Replacing synthetic texturizing polymers with natural raw materials in cosmetic formulations

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Abstract

Background: The aim of this work was to evaluate the possibility to replace synthetic texturizers, namely nylon-12 and polymethylmethacrylate (PMMA), with natural biodegradable polymers, without losing their stability characteristics and sensorial performances.

Methods: Nine natural-origin texturizing materials were incorporated in oil in water emulsions and analyzed by means of rheological and texture analyses. The rheological tests, performed in continuous and oscillatory flow condition using a rotational rheometer, allowed characterizing the samples' flow behavior and viscoelasticity. The texture parameters, such as firmness, consistency, adhesiveness and stringiness, were measured through an immersion/de-immersion test conducted with a Texture Analyzer. The raw materials that were found to have more similar texturizing properties to nylon-12 and PMMA, have then been inserted in finished products in order to evaluate their applicative performances. A double-blind sensory test was performed using a paired samples t-test.

Results: The starch-based polymer in an acne-prone skin product, has proved to have great stabilizing capacity, leading to elastic systems with good film-forming properties. Silica showed great adhesiveness and low pick-up, suitable for the formulation of a body butter and similar to those conferred by the synthetic polymers.

Conclusion: Rheological and texture analyses proved to be two complementary techniques useful to study the physico-mechanical characteristics of cosmetic formulas, helping formulators to easily forecast the contribution of new raw materials, when they are faced with the need to reformulate cosmetic products in a green and sustainable perspective.

Keywords: sustainability, polymers, texture, rheology

Introduction.

Microplastics are solid synthetic non-biodegradable polymer particles smaller than 5mm in size. They are used in consumer and professional products in multiple sectors, including cosmetic products, detergents, paints and coatings, construction materials and medicinal products, as well as fertilizers and in the oil and gas sectors. [1] The persistence and the potential bioaccumulation of microplastics is a cause of great concern for the aquatic environment and our ecosystem. [2] However, the effects on human health are uncertain and still not well understood. Cosmetic industries were among the first to address the issue of the consequences of microplastics on the aquatic ecosystem, severely limiting the use of microplastics intentionally added to products. In Italy from 2020 rinse-off products containing microplastics with exfoliating abrasive function are not salable. [3] The European Chemicals Agency has recently proposed to include in the definition of microplastic also a large number of non-biodegradable non-solid synthetic polymers, which can be dispersed or emulsified in cosmetic leave-on formulas with functional purposes. [4] The proposed new restrictions are forcing manufacturers to re-think entire product lines, finding new solutions to replace synthetic raw materials, such as nylon-12 and polymethylacrylate (PMMA), conventionally used in skin care products as texturizers and film-forming agents. Natural raw materials are often proposed as biodegradable and less impactful alternatives, even if matching the applicative performances of synthetic polymers can be quite challenging.

In this context of urgency, the priority for manufacturers is to study and characterize, with time-saving and reproducible tools, these natural raw materials proposed on the market, evaluating the potentiality of their use as alternatives to synthetic polymers.

Physico-mechanical characterization of cosmetic formulas by means of rheological and texture analyses is useful to predict the contribution of new raw materials to the formulations and they can be successfully used to help the cosmetic product design. [5] Rheological measurements, performed both in continuous and oscillatory flow conditions, are performed to study the flow behavior and the viscoelastic properties of semi-solid materials and hence to evaluate the stability properties of the products. [6] Texture analysis, commonly used in the food industry, has been introduced in the cosmetic field to study the mechanical properties of products during pick-up and application, which are linked to their sensory characteristics. [7]

The aim of this work was to evaluate the possibility to insert some natural texturizing polymers in cosmetic skin-care formulas replacing conventional synthetic polymers, without losing their sensorial and applicative performances that have an impact on consumers' acceptability. After an initial screening phase, in which the selected natural texturizers have been inserted into simplified oil-in-water emulsified systems and characterized by means of rheological and texture analyses, those whose contribution was more similar to that conferred by synthetic polymers nylon-12 and PMMA, in terms of mechanical and texture properties, have been incorporated into three different more complex finished products, to evaluate the actual possibility of substituting conventional synthetic polymers. Finally, the double-blind sensory test allowed verifying whether the substitution allowed to preserve the tactile and sensory properties of the original products.

Materials and Methods.

Two synthetic and nine natural texturizing raw materials were selected. Synthetic texturizers: X (Nylon-12), Y (PMMA). Natural organic texturizers: A (Zea mays starch, Polyvinyl alcohol, Glycerin), B (Distarch phosphate), C (Maltodextrin), D (Hordeum Vulgare Seed Flour), E (Cellulose). Natural inorganic texturizers: F (Calcinated kaolin), G (Sodium Potassium Aluminum Silicate, Titanium Dioxide Silica), H (Mica), and I (Talc).

These raw materials have been incorporated at 5% w/w in an oil in water emulsion, with potassium cetyl phosphate as emulsifier and an oily phase (12% w/w) consisting of Triethylhexanoin and Dicaprylyl carbonate in equal parts. The oil phase (75°C) was added to the water phase (70°C) using a Silverson L5T laboratory mixer and homogenized for 5 min at 4500 RPM.

The materials that were found to have similar texturizing properties to nylon-12 and PMMA, have then been inserted in three commercial finished skin care products, provided by Unifarco S.p.A., in replacement of synthetic polymers. PRODUCT 1 is an acne-prone skin serum, with mattifying and anti-shine effect, containing an anionic emulsifier, acrylic rheological modifiers, a light oily phase and nylon-12 and PMMA as texturizers; PRODUCT 2 is a gel-cream with a fresh and light texture, fast absorbing to be applied on the eye contour and composed by an association of non-ionic emulsifiers and PMMA as texturizer;

PRODUCT 3 is a body butter formulated with rich and nourishing emollients, an association of non-ionic and anionic emulsifiers with fat alcohols and PMMA as texturizer.
The morphology of the emulsions was evaluated using a LEICA DM1000 optical microscope with 40X objective and 100X immersion oil objective.

The rheological tests were performed with a Rheometer Physica MCR e302 from Anton Paar at a controlled temperature of 23°C ± 0.05°C. Tests were conducted both in continuous and oscillatory flow conditions using PP50-P2 sensor (parallel plates with serrated surfaces) with a fixed gap of 1 mm. The viscosity values (η) and the flow properties were measured with controlled shear rate tests (CSR), at increasing shear rate, ranging from 0.001 to 1000 s-1. Amplitude sweep tests (AS) were performed increasing strain (γ) from 0.01% to 1000%, at a fixed frequency of 1 Hz, to identify the samples' linear viscoelastic region (LVER) and the critical strain ($\gamma_{G'=G''}$). Frequency sweep tests were performed decreasing frequency from 10 Hz to 0.01 Hz, at a fixed strain inside the LVER, to analyze the emulsions' inner structure and the trend of storage (G') and loss (G'') moduli.

An immersion/de-immersion test was conducted at room temperature by means of a Texture Analyzer TMS-Pro, from Food Technology Corporation, equipped with a 2 cm diameter, nylon, spherical probe, using a load cell of 10N. The probe moved vertically to a depth of 10 mm at a rate of 80 mm min^{-1} inside the emulsions loaded in 50 mL containers (5.3 cm diameter) and then returned to its start position. Texture Lab Pro was used to collect the data and elaborate a curve plotted as load (N) vs cumulative displacement (mm). Firmness (N) is the maximum value of force; consistency (N.mm) is the area under the positive curve; cohesiveness (N) is the negative peak; adhesiveness (N.mm) is the area under the negative portion of the curve; stringiness (mm) is the extension of the filament the sample formed during the de-immersion phase.
The adhesive properties of the residual film formed by 0.5 g of the products after application on a silicon surface were evaluated, by measuring the work needed to unstick a steel spherical probe (1 cm diameter) at a speed of 80 mm/min (work of adhesion).

Thirty-two volunteers were selected to evaluate the sensory characteristics of the formulations, comparing those with synthetic texturizers as references with those modified with natural polymers. They were instructed to observe the samples under study, placed in 30 ml white containers, and to apply them on the skin. They answered a sensory questionnaire to evaluate, giving a score from 1 to 7, the appearance (color and shine), the consistency, the spreadability, the rate of absorption, the stickiness, the after-feel (glow or matte effect, and softness of the skin). The experimental data obtained were submitted to statistical analysis, namely a paired samples t-test.

Results.

A screening of the natural texturizers was carried out incorporating them at a concentration of 5% w/w in an oil-in-water emulsion and studying the mechanical characteristics by means of textural and rheological analyses. Using XLSTAT software, a Principal Component Analysis (PCA) was performed on the data set containing the emulsions as observations and the textural (firmness, consistency, cohesiveness, adhesiveness, stringiness, and work of adhesion) and rheological parameters (η, G*) as variables (Fig. 1). The first two principal components (F1 and F2) accounted together for 91.99% of the total variance (83.48% and 8.51% respectively). F1 was positively related to all the rheological and textural parameters, except for stringiness; F2 was positively related to stringiness.

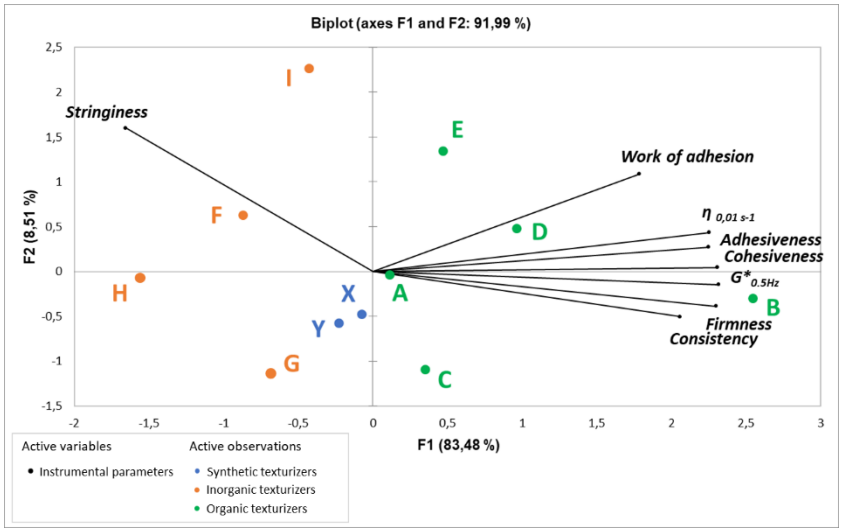

Figure 1: PCA loading biplot with rheological and texture parameters (variables) measured for the emulsions containing 5% of synthetic (in blue), organic (in green), and inorganic (in orange) texturizers.

The PCA showed the correlations between these two instrumental techniques: η and G* were positively correlated to firmness, consistency, adhesiveness, cohesiveness and negatively correlated to stringiness. The inorganic polymers F, H, and I formed fluid and viscous emulsions, with high spreadability and stringiness, but low adhesiveness. Among the organic polymers, B formed firmer systems with higher elastic G' modulus, while D, and E showed higher adhesive properties. Polymers A, G, and C conferred more balanced rheological and texture parameters, similar to those conferred by the synthetic polymers X and Y.

For the next step of this work, the organic polymers A and C and the inorganic polymers H and G were chosen to be used as alternatives to synthetic texturizers in the formulations of more complex skin care emulsions, since the preliminary data showed how these materials conferred medium-low texture properties and did not affect the structure and viscosity of the system.

PRODUCT 1 (P1) containing 1% w/w of nylon-12 and 1.5% w/w of PMMA has been reformulated replacing the synthetic texturizers with the selected natural ones at the same total amount (2.5% w/w). The texture curves in Figure 2 reveal that the parameters measured for the emulsions containing A and C as texturizers did not show significative differences with those measured for the reference product containing X and Y. On the contrary, the samples formulated with the inorganic texturizers G and H were characterized by higher values of firmness, consistency, cohesiveness and adhesiveness, and lower values of stringiness.

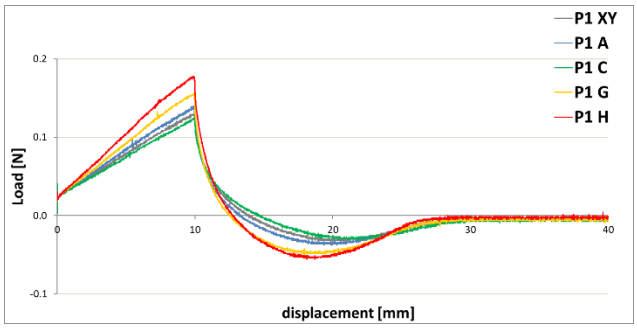

Figure 2: texture curves from an immersion/de-immersion test.

Moreover, the analysis of the residual film formed after application confirmed that the inorganic polymers G and H conferred higher adhesive properties than PRODUCT 1, while

on the other hand there were no significant differences using the organic polymers A and C (Fig. 3).

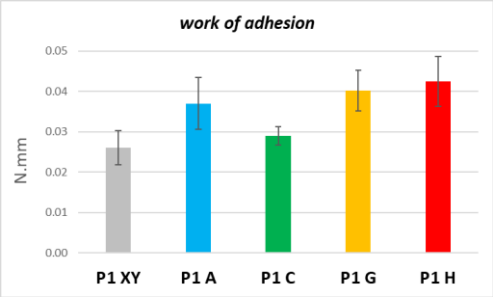

Figure 3: work of adhesion measured with the texture analysis of the residual film after application on a silicone surface.

The rheological curves (Fig. 4), whose trend is typical of a weak-gel structure, show that the organic polymers G and H caused a slight increase of the elastic component, whereas the use of C determined a decrease of both G' and G''. The moduli of polymer A were superimposed on those of the sample formulated with the synthetic polymers, demonstrating that A can be considered as a valid alternative to the synthetic polymers in this product.

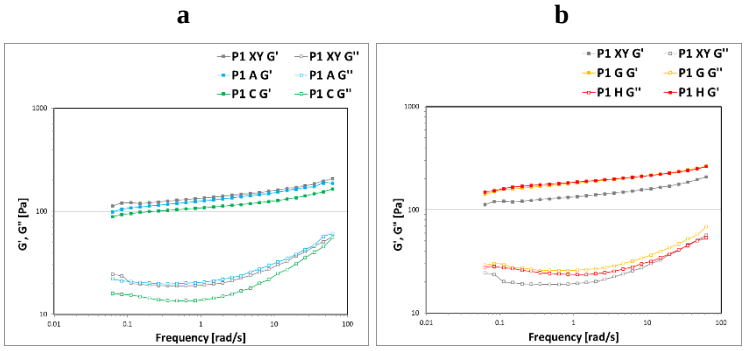

Figure 4: trend of elastic G' and viscous G" moduli in function of the oscillation frequency for samples P1 XY, P1 A, and P1 C **(a)** and samples P1 XY, P1 G, and P1 H **(b)**.

PRODUCT 2 (P2) containing 1% w/w of PMMA has been reformulated replacing the synthetic texturizer with the selected natural ones at the same total amount. The results obtained from the texture analyses show that the incorporation of natural polymers instead of the synthetic one caused a decrease of the emulsions' consistency (Fig. 5a). The most significant decrease occurred when the synthetic texturizer was replaced with polymer A, which also caused a significant decrease of the adhesive properties of the residual film after

application (Fig. 5b). Among the polymers C, G, and H there were no significant differences in terms of work of adhesion.

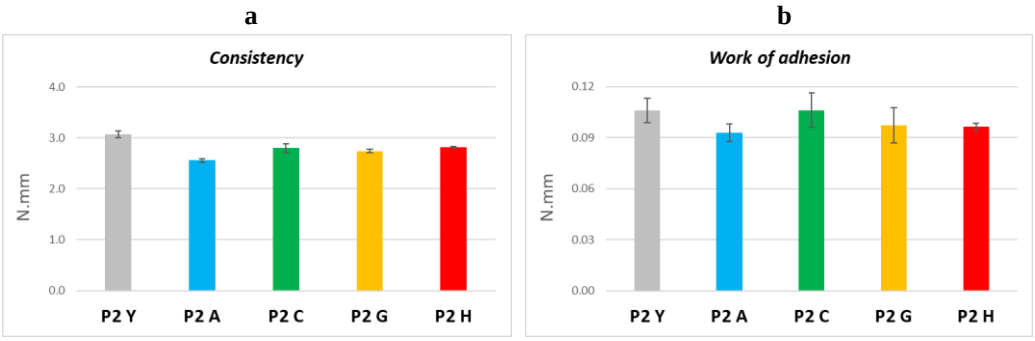

Figure 5: texture parameters: consistency measured by means of an immersion test **(a)** and work of adhesion of the residual film after application **(b)**.

The mechanical spectra obtained with the frequency sweep analyses did not show significant quantitative differences between the reference product with PMMA as texturizer and the emulsions formulated with the natural ones (Fig. 6). They all showed a weak gel rheological pattern with G' always dominating over G'' in the entire frequency range investigated, whose values are settled between the second and the third decades.

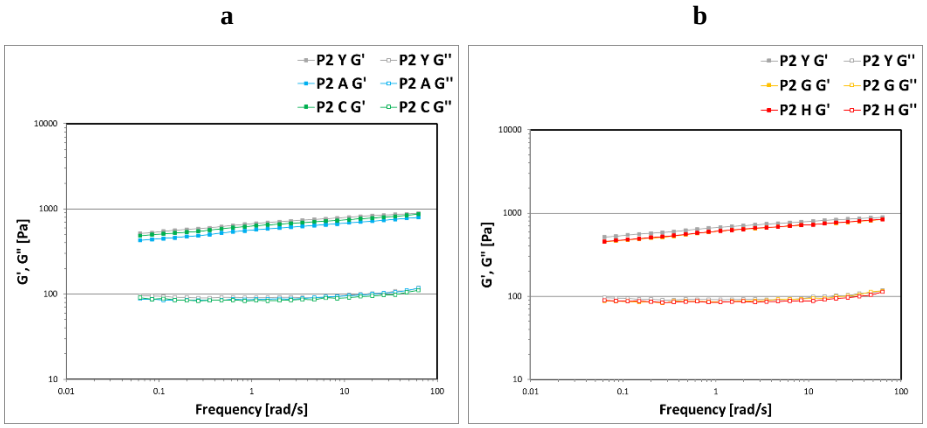

Figure 6: trend of elastic G' and viscous G" moduli in function of the oscillation frequency for samples P2 Y, P2 A, and P2 C **(a)** and samples P2 Y, P2 G, and P2 H **(b)**.

Observing the damping factor (tanδ) values in function of frequency, reported in Figure 7, we can appreciate a different structure of the emulsion P2 A. In fact, the damping factor tanδ is the rheological parameter that measures the ratio between the viscous modulus G'' and the

elastic modulus G' in the material: P2 A showed higher values than those of the other samples, due to the more relevant viscous behaviour.

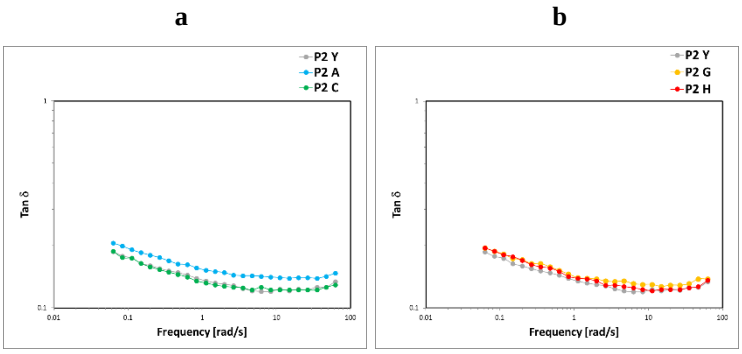

Figure 7: trend of the damping factor tanδ in function of the oscillation frequency for samples P2 Y, P2 A, and P2 C **(a)** and samples P2 Y, P2 G, and P2 H **(b)**.

PRODUCT 3 (P3) containing 3% w/w of PMMA has been reformulated replacing the synthetic texturizer with the selected natural ones at the same total amount. The analyzed samples differ greatly from the P3 reference sample in terms of texture parameters (Fig. 8). The samples P3 A, P3 G and P3 H showed higher values of firmness, consistency and cohesiveness than the reference sample P3 Y, but lower values of stringiness. P3 H had also higher adhesiveness. On the contrary the sample P3 C showed significative lower textural parameters.

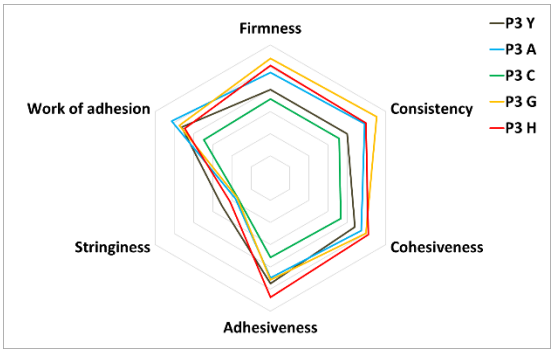

Figure 8: comparison between the texture parameters measured for P3 with synthetic and natural texturizers.

Since the emulsion P3 G was the one that showed to have adhesive properties of the residual film almost equal to those of the reference P3 Y, we decided to decrease the silica concentration to 1.5% w/w to get as close as possible to the texture parameters shown by the emulsion with the synthetic texturizer. Looking at the first part of the texture curve in Figure 9 a, it can be noted that the firmness and the consistency of the emulsion decreased by

reducing the concentration of silica; the second part of the curve, registered during the de-immersion phase, which includes the values of adhesiveness, cohesiveness and stringiness, had the same trend registered for the reference emulsion with PMMA as texturizer. The rheological curves obtained with the amplitude sweep analysis (Fig. 9 b) did not show significant quantitative differences in terms of G' and G'' values, although halving the silica concentration resulted in a reduction of the LVER and a shift of the critical strain to lower values. Probably the greatest quantitative differences found in the texture analysis are due to a different interaction between the silica in higher percentages and the lipid phase of the emulsion, which influence the surface mechanical properties more than bulk properties measured with rheology.

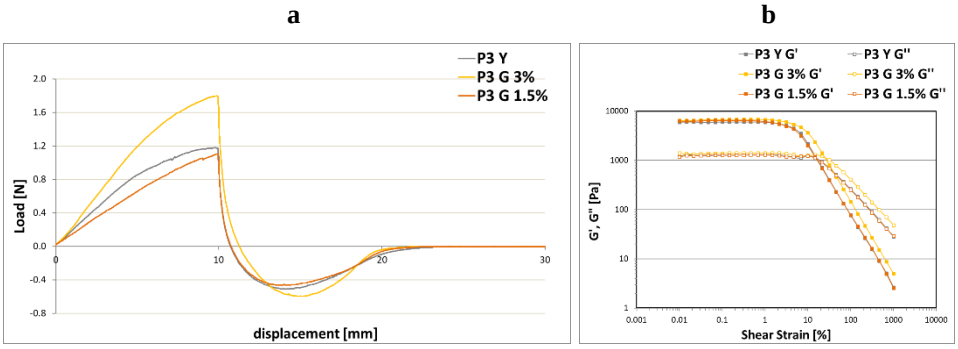

Figure 9: texture curve from a immersion/de-immersion test **(a)** and trend of the G' and G'' moduli in function of the shear strain **(b)** for samples P3 Y and P3 G.

The results obtained from the double-blind sensory test are summarized in Table 1. The volunteers were asked to compare the samples giving a score from 1 to 7 to the sensorial parameters concerning the visual appearance, the application phase and the after-feel. Each reference product was compared to the samples formulated with the natural texturizers which have shown to confer, through texture and rheology instrumental tests, the most similar mechanical parameters to those of the synthetic texturizers X and Y. The emulsion P1 XY was compared to the sample P1 A containing the organic texturizer zea mays starch: no significant difference was detected between the two samples. The reference product P2 Y was compared to the sample P2 C formulated with the organic texturizer maltodextrin: the only difference detected was the color, since in a scale from 1 to 7, where 1 indicated white/yellow, 4 indicated white, and 7 indicated white/gray, P2 Y had an average rating of 2.7 and P2 C had an average rating of 1.7. The reference product P3 Y was compared to the

sample P3 G formulated with the inorganic texturizer silica at 1.5% w/w: the two samples differ not only in color, as P3 Y has an average rating of 3.5 and P3 G has an average rating of 4.3, but also for consistency, since on a scale from 1 to 7 where 1 indicated a fluid system and 7 indicated very consistent or solid system, P3 Y had an average rating of 4.3 and P3 G had an average rating of 4.8.

Table 1: results obtained from the paired samples t-test: green boxes indicate that no differences were perceived, red boxes indicate a significative perceived difference. The average values of differences are reported.

Significative difference	ASPECT	COLOUR	CONSISTENCY	SPREADABILITY	ABSORPTION	GREASINESS	STICKINESS	GLOW EFFECT	MATTE EFFECT	SKIN SOFTNESS
P1 XY vs P1 A										
P2 Y vs P2 C		1 (P2 Y 2,7 – P2 C 1,7)								
P3 Y vs P3 G		- 0,8 (P3 Y 3,5 – P3 G 4,3)	- 0,5 (P3 Y 4,3 – P3 G 4,8)							

Discussion.

The results of this study demonstrate how the replacement of raw materials of synthetic origin is a very complex job for the formulator, as most of the natural raw materials have peculiar and different application and sensory characteristics, which need to be characterized and well understood. The physical and mechanical properties of polymers inevitably have an impact on the rheological and texture characteristics of the finished products, and this can change the consumers' perception and affect their acceptability.

PRODUCT 1 is a serum formulated for acne-prone skin with a mixture of nylon-12 and PMMA as texturizer and is characterized by a fluid texture with low firmness and consistency, high spreadability and pick-up properties. In this case, the replacement of synthetic texturizers with natural organic texturizers, in particular with zea mays starch, has proved to be the best choice, as these polymers, due to their hydrophilic nature, are able to interact with the water of the system, improving the structure properties and skin feel of the product. The use of zea mays starch as texturizer does not change the rheological and texture properties of the product and does not interfere with the sensorial aspects and the acceptability, as detected by the sensory test performed in this work.

PRODUCT 2 is a cream gel with smooth and firm texture. For this product, the replacement of PMMA with the natural texturizers selected in this study does not alter the mechanical and application properties. Maltodextrin was chosen as the best candidate to replace the synthetic texturizer since it confers high adhesive properties suitable for the application on the eye contour. However, the substitution with maltodextrin involves a slight variation in the color of the formulation, which is perceived by panelists as tending to yellow when compared with the reference product.

PRODUCT 3 is characterized by high values of firmness, consistency and adhesiveness and low values of stringiness, which is a typical characteristic of a body butter with rich texture and low pick up. The high content of oils in the formula makes the natural inorganic texturizers, which have a greater oil absorption capacity, more performing, increasing the structure properties of the emulsion, as shown by the higher rheological moduli and texture parameters of firmness, consistency and cohesiveness. The replacement of the PMMA, used in the product at a concentration of 3% w/w, with the silica-based texturizer at 1.5% w/w allows obtaining a system with a texture similar to that of the original product, as confirmed by the curves obtained with the immersion test. The sensorial analysis did not show significative difference between the reference product and the formulation with silica during the phase of rub out and after-feel on the skin. However, significative differences were found in the appearance of the samples and during the pick-up phase, since the introduction of silica caused a slight variation in color and a slight increase in the perception of consistency.

Conclusion.

The combined use of rheology and texture analysis is useful to characterize the applicative properties of cosmetic formulas, evaluating the influence of the vehicle composition and the replacement of raw materials on spreading properties and adhesive characteristics. These two complementary techniques could provide a scientific support for cosmetic industries to easily reformulate cosmetic products in a green and sustainable perspective, without losing the sensorial performances impaired by the conventional synthetic ingredients.

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Conflict of Interest Statement.

NONE.

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