Reformulation of hair conditioner to improve sustainability and usability with the help of rheology

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Abstract

Background: Looking ahead to industrial production and big volumes of hair conditioners, promoting cold manufacturing processes represent a substantial opportunity to reduce carbon dioxide emission. This study aimed to reformulate a hair conditioner, containing waxy components and manufactured with a hot process, using a liquid thickening-stabilizing-conditioning polymer that enables a cold process. A second objective was to keep similar textural and sensory properties.

Methods: Waxy components were replaced one by one looking for a cold process. Rheology experiments were carried using a controlled stress rheometer (DHR2 from TA Instruments). Texture of the selected formula was analyzed compared to the reference (TA XT- PLUS from Stable Micro System). The effects on hair tresses were evaluated by dedicated expert panelists.

Results: The changes in composition influenced both the flowing profile and the internal structure of the hair conditioner. The cold-processed formula with the liquid polymer provided equivalent macroscopic stability than the hot-processed Reference and better stability of the microstructure to temperature variations. Flowing profile was also visibly improved while similar effects were obtained on hair tresses according to the 5 selected descriptors (95% confidence interval).

Conclusion: Rheology experiments helped to screen the impact of changes in the composition and highlighted some assets of the cold-processable formulation that would not have been expected using usual viscosity and stability characterization. The cold processable hair conditioner permitted reduced energy consumption by 95%. The time required for production was also divided by 3.

Keywords: Hair care; Conditioning; Sustainability; Rheology; Sensory

Introduction.

Sustainability can be approached through different perspectives and challenge our formulation habits and manufacturing practices. When big production volumes are involved, such as for hair conditioners (hair conditioners reached a volume of 1.48 millions tonnes worldwide in 2020 according to Euromonitor International report and was predicted to be the most dynamic hair care category up to 2025), the manufacturing process has a particular significance in improving the carbon footprint. Indeed, conventional hair conditioners, containing waxy components such as fatty alcohols and cationic agents, require hot manufacturing [1, 2]. In addition, this type of formulation has largely demonstrated its effectiveness but it also has certain constraints related to a change in consistency over time [3]. Viscosity variations after manufacturing were also explained by time sensitivity to shearing action and inaccuracies in the manufacturing process such as on the melting time of fatty alcohols, cooling time and cooling gradient [4, 5]. A sensitivity to temperature variations during storage was also reported. These inconveniences can finally disturb the distribution outside the packaging during use, especially from spray pumps and affect the formulation spreadability on hair. The purpose of this work was to reformulate a hot-processed hair conditioner in a cold-processed formulation while maintaining its stability and improving its usability. Rheology experiments were carried out to analyze the effects of ingredient substitution, to screen formulation behavior during use at this early stage of the formulation development and select the composition to the most favorable profile. Texture and sensory analysis on hair completed the evaluation of the most appropriate formula option when used.

Materials and Methods.

Optimization of hair conditioner formulation

Reformulation of a classical hot-processed hair conditioner (called Reference) was done by removing one by one the waxy components and replacing their association by a liquid thickening-stabilizing-conditioning polymer (Acrylamidopropyltrimonium Chloride/ Acrylates Copolymer & Isohexadecane & Coceth-7), looking for the optimized dosage and a cold manufacturing process. Formula stability and usual characteristics were monitored (Table 1).

INCI name/% (w/w)		Reference	HC1	HC2	HC3
A	Water	90.5	90.5	90.5	90.5
	Acrylamidopropyltrimonium Chloride/Acrylates Copolymer & Isohexadecane & Coceth-7	-	1.5	3.0	3.5
B	Steartrimonium Chloride & Water & Isopropyl alcohol (25% Active Matter)	3.0	2.0	3.0	3.0
	Cetearyl Alcohol	3.0	2	-	-
	Steareth-20	0.5	0.5	0.5	-
C	Glycerin	2.0	2.0	2.0	2.0
	Preservative	1.0	1.0	1.0	1.0
Manufacturing procedure - Homogenization with rotor/stator turbine 4 minutes at 4000rpm, - Stir with an anchor stirrer at 50 rpm for cooling down or during 10 minutes for the RT procedure and add ingredients of phase C one by one; stir until homogeneous.		at 80°C*	at 80°C**	at 80°C**	at Room Temperature (RT)***
pH		≅ 5.3	≅ 5	≅ 5	≅ 5
Brookfield viscosity 1 month after manufacturing (mPa.s, Spindle 4; Speed 6)		≅ 8,100	≅14,500	≅ 12,500	≅ 13,000
Stability at RT & 45°C		Stable > 3 months at RT and 1 month at 45°C			

* Addition of water at 80°C in phase B followed by homogenization.
** Mixing of phase A until Homogeneous followed by heating to 80°C; addition of ingredients of phase B one by one into phase under homogenization.
** Mixing of phase A until Homogeneous at room temperature; addition of phase B followed by homogenization.
**** Mixing of phase A followed by homogenization.

Table 1 - Hair conditioner formulation and characteristics

Rheology analysis

Rheology experiments were conducted on the different formulations using a rotational Controlled stress/ strain (DHR2 from TA Instruments; Aluminum cone 40mm/2°). Flowing experiments were performed at 20°C to evaluate the global flowing profile. Rate index (with best fit model shown to be Herschel-Bulkley analysis, consistently with previous publication on hair conditioners [6]) and yield stress (steady state flow protocol; Onset mode) were determined. Viscoelasticity was analyzed using oscillatory experiments in different conditions: frequency sweep at 20°C (0.1 to 100 rad/s) and temperature sweep from 0°C to 80°C, then 80°C to 0°C (frequency 1Hz/ anti-evaporation cap). Evolution of storage modulus (G') and mean G'/G" ratio were followed.

Texture profiles

Texture analysis was realized (TA XT- PLUS from Stable Micro System) using an hemispheric probe going down into the product packaged in a petri dish filled to the brim, then up (diameter: 50mm; Standard cycle protocol at 20°C up to a depth of 4 mm). Force profile was followed as a function of time. Maximum force and compression energy were determined as indicators of the product firmness/ consistency during use (mean of 5 replicates at different positions of the sample; samples were placed in the petri dish at least 30 minutes before the measurement). Adhesion energy during the upturn movement was also assessed. The ratio Adhesion energy/ Compression energy was calculated as representative of behavior during the product pick-up [7].

Sensory evaluation

A triangular sensory random test was conducted with an expert panel specifically dedicated to hair care and trained since 2017 [8]. The evaluation was conducted on bleached caucasian hair tresses (Level II; 10 panelists; Statistical analysis using Tastel® software). After a standard pre-washing, hair conditioner was spread on wet hair (0.4g of product/tress), left on for 5 minutes, then rinsed. The tresses were dried at room temperature for 24 hours with 45% Relative Humidity. 5 attributes were examined in a standard sensory booth (cool daylight), according to trained gestures: ease of combing, shine, volume, sliding effect, residual oily sensation, natural feeling.

Results.

Rheology experiments have helped to monitor the influence of the replacement of waxy materials on the behavior of the formulation. Flow experiments initially demonstrated that all formulations exhibited shear thinning behavior, slightly less pronounced for HC2 and HC3 containing a high amount of liquid polymer, as shown by the slope of the curves in Figure 1. This shear thinning behavior with a low viscosity in the shear range corresponding to that applied when spreading the formula on hair (>500s^{-1} based on data on skin; 950s^{-1} mentioned in a previous publication as representative of shear rate during conditioner spreading [9]) promotes a perception of easy spreading, despite significant increasing in Brookfield viscosity of HC1, 2 and 3 compared to the Reference (with 20% of variations considered). Due to close results, spreadability of the formulations on hair were not expected to be different.

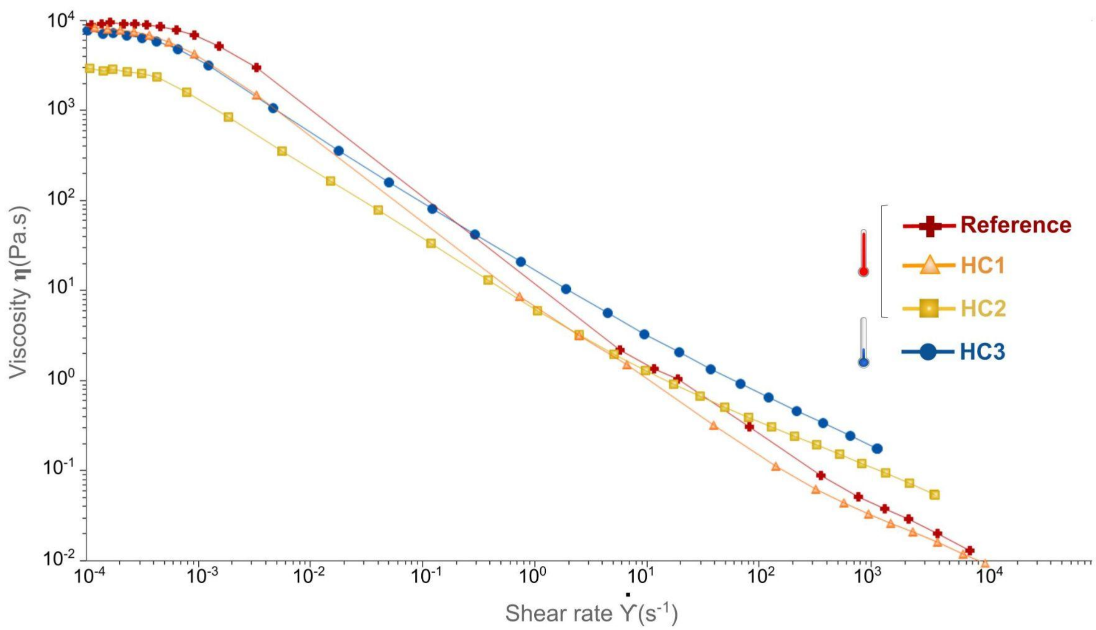


Figure 1 - Flow curves

The hot-processed reference provided a significant yield stress, despite its lotion-like texture, which on one hand helped the product stability but, on the other hand, could explain the reported distribution issues from packaging. The gradual reduction of waxy components to the increase of the liquid thickening-conditioning polymer led to a reduced yield stress (Figure 2). A lower yield stress was expected to promote easier flow out of the packaging, especially in the cases of free flowing from bottles and pump dispensers. HC3 formula seemed to provide a good compromise.

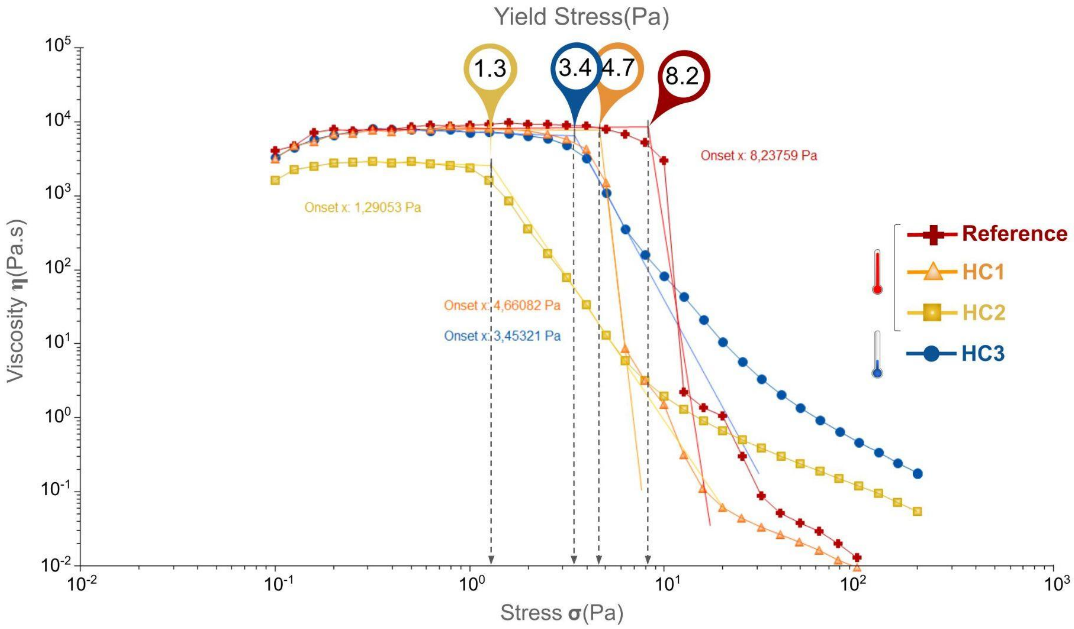


Figure 2 - Yield stress

Oscillatory experiments demonstrated the predominant elastic structure of the trials, contributing to stability, as indicated by the predominant G'modulus and the G'/G" values superior to 1. Total replacement of fatty alcohols by the liquid polymer (HC3) led to a similar level of structure than the reference. Only HC2 showed a weaker internal structure.

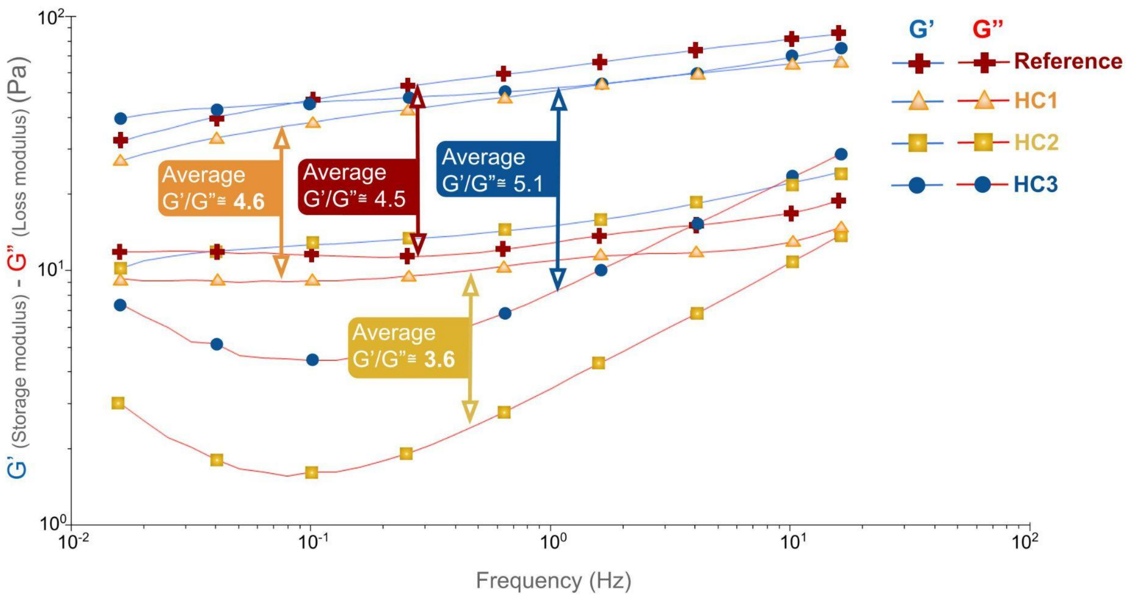


Figure 3 - Viscoelastic character - Frequency sweep

Temperature sweep experiments highlighted significant differences according to the formula composition. The formula reference and HC1, rich in fatty alcohols, presented a structure breakdown between 55 and 80°C (Figure 4). Destructuring above 60°C reflected melting of fatty alcohols. When the temperature decreased below 55°C, the recovery of the structure was observed.

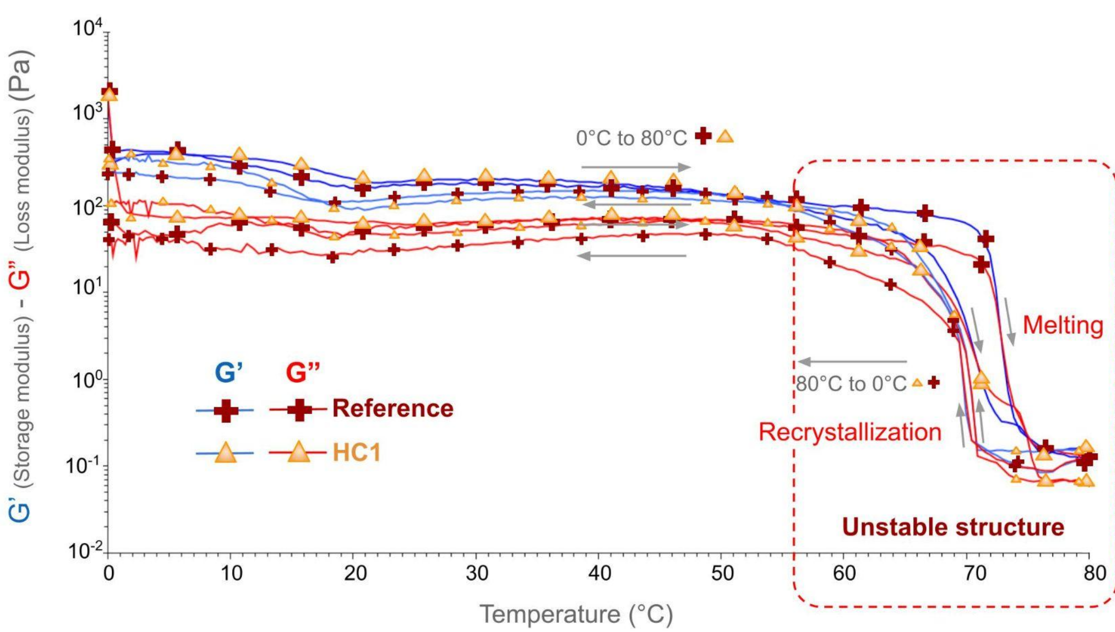


Figure 4 - Viscoelasticity according to temperature sweep

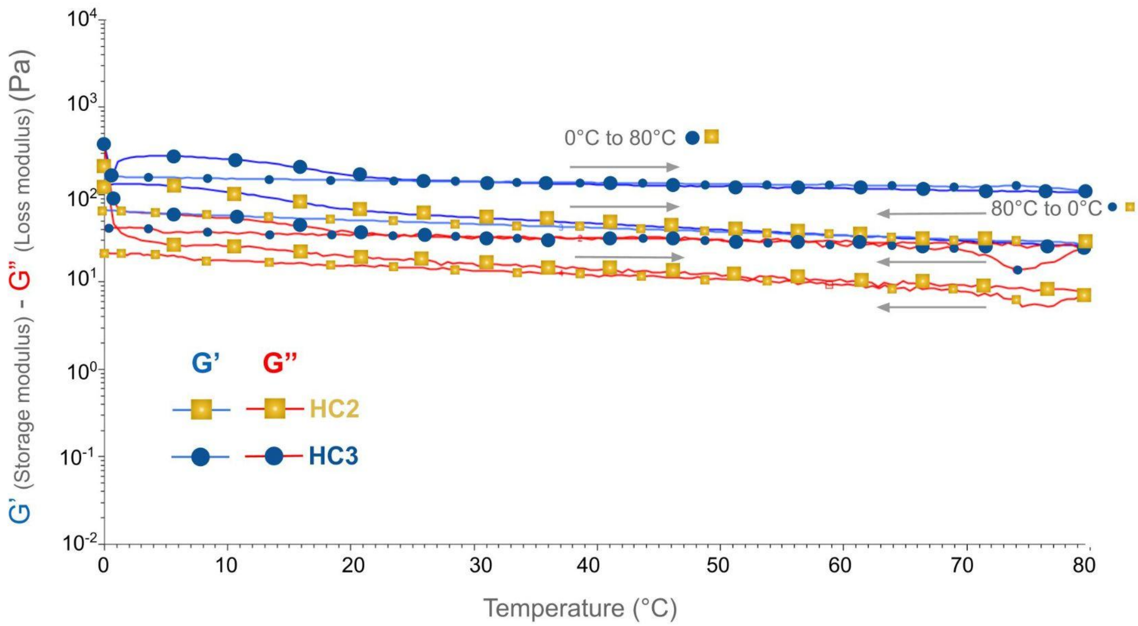
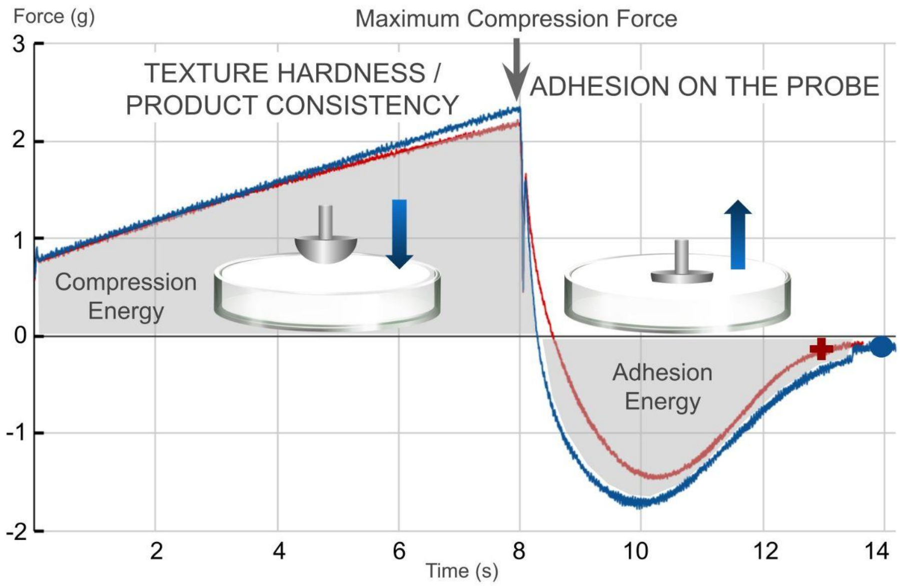


Figure 5 - Viscoelasticity according to temperature sweep

On the contrary, the two formulations mainly based on the liquid polymer, without fatty alcohols (HC2 combined with a low amount of waxy surfactant and HC3 based only on the liquid polymer), demonstrated to be robust when submitted to temperature variations (Figure 5). These results reinforced the interest of the cold-processed formulation alternative.

Texture analysis highlighted similar profiles of HC3 and the hot-processed reference (Figure 6). Both products had similar consistency during penetration of the probe as pointed out by respective compression energies and maximum compression forces values. The adhesion properties were considered to be similar, as indicated by the close adhesion energy/compression energy ratios. No sticky effect was expected given the rather low value of the ratios.



	Maximum Compression Force	Ratio of Energies Adhesion/ Compression
Reference	2.24 g ± 0.12	0.3
HC3	2.38 g ± 0.09	0.4

Figure 6 - Texture profiles of the formulations

Regarding the sensory evaluation, 8 out of 10 panelists didn't find any difference between tresses treated by the Reference and HC3. The two who perceived a difference noted it on a very low intensity, meaning that they were not sure of their answer. The two formulas were thus perceived as having a similar effect, at 98.93% on combing, shine, volume, sliding and residual feeling (considering alpha risk of 5%). The two hair experts who applied the products on wet hair noticed a difference in application: HC3 product had a very light texture and provided a quick break effect, compared to the body given by the reference.

Discussion.

Rheology experiments, summarized in table 2, highlighted some assets of the cold-processed alternative formula: HC3, using a liquid thickening-stabilizing-conditioning polymer instead of a combination of fatty alcohols.

Combining shear thinning and a lower yield stress, HC3 could prevent reported distribution issues from packaging. Similar values of rate index and yield stress (0.45 and 3 respectively) have been obtained after one month of storage of HC3 in freeze-thaw cycles from -5°C to 40°C. Easier and smooth flowing compared to the Reference were confirmed in practice as shown in figure 7. The non-smooth jerky flow of the Reference could also have been analyzed by a deep look on the flowing curve (Figure 2) showing several slope changes, thus indicating product fracturing during shearing. These results could not have been expected when looking at usual viscosity characteristics with a higher value for HC3 (Table 1). After 3 months of storage at room temperature, it was also checked that HC3 did not have any thixotropic character, while slight thixotropy could be seen for the Reference (Figure 8). The absence of thixotropy of HC3 allowed a high degree of flexibility in manufacturing with no expected viscosity evolution after shearing. Considering the behavior during use, the absence of thixotropy is balanced by the quick break effect, which facilitates the application on the hair.

As a second interest, HC3 benefited from an internal elastic structure, at a similar level than the Reference but stable in an extended range of temperature. This robustness brings a great safety of use for the formulator and the whole supply chain. Moreover, the structure given by the polymeric network was confirmed to be quite constant after one month of storage in freeze-thaw cycles conditions (Table 2). On the contrary, the reference showed a booming G’ value in the same conditions (from 59 to 242), testifying some evolution in the internal organization (change in conformation of the gel phase described with several systems containing cationic surfactants and fatty alcohols [10]), that can be related to the changes in consistency over time reported for this type of product containing high fatty alcohol dose.

		Reference	**HC3**
Manufacturing process		at 80°C	at RT
RHEOLOGY PROFILE 7 days after manufacturing			
Flowing profile	Shear thinning character: Rate index	0.34	0.41
	Yield stress (Pa)	8.2	3.4
Elastic structure	Frequency sweep G’ (Pa) G’/G”	59 4.5	51 5.1
	Temperature sweep Stability domain	0-55°C	0-80°C
Structure stability after 1 month of storage in cycles oven-5/40°C			
Elastic structure	Frequency sweep G’ (Pa) G’/G”	242 3.5	47 2.2

Table 2 - Summary of Rheology profile

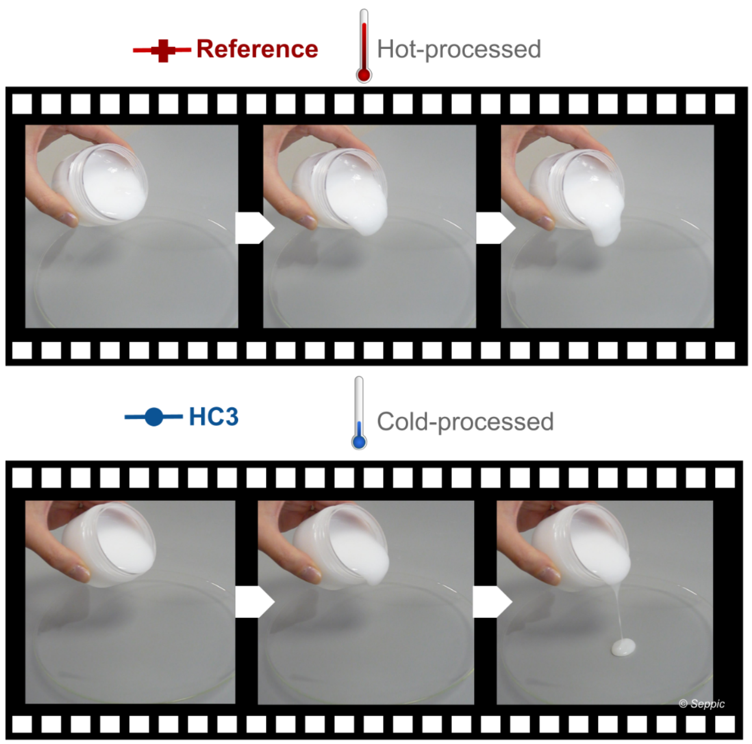


Figure 7 - Compared flowing behavior

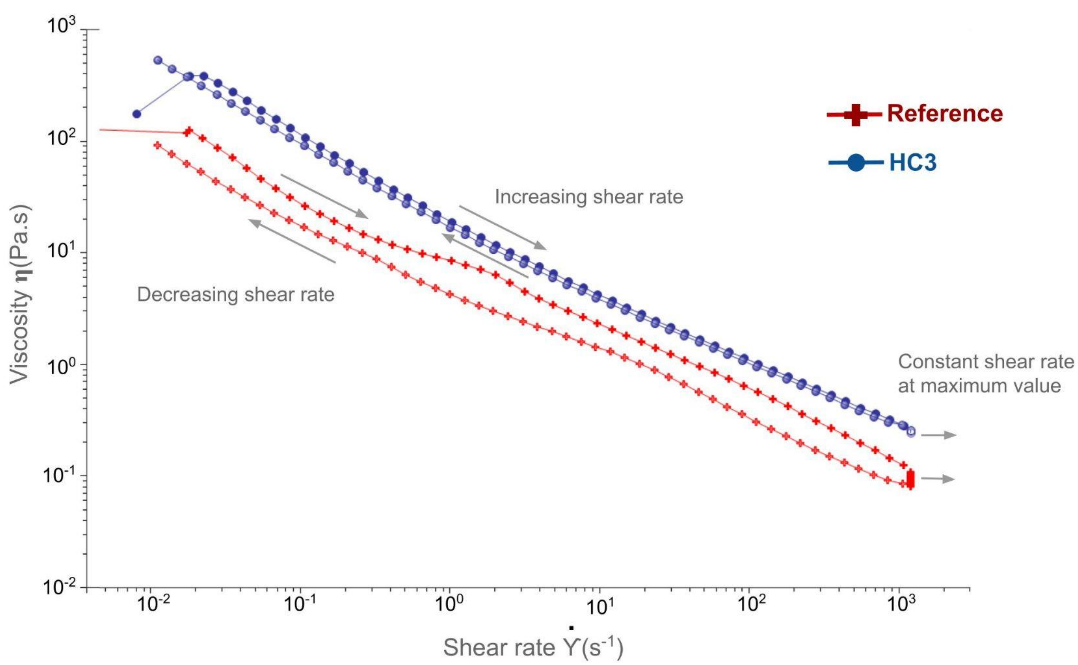


Figure 8 - Thixotropy visualization

Taken altogether with the similar profiles from texture analysis and finish on hair tresses, HC3 formula was revealed as a promising alternative that would have to be evaluated *in vivo* on a larger hair panel. The different texture noticed by the experts during application on the tresses, especially the more aqueous texture with less body, seemed to mean that the products will still not be exactly similar to the use and may require adaptation. However, this lighter texture could also be seen as an opportunity for fine hair or warm climates. The formulation could also be tuned by adding bio-based light emollients or polymers to reduce hair surface hydrophilic character. Indeed, the liquid thickening-stabilizing-conditioning polymer is able to stabilize this type of ingredients without the addition of other surfactants.

Time and energy consumed during the production of a 5 Kg pilot batch (Trimix 10L equipment from VMI Rayneri) were estimated considering the full energetic power of each mixing device as default value. Energy consumption was reduced from around 13.5 Kwh for the Reference produced at 80°C to less than 1 Kwh (0.7 calculated) for the cold-processed hair conditioner, corresponding to 95% reduction. Moreover, production time decreased from 1h30 to 20-25 minutes (without taking into account the cleaning operations).

Conclusion.

Rheology helped to better understand the effects of the substitution of hair conditioner waxy components (fatty alcohols) and support the optimization of a cold-processed formula using a liquid thickening-stabilizing-conditioning polymer. The resulting hair conditioner showed similar effects on hair tresses than the Reference and improved usability: stable structure up to 80°C and under freeze-thaw cycles, smoother flowing and improved distribution from pump packaging. The cold manufacturing process reduced energy consumption by 95% compared to the Reference and divided the production time by 3, on the basis of a 5 Kg pilot batch.

Conflict of Interest Statement.

Authors are Seppic employees. Authors have no other conflict of interest to declare.

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