6. Clinical in Vivo Studies on ASO

In order to test a cream containing ASO at 3%, a total of 12 women were subjected to a facial sting study. Inclusion criterion for the women was the fact that, they were identified as “stingers” (reacting to 10% lactic acid aqueous solution). None of the subjects, however, had any evidence of hypersensitivity to topical products or any dermatological disease. In these tests, the cream was applied to the subject’s labial fold of the nose. Then, subjective stinging was assessed at 2.5 and 5 minutes after the application. Reactions were scored in a 0-3 scale. Then, a cumulative score was calculated by summing up the individual scores from both evaluations for each woman. Accordingly, the highest individual and cumulative scores were found to be 6 and 72, respectively. Corresponding cumulative score to the 3.0% crème was 5; it was based on reactions by two women (one with an individual score of 4 and another one with a score of 1). The crème was supposed to have “little or no potential for sting during normal intended use” [24]. A 1.0% ASO-containing crème was subjected to chamber scarification test wherein a total of 10 women with Fitzpatrick skin types II and III participated. For this purpose, specific sites on the women’s forearm were needle-scratched without drawing blood; the study further undertaken with five other materials. 0.3 ml of the crème was applied for a period of 24 hours. The sites were rinsed after removing the patch followed by

erythema assessment at 30 minutes later. Accordingly, the sites were scored on a 0-4 scale. Mean score on day 3 (for irritancy potential determination) was 1.4, so that the cream was considered as being of “slight” irritation potential [25]. Irritation potentials of the two formulations containing ASO at 2.23% and 2.5% were examined using 9 or 10 subjects with “sensitive skin”. For this purpose, occlusive patches were applied for two consecutive 24-hour periods. None of the lotions resulted in erythema. However, the crème containing ASO at 2.23% showed some insignificant increase in trans-epidermal water loss (*TEWL*). *TEWL* was not measured for the other sample because of equipment failure [26], [27].

## 4. Conclusion

This our study, in contrary to previous works, corn starch was modified and the results were confirmed through application. Our results are greatly important for the researchers who are seeking to enhance hydrophobicity and flowability of modified starches, so as to improve their applications in food, pharmaceutical, and cosmetic industries. In conclusion, ASO can introduce new functional properties and strengthen some of the current starch properties, so that the modified starch can replace some expensive chemicals without losing performance. This is while, the production of starch products from natural starch does not go through complex processes. Application of starches in plants can increase economic value of the product and hence overall profitability. ASO is a white powdered material which exhibits hydrophobicity and has found applications as moisture absorbent, anti-wrinkle agent, viscosity enhancing agent, non-aqueous agent, fast spreading of cream, and sun protection factor in cosmetics and hygiene products; it can be used in such products as hair conditioners.

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