“Instrumental approach for the eco-design of hair styling products: rheology and texture analysis”

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1. Introduction

Ecodesign formulation faces the challenge of minimizing the environmental impact while satisfying consumer expectations for high-performance products [1]. The recent microplastics ban [2] has intensified the search for viable alternatives to synthetic polymers, especially in categories such as hair fixatives in which natural materials often show limitations in properties like long-lasting hold, hair stiffness and film-forming ability.

This study aimed to develop an instrumental protocol to evaluate the impact of ecodesign-driven reformulation on the structural and application performance of hair styling products. The reformulation process focused on the selection of natural origin and biodegradable fixative and suspending materials, seeking the best possible compromise between environmental sustainability, stability, and application properties that determine consumers’ satisfaction. In the first phase of this project a pool of film-forming polymers at different concentrations in gel formulations have been characterized and clustered according to their structure properties, adhesive ability, hardness, and elasticity of the treated hair. The results of this preliminary phase have been presented at the Annual European Rheology Conference AERC 2025 [3].

Subsequently, commercial hair fixative products have been reformulated in an ecodesign perspective by totally or partially replacing synthetic film-forming polymers, which are considered microplastics with a toxicity profile for the marine fauna, with associations of plant-origin materials. Non-biodegradable acrylic rheological modifiers, whose persistence in the environment is problematic, have been replaced with associations of polysaccharides. The physico-mechanical characterization of cosmetic samples by means of rheological and texture analysis plays a crucial role in helping manufacturers to quickly make formulation changes and replace commonly used raw materials with more sustainable alternatives, evaluating their contribution within the finished product.

Rheological tests, performed both in continuous and oscillatory flow conditions, allow characterizing the samples’ structure, flow behavior, and viscoelastic properties [4-6]. Texture analysis is used to study mechanical parameters, such as firmness, consistency, adhesiveness, and stringiness, which are linked to the products’ application properties and hence to consumers sensory perception [7, 8]. The three-point cantilever bending technique is employed to evaluate the mechanical properties of treated hair tress [9, 10]. These data are essential for the

development and quality control of new cosmetic products and the optimization of existing formulations. They can also be used to support marketing claims of performance and sensorial properties, in an objective and scientific way.
This approach can significantly accelerate the development of innovative, eco-friendly hair styling products, meeting consumers' expectations and moving beyond traditional trial-and-error methods.

2. Materials and Methods

Synthetic polymers: PV (polyvinyl pyrrolidone), AQ and CQ (quaternary polymers), LV, AD, and SC (vinyl pyrrolidone copolymer), SM (acrylic copolymer).
Natural polymers: AG, XL (starch derivatives), AM (polymer derived from succinic acid), AL (alginate), SD and SF (quaternary ammonium guar derivative).
The polymeric raw materials were dispersed at different concentrations in a gel base formulation containing 1% w/w of Hydroxyethyl-cellulose.

Three commercial hair styling products have been re-formulated by totally or partially replacing synthetic polymers with naturally derived materials (Table 1).

Table 1: Synthetic styling polymers contained in hair styling products and natural alternatives used for the reformulation in eco-design.

Products	Description	Synthetic polymers	%w/w	Natural alternatives	%w/w
Product A	Moisturizing gel with medium hold on hair	LV	8.5	SD SF	3 3
Product B	Elasticizing and shining curly hair serum	AD SC	18 1.8	SD AG	1.3 1
Product C	Hydrating anti-frizz gel-to-oil texture for curly hair	AD	2	SD	1.3

The rheological analyses were performed using a Rheometer Physica MCR e302 from Anton Paar at a controlled temperature of 23°C ± 0.05°C. Tests were conducted in oscillatory flow conditions using PP50-P2 sensor with a fixed gap of 1 mm. 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). Frequency sweep tests were performed decreasing frequency from 10 Hz to 0.01 Hz, at a fixed strain within the LVER, to analyze the trend of storage (G') and loss (G'') moduli.

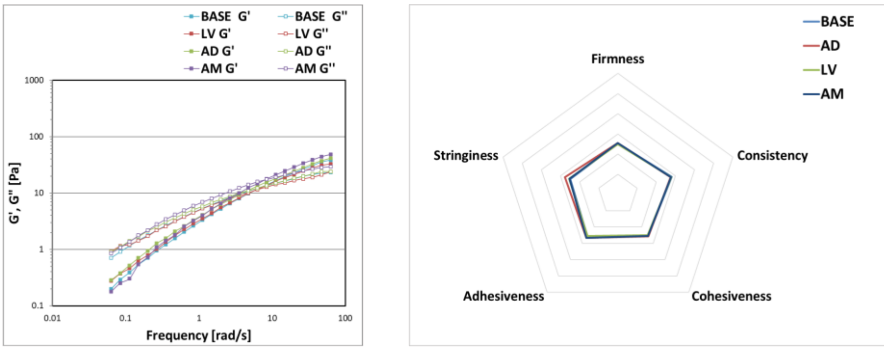
An immersion/de-immersion test was conducted at room temperature by means of a Texture Analyzer TMS-Pro, from Food Technology Corporation, equipped with load cells of 5 and 10N. The 2 cm diameter, nylon, spherical probe moved vertically to a depth of 10 mm at a constant speed inside the samples loaded in 50 mL containers and then returned to the initial position. Texture Lab Pro was used to measure the following parameters: firmness (N); consistency (N.mm); cohesiveness (N); adhesiveness (N.mm); stringiness (mm).

The three-point bending technique was used to measure the strength and flexibility of the polymeric film deposited onto the hair. Hair tresses were treated with 2 g of polymer solutions and dried overnight in a 40% RH and 25°C environment. A texture analyzer equipped with a custom-designed probe was mounted to the instrument, TA.XT plus from Stable Micro Systems. Hair tresses were fastened to a clamp and rested on cantilevers positioned 4 cm from each other. The probe was positioned in the middle above the hair tress. It travels downward at a speed of 2 mm/s making a 1 cm deformation into the hair tress. Each tress underwent 10 cycles of deformation, which results in a force vs. distance curve containing 10 peaks allowing for the determination of parameters including: maximum force (F1) related to the hardness of tress; distance at the maximum peak (P1) related to flexibility; ratio between the peak force of the 10th cycle and that of the 1st cycle (F10/F1) linked to hair elasticity.

3. Results

3.1. Characterization of hair styling polymers

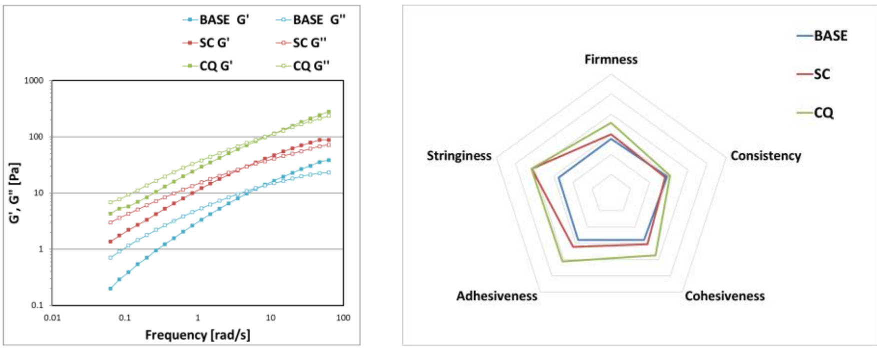
The polymeric gel formulations were analyzed by means of rheology, texture analysis and the three-point bending technique after the application on hair tresses. LV, AD, AM, AQ, PV, AG formed non-structured samples with liquid viscous behavior. These polymers did not have an impact on the viscoelastic properties of the base gel formulation and exhibited low texture parameters. Figure 1 shows as an example the viscoelastic behavior and the texture parameters measured for some of these polymers.



(a) **(b)**

Figure 1: (a) Mechanical spectra and (b) texture parameters of base gel and gels with 5% w/w of polymers LV, AD, AM.

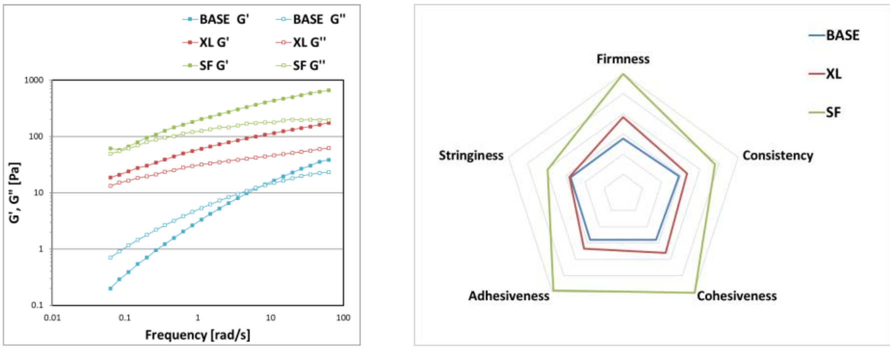
SC, CQ, AL, SD, increased the moduli of the base gel formulation since the samples were more structured. They formed adhesive gels with high pick-up characteristics. Figure 2 shows as an example the viscoelastic behavior and the texture parameters measured for some of these polymers.



(a) **(b)**

Figure 2: (a) Mechanical spectra and (b) texture parameters of base gel and gels with 5% w/w of polymers SC and CQ.

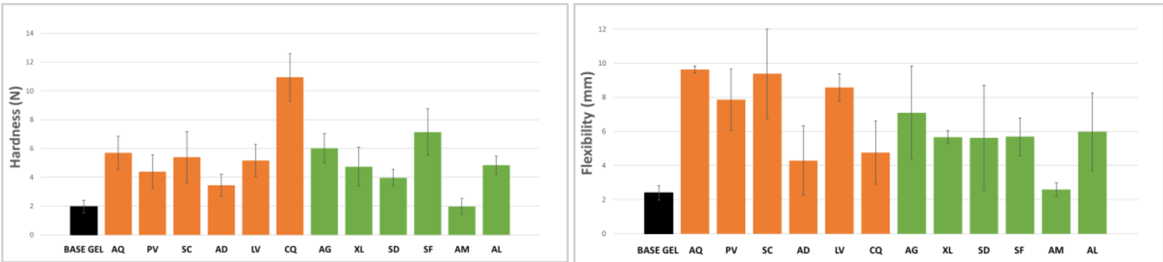
XL and SF showed weak-gel rheology with the elastic modulus G’ higher than the viscous modulus G’’ and solid-like behavior by increasing concentrations. They formed firm and consistent gels with high elasticity. Figure 3 shows the viscoelastic behavior, and the texture parameters measured for these polymers.



(a) (b)

Figure 3: (a) Mechanical spectra and (b) texture parameters of gels with 5% w/w of polymers: base gel, XL, SF.

All polymers formed a film on hair tresses that enhances their mechanical properties (Fig. 4). Synthetic polymers imparted more flexibility. The cationic polymer CQ and the natural one SF formed the hardest protective film after application. AM formed the softest and least flexible film.



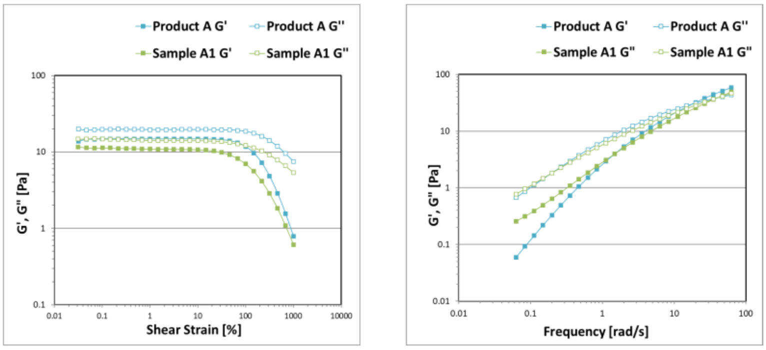
(a) (b)

Figure 4: (a) Values of hardness and (b) flexibility measured with a three-point cantilever bending test for polymeric gels at 5% w/w.

3.2. Reformulation of Product A

Product A is a hair styling gel with medium hold containing 1.5% of Polyquaternium-10 as a cationic conditioning polymer with high viscosifying properties and 4.5% w/w of synthetic vinyl pyrrolidone copolymer (LV) as film-forming agent. These polymers were replaced with an association of PV film-forming polymer and the quaternary ammonium guar derivatives SD and SF at 3% w/w (Sample A1).

The Amplitude sweep test showed a very similar moduli trend among the samples with the viscous modulus G'' higher than the elastic one G' (Fig. 5a); Sample A1 showed lower moduli values. The Frequency sweep test highlighted the viscoelastic behavior for the samples, in which G' was higher than G'' at higher frequency, whereas G'' was higher than G' at lower frequencies (Fig. 5b); however, the cross-over point of the original formula was settled at lower frequencies than the reformulated Sample A1, indicating a more structured network.



(a) **(b)**

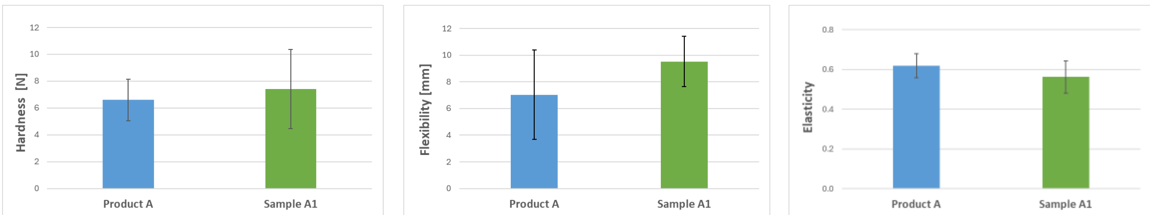
Figure 5: Trend of visco-elastic moduli in function of (a) shear strain and (b) oscillation frequency for Product A and Sample A1.

In Table 2 the values of the texture parameters for Product A and Sample A1 are shown, along with the standard deviations from the mean of five measurements. The new formulation showed higher values of cohesiveness and adhesiveness compared to the original formulation. This results in a higher pickup and film-forming properties.

Table 2: Values of texture parameters measured for Product A and Sample A1

	Firmness (N)	Consistency (N.mm)	Cohesiveness (N)	Adhesiveness (N.mm)	Stringiness (mm)
Product A	0.105 ± 0.001	0.601 ± 0.009	0.031 ± 0.001	0.123 ± 0.001	20 ± 5
Sample A1	0.133 ± 0.006	0.690 ± 0.050	0.049 ± 0.001	0.193 ± 0.003	24 ± 2

Additionally, the three-point bending analysis revealed that the values of hardness (Figure 6a), flexibility (Fig. 6b), and elasticity (Fig. 6c) did not show significative differences between the original formula and the reformulated one. This highlighted that the substitution of synthetic polymers in this case has led to a result that closely replicates the original formulation.



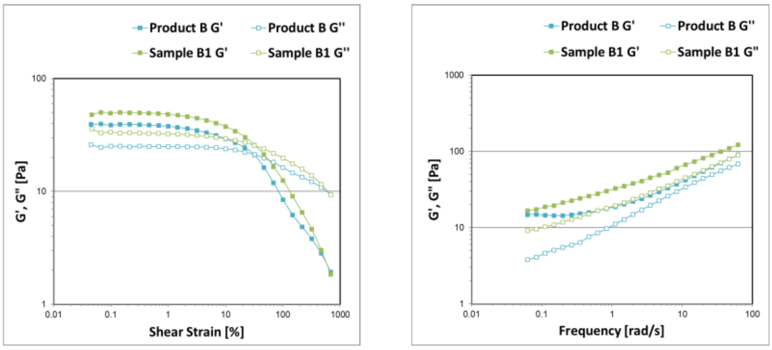
(a) **(b)** **(c)**

Figure 6: Comparison between hardness (a), flexibility (b) and elasticity (c) calculated with the three-point bending test for Product A and Sample A1

3.2. Reformulation of Product B

Product B is a serum for curly hair, which contains Poliquaternium-37 and two styling copolymers of vinyl pyrrolidone and acrylates copolymers SC at 9% w/w and AD at 0.5% w/w. This product has been reformulated (Sample B1) by reducing the concentration of SC at 5% and replacing Polyquaternium-37 and AD copolymer with quaternary ammonium guar derivative SD at 1.3% w/w and a starch derivative AG at 1% w/w. The polysaccharide Sclerotium gum at

0.2% w/w was inserted as a rheological modifier to increase the consistency and the elasticity of the formula.
In the Amplitude sweep test the moduli of Sample B1 were slightly higher compared to the ones of the original formula (Fig. 7a). This behaviour was confirmed by the Frequency Sweep analysis, where G' was always higher than G'' (Fig. 7b), showing a weak-gel pattern. The fact that the reformulated sample was more structured and elastic could represent an advantage in terms of long-term stability.



(a) **(b)**

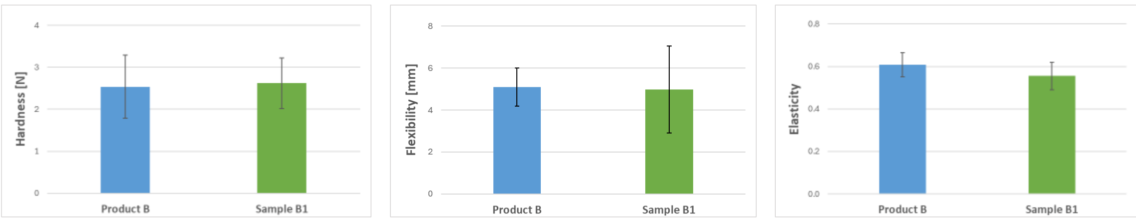
Figure 7: Trend of visco-elastic moduli in function of (a) shear strain and (b) oscillation frequency for Product B and Sample B1.

From the texture analysis, which values are shown in **Table** 3, the new formulation exhibited higher values of all the parameters, in particular adhesiveness, consistency, and stringiness. This indicated that the formula was more compact and structured compared to the original one. This observation agree with the rheological analysis, which showed that the new formulation was indeed more structured.

Table 3: Values of texture parameters measured for Product B and Sample B1

	Firmness (N)	Consistency (N.mm)	Cohesiveness (N)	Adhesiveness (N.mm)	Stringiness (mm)
Product B	0.151 ± 0.002	0.760 ± 0.020	0.039 ± 0.001	0.148 ± 0.002	12.3 ± 0.4
Product B1	0.197 ± 0.002	0.916 ± 0.006	0.069 ± 0.001	0.243 ± 0.009	18.0 ± 2.0

For product B, the three-point bending test showed that all the parameters remained very similar to the original formulation, reflecting that the reformulation maintained the same *mechanical profile, keeping consistent the performance of the original product* ***(Fig. 8)*****.**



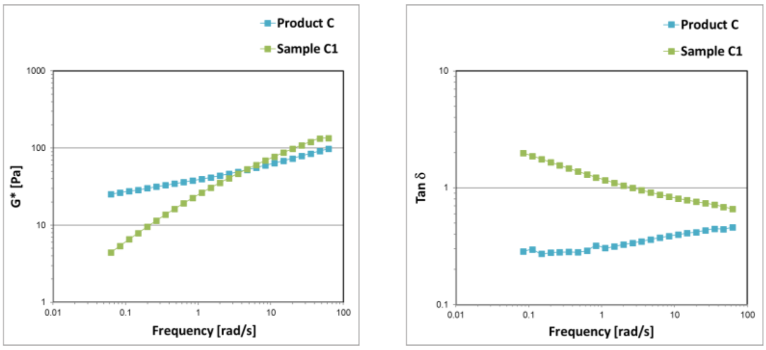
(a) **(b)** **(c)**

Figure 8: Comparison between hardness (a), flexibility (b) and elasticity (c) calculated with the three-point bending test for Product B and Sample B1.

3.3. Reformulation of Product C

Product C is a gel for curly hair containing AD synthetic copolymer at 2% as a film forming agent and carbomer polymer at 0.3% as a gellyfing agent. The goal of this reformulation was not only to improve the product's sustainability, but also to enhance its applicability and performance in terms of curl definition. This product has been reformulated with a combination of quaternary ammonium guar derivative SD at 1.3% w/w and Hydroxyethyl-cellulose to obtain the desired consistency and the elasticity of the formula, crucial in products meant for curlier textures.

While the values of complex moduli G* of the two formulas were settled within the same decade (Fig. 9a), the trends of the damping factor tanδ, derived from the ration between G'' and G', were very different. For the original product it followed the typical pattern associated with carbomer structures that have a more elastic behavior, whereas Sample C1 exhibited higher values in function of the frequency applied (Fig. 9b) and a liquid-viscous behavior typical of guar derivatives.



(a) (b)

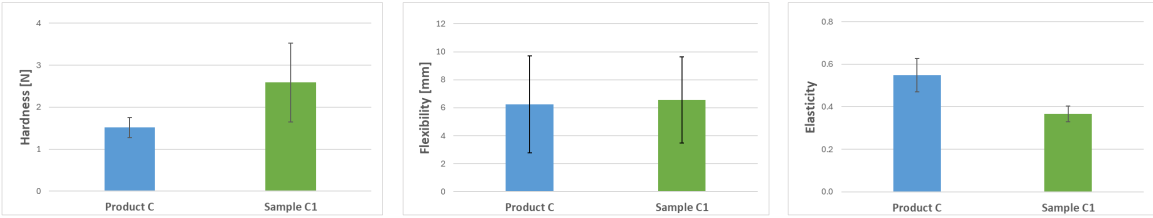
Figure 9: Trend of complex modulus G* (a) and damping factor tanδ (b) in function of oscillation frequency for Product C and Sample C1.

From the texture values (Table 4), it can be observed that the reformulation with natural alternatives caused a reduction in firmness and consistency and an increase in adhesiveness and stringiness. This was also highlighted by the rheological measures and emphasizes that it is not always possible to achieve a substitution that leads to an identical result. However, in this case, the higher adhesive properties demonstrate that, in terms of film-forming properties, improvements have been made.

Table 4: Values of texture parameters measured for Product C and Sample C1

	Firmness (N)	Consistency (N.mm)	Cohesiveness (N)	Adhesiveness (N.mm)	Stringiness (mm)
Product C	0.149 ± 0.001	0.750 ± 0.020	0.039 ± 0.001	0.128 ± 0.001	13 ± 4
Product C1	0.126 ± 0.005	0.620 ± 0.019	0.058 ± 0.002	0.281 ± 0.032	24 ± 1

In fact, this trend was also highlighted by the results from the three-point bending test where the hardness (Fig. 10a) of the film has been significantly improved.



(a) (b) (c)

Figure 10: Comparison between hardness (a), flexibility (b) and elasticity (c) calculated with the three-point bending test for Product C and Sample C1

4. Discussion

The substitution of synthetic polymers without compromising their functional properties is a significant challenge, especially in the formulation of hair styling products, where consumers demand high performance and particular application characteristics. Synthetic materials are designed to produce specific effects in cosmetic products, influencing structure and sensory perception. When replacing these ingredients with natural raw materials, careful selection of the type of material, its concentration, and combinations becomes essential to achieve the desired performance without noticeable changes in the formulation.

The eco-design approach proposed in this study includes both rheology and texture analysis to identify optimal ingredient concentrations and combinations, enabling comparisons between products, starting with the characterization of individual polymers dispersions. Technical data sheets for cosmetic ingredients often lack key chemical information, such as molecular weight and crosslinking degree, as well as their effects in formulations. This highlights the need to study polymers' behavior using instrumental techniques to understand their contributions, make comparisons and, therefore, make rational formulation decisions, ensuring the desired product properties.

Synthetic polymers have demonstrated to create strong, flexible protective films on hair without affecting the system's rheology or structure. In contrast, polysaccharide blends that perform well on hair tend to swell and alter the product's viscoelastic properties. Notably, starch derivatives (XL) and quaternized guar gum derivatives (SF and SD) formed firm, consistent samples with high elasticity, exhibiting good film-forming properties that imparted flexibility and elasticity to hair.

When replacing synthetic polymers in the three formulas, it became clear how the different interactions between polysaccharides and synthetic polymers with water impacted the product's rheological and structural properties. In Product A, a hair styling gel, maintaining the high viscosity provided by polyquaternium-10 was essential for spreadability, ease of application, and medium hold. Therefore, a combination of natural-derived polymers (SD and SF) was necessary to ensure firmness, viscosity, and high adhesiveness, while little amount of synthetic polymer PV retained hair elasticity and flexibility. In Product B, a curly hair serum, the performance of the synthetic acrylic copolymer SC could not be entirely replaced. Its concentration was reduced, and AD polymer was substituted with a blend of potato starch AG and guar gum derivatives (SD and SF), providing film-forming properties, cohesiveness, and adhesiveness. Elasticity was preserved by introducing sclerotium gum polysaccharide, which also acted as a rheological modifier, ensuring long-term stability. In product C, a gel-to-oil texture product, vinyl pyrrolidone copolymer AD was replaced with a combination of guar gum derivative (SD) to give definition and hold to the curl and hydroxyethylcellulose to give viscosity to the formulation. Even if the elasticity of carbomer could not be replicated with natural derivatives, their synergy

helped us to reach the desired performance in terms of adhesiveness and hardness while ensuring long term stability.
This instrumental approach represents a valid tool to rationalize the use of polymers, helping formulators to compare and carefully choose or replace them to keep the same level of performance and enhance sustainability of hair styling products.

5. Conclusion

Although it was not possible to perfectly replicate the structural and application properties of the original hair styling products, the combined use of rheology, texture immersion/de-immersion analysis, and the 3-point bending test enabled the selection of the most suitable fixative polymers that can closely mimic the performance of the synthetic ones, offering similar applicative and sensory characteristics. This instrumental approach offers formulators an efficient alternative to the traditional trial-and-error method, enabling them to find cost-effective and time-saving solutions, especially when reformulating products with a focus on sustainability. To further validate the method, sensory panel tests should be conducted to confirm the correlation between instrumental analysis and consumer perceptions.

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