Linking Sensory and Rheology Characteristics

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ABSTRACT: *The authors introduce a method to use rheological properties (such as dynamic viscosity and yield stress) to describe and predict skin sensory attributes (such as cohesiveness) of cosmetic products. This is a first step in learning to use emulsion structure to predict sensory attributes.*

At present, most sensory evaluations of personal care products are carried out using well-trained panels. Sometimes this is supplemented by various instrumental methods such as viscosity, corneometry, polarity, etc. The objective of this study is to investigate the relationship between rheological properties and sensory attributes. We view this as a first step to understanding the influence of emulsion structure on sensory characteristics.

In this paper we demonstrate a methodology to use rheological properties to describe and predict skin sensory attributes. Rheological data is analyzed by Principal Component Analysis (PCA) and clear correlations were found between several rheological properties. Partial Least Squares regression showed cohesiveness can be predicted by two rheological properties: dynamic viscosity and yield stress.

Some sensory and rheological properties clearly depend on the emulsion structure. In colloid chemistry, scientists are using models to correlate emulsion structure with rheological characteristics. In contrast, there is far less knowledge about sensory-emulsion structure relationships, but the development of rheology-sensory relationships can be the first step in building understanding about how sensory attributes are influenced by changing the emulsion structure.

Theory

Sensory properties of cosmetic products are key characteristics and many of these properties are often related with rheological properties. The appearance is the customer's first visual contact with the product and therefore very important. Then the product is applied on the skin and rubbed out. In this phase the skin feel properties of the product are important. For instance, the thickness of a product may play an important role in the sensory impression. The customer expects a thicker product for a facial cream, whereas a body lotion is expected to be less thick. The latter should be easily applied on larger parts of the body. Thickness also plays an important role during production.

Proper evaluation of sensory characteristics is time-consuming and consequently expensive. In order to save time and cost, instrumental methods could be useful to replace sensory tests. It is generally accepted that instrumental methods (such as rheology) could be very useful to increase knowledge about why different products have different sensory characteristics and others don't. Surprisingly, the amount of information found in literature about rheology-sensory correlations for cosmetic products is very limited.

Meloni[1] used rheological properties to explain unexpected moisturization properties of hydrophilic polymers, showing how ingredients can be used to change the emulsion structure. A few papers assert that sensory-rheology correlations are not noticeable in one-to-one relations. Barry[2] studied the correlation of sensory tests of cosmetic emulsions with rheology, but concluded that sensory tests do not correlate with

> Univariate methods are not capable of identifying a proper [sensory-rheology] correlation. Multivariate methods are much more powerful.

stationary viscosity alone. Brummer[3] concluded that shear stress at the onset of flow alone is not an unambiguous criterion to distinguish between product types. Both Barry and Brummer are indicating that rheological properties cannot be sufficiently described by sensory property. In other words univariate methods are not capable of identifying a proper correlation. Multivariate methods are much more powerful. These methods are described elsewhere.[8]

The power of multivariate methods has been shown in several application areas. The food industry is a good

MULTIVARIATE ANALYSIS

Univariate techniques are most often used to calculate the correlation between one dependent variable and an independent variable. A famous example is the relation between absorbency and concentration according to the Lambert-Beer law. Unfortunately, some references[2-3] have shown that sensory-rheology relations cannot be explained by one-to-one correlation. Therefore more advanced techniques are applied. Two examples are Principal Component Analysis (PCA) and Partial Least Squares (PLS).

Principal Component Analysis: The basic principle of PCA is to reduce the number of dimensions by identifying linear relationships between the variables. Latent variables (principal components) are calculated to explain the variance in the data set optimally. The most important visual results of the calculation can be described by the loading and score plots.

A loading plot provides information about the variables and how these are related. For instance, this plot enables one to identify the existence of positive or negative relations between the variables. A score plot shows the similarities and differences between the products.

Partial Least Squares: PLS is a regression method that has some similarity with PCA. Instead of maximizing the explained variance in the data set, PLS maximizes the explanation of the dependent value (y-value). This process is much more focused on the dependent variable and therefore more efficient to describe the variable of interest.

example because there is clear overlap with cosmetic applications.[4] Both applications areas often work with emulsions and in both areas sensory characteristics are very important. Nevertheless, multivariate methods are not often described in literature in combination with cosmetic applications. Wortmann[5] used PCA to study the influence of co-surfactants and conditioning agents in shampoo. Wiechers[6] and Wortel[7] described several multivariate techniques to evaluate sensory attributes of both emollient and formulated products.

The scope of the article before you is to demonstrate a method to describe sensory attributes with rheology properties. It is not possible to give a complete theoretical introduction to either multivariate analysis or rheology. However, some basics of these techniques are required to understand this work (see sidebar). In this article we will focus on the advantage of multivariate analysis and use the output of its calculations without explaining the mathematics behind it.

Materials

In this study we measured 85 different formulations from both commercial products and in-house formulations. These samples were tested by a trained sensory panel. The samples were also measured with a rheometer[a] to obtain information on how the emulsion behaves when a certain force is applied.

The data evaluation and the regression is done by several software packages, such as SAS version 8.2[b] and Unscrambler[c].

Sensory Methods

All 85 samples are evaluated using the Spectrum Descriptive Analysis method.[9] This sensory technique relies on obtaining accurate numbers by a well-trained sensory test panel. This panel consists of approximately 10 members and each panelist evaluates each product three times using well-defined attributes with a fixed meaning. The 21 attributes can be subdivided in several groups: appearance, pick-up, rubout, immediate after-feel and after-feel after 20 minutes. This study mainly focuses on the pick-up and rubout phase because these are obviously most related with rheology.

Cohesiveness is used as a typical example to explain the applied methodology. This sensory attribute is evaluated during the pick-up phase and is evaluated by compressing the product slowly between index finger and thumb, after which the fingers are separated. The degree to which the sample strings rather than breaks when fingers are separated is defined as cohesiveness. A stringy product has a high cohesiveness number.

Rheology Methods

Various rheological techniques are applied, namely steady state (constant shear rate), constant stress (creep) and dynamic measurement (oscillatory). This allowed us to obtain 20 rheological properties, such as high shear rate viscosity, yield value (obtained from fit of the flow curve), zero shear viscosity, storage and loss modulus. For all measurements the samples are placed in the gap between a 2° cone and a 5 cm plate. Depending on the measurement, a different force (shear or stress) is applied on the sample.

Steady state (constant shear rate) measurements: For these measurements the rheometer is used as a constant shear rate instrument by rotating the cone at increasing rate. All samples are measured at a temperature of 29°C. The flow profile is measured from 0-500-0 s^{-1}, using 180 measuring points (0.5 sec/point) and 240 measuring points (2 sec/point). The torque on the plate is measured to give the shear stress.

The shear stress-shear rate curves are analyzed using several models to obtain the yield value and the plastic viscosity. In this study the yield stress is calculated using the Bingham model (Equation 1). According to this model the yield stress (intercept) is calculated by extrapolation to zero shear rate. This extrapolation is carried out using four points after the first measurement.

$$\sigma = \sigma_\beta + \eta_{pl}\,\dot{\gamma} \qquad (1)$$

where σ = shear stress
σ_β = yield stress
η_{pl} = plastic viscosity
$\dot{\gamma}$ = shear rate

Constant stress (creep) measurements: A constant stress is applied on the sample (at 25°C) and the deformation or strain is measured as a function

of time for t = 120 seconds. Then, the stress is removed and the strain (which reverses sign) is measured for 120 seconds; this gives the recovery curve. Before the yield stress is reached, near complete recovery is obtained, i.e., the strain in the recovery curve approaches zero. When the applied stress exceeds the yield stress, the strain continues to increase with time (during time of application, t = 120 sec) and only partial recovery is obtained, i.e., the strain reached after t = 120 sec in the recovery curve is no longer zero. From the slope of the strain versus time one obtains the shear rate.

When the applied stress is divided by shear rate, one obtains the viscosity η_σ at this applied stress. A plot of viscosity η_σ versus stress σ shows a curve with two Newtonian regions: one in the low shear rate regime $\eta(0)$ (the residual or zero shear rate viscosity) and one in the high shear rate regime $\eta(\infty)$. These low and high shear viscosities are separated by a shear thinning region. The value of the stress at which the viscosity begins to decrease is sometimes referred to as the critical stress σ_{cr}.

Dynamic (oscillatory) measurements: For these measurements a sinusoidal strain with frequency ω (rad/sec) and amplitude γ_o is applied on the sample (at 29°C) and the stress is simultaneously measured. For a viscoelastic system, the stress and amplitude oscillate with the same frequency but out of phase. The stress and strain amplitudes are shifted by a time Δt and this allows one to calculate the phase angle shift δ ($\delta = \omega \Delta t$). From the amplitudes of the stress and the strain and the phase angle shift one can obtain the complex modulus $G^\star$:

$$G^\star = (\sigma_o / \gamma_o) \tag{2}$$

where $G^\star$ = complex modulus

σ_o = measured stress

γ_o = amplitude

The elastic modulus or storage modulus (G') and the loss or viscous modulus (G'') can be calculated from the complex modulus:

$$G' = G^\star \cos \delta \tag{3}$$
$$G'' = G^\star \sin \delta \tag{4}$$

Finally, the dynamic viscosity η' can be calculated from the loss modules:

$$\eta' = G'' / \omega \tag{5}$$

In oscillatory measurements one initially fixes the frequency, for instance at 1 Hz, and measures $G^\star$, G', G'' and η' as a function of strain amplitude. The rheological parameters are virtually constant up to a critical strain γ_{cr}. This constant region is referred to as the linear viscoelastic region (LVER). Above γ_{cr} the values of $G^\star$ and G' start to decrease whereas G'' and η' start to increase with further increase in strain amplitude. In the present study, the value of η' was calculated using the values of the rheological parameters at the end of the LVER.

Multivariate Methods

In the first part of the study we aimed to understand the uniqueness of the rheological properties by using PCA. The visual output of this method enables the identification of similarities and differences between rheological properties. This can play an important role for the pre-selection of these properties. This step is useful to increase information density of the dataset and
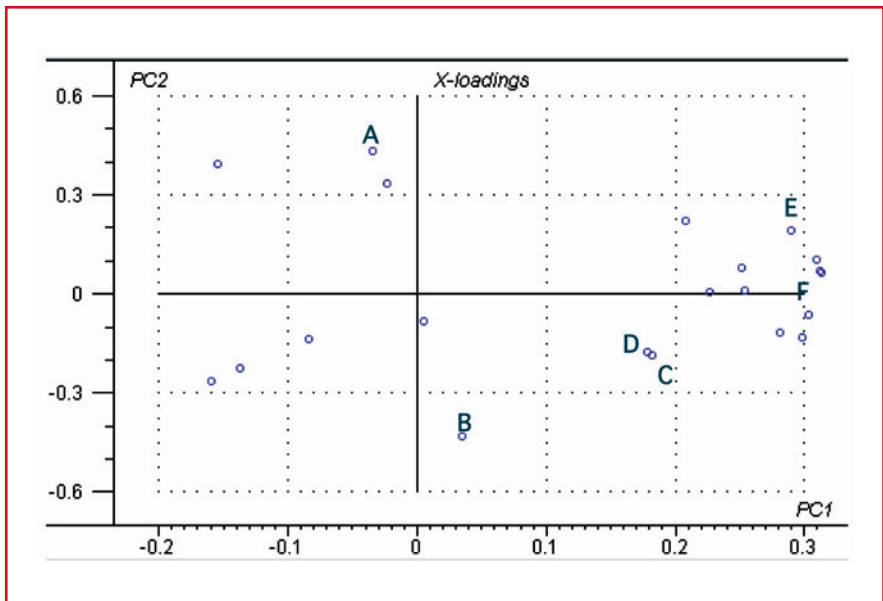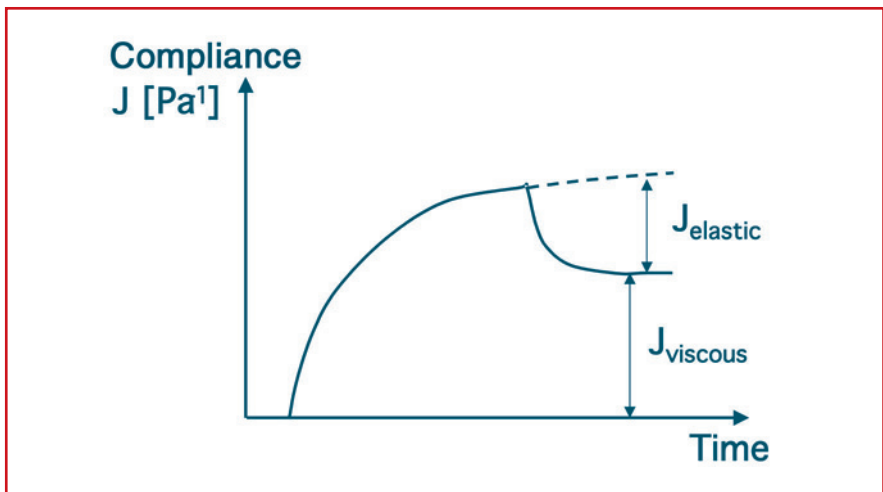
Figure 1. PCA loading plot

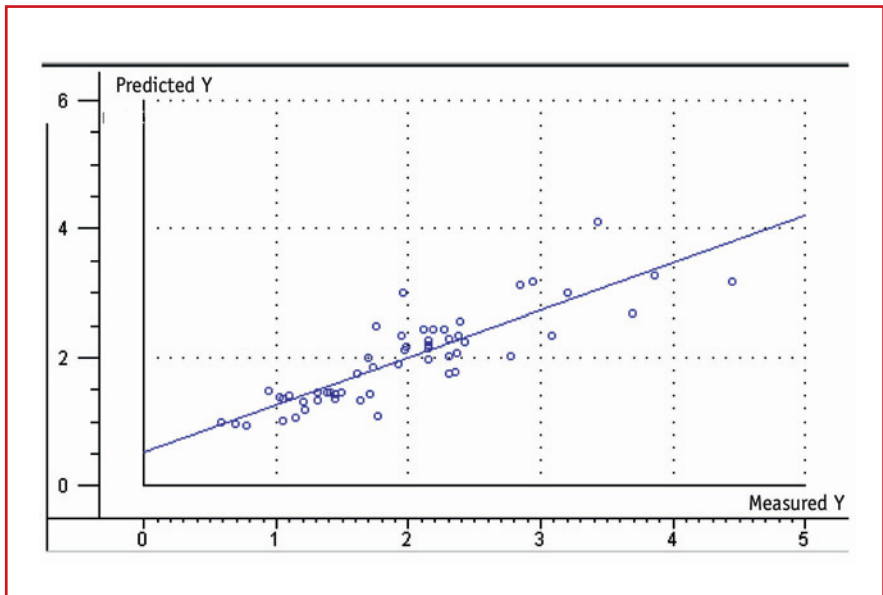*Figure 2. Elastic and viscous components of compliance creep*

Figure 3. PLS-measured values vs. predicted values

improve the quality of the regression (part 2). The PCA calculation is applied on the complete data set including all 20 rheological properties calculated from all three rheology measurement techniques. Loading plots are created to show which rheological attributes contained unique information and which properties are related in order to reduce the number of rheological attributes and to get a better overview.

In the second part, PLS regression is applied to correlate sensory attributes with rheological properties. Cohesiveness is used as an example to illustrate the prediction of a sensory attribute from rheological properties. A stepwise procedure is used to select the most significant rheological properties that are related with cohesiveness. These selected properties are used for the calibration of the model. An independent test set validation is used in order to validate the PLS model. This test set contained 10 new products. The cohesiveness was predicted by the cohesiveness model and evaluated by the sensory panel. The comparison of these results will show the reliability of the PLS model.

Results

Rheology: The rheological properties that are mentioned in the experimental part were calculated and evaluated. The data was used as an input for the PCA calculation. For some properties a logarithmic transformation was applied in order to obtain better distributions. The loading plot (Figure 1) visualizes the relations between the rheological properties.

The interpretation of this plot can be explained by two clear examples. First, compare points A (elastic component) and B (viscous component); both are attributed to creep measurements. According to the loading plot these two properties are inverse correlated, i.e., if A is increasing, B must be decreasing. This can easily be explained by rheology. The creep compliance J is the deformation per stress unit and consists of a viscous component and an elastic component (Figure 2). The more elastic a formulation's behavior is, the less viscous it is, and vice versa.

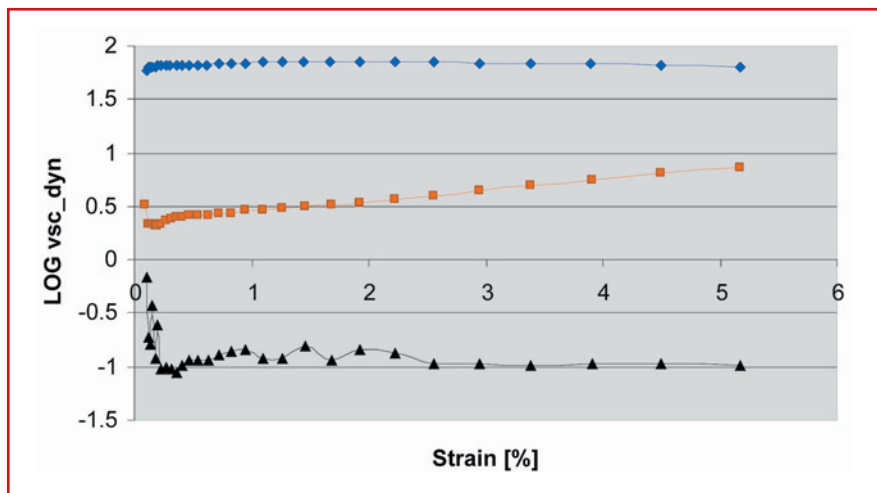The second example studies two properties that are close to each other

Figure 4. Dynamic Viscosity vs. strain amplitude (♦=sample A, ■=sample B, ▲= sample C)
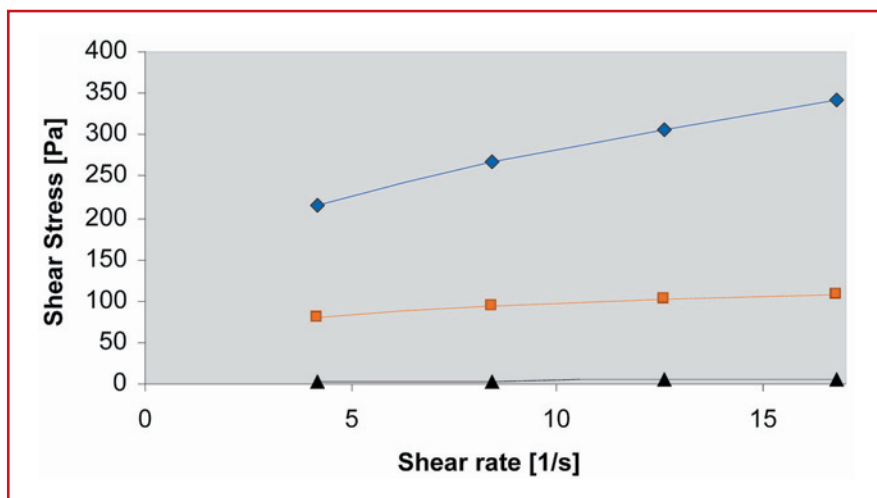

Figure 5. Shear stress versus shear rate (♦=sample A, ■=sample B, ▲= sample C)

in the loading plot; this means that these properties are directly correlated. A direct correlation means that if one property is increasing the other is also increasing. A good example is points C (cohesive energy, amplitude sweep) and D (thixotropy index, rotation measurement) in Figure 1. These rheological properties contain similar information (for the current data set) but are results of different measurement techniques and independent calculations. Surprisingly, from a rheological point of view this correlation is unexpected, but might be a good learning point for the properties of the samples. Obviously, time can be saved by not measuring redundant rheological properties.

Regression: The stepwise regression shows that the dynamic viscosity and yield stress (points E and F, respectively, in Figure 1) are the most suitable to apply for the cohesiveness model. These properties are used to calculate the PLS model. The correlation coefficient of this model is 0.85, which is not very high. However, the model is based on a sensory panel evaluation, which usually contains a considerable amount of noise. The model shows that both rheological properties are directly correlated with the cohesiveness.

The selected rheological properties are from different rheological techniques. Dynamic viscosity is measured with oscillatory measurement, whereas yield stress is measured under steady state conditions. According to the PCA loading plot (Figure 1) these properties mainly differentiate on the seconds PC (y-axis). The yield stress contains information about how much force is required to move the product. More details about the physical interpretation are written in the discussion. The independent test set validation of the PLS

model shows that most of the products were predicted with the same accuracy as the calibration (Figure 3).

Discussion

Colloid models can be used to describe the relation between rheology and emulsion structure. As a first step, we chose three samples A, B, and C that are characterized by a wide range in rheological properties. As an illustration, Figure 4 shows the variation of dynamic viscosity η' with strain amplitude. Figure 5 shows the shear stress-shear rate curves for these samples. From this curve, yield value σ_β was obtained by extrapolation to zero shear rate. The dynamic viscosity (Figure 4) of these samples is 69.2, 2.6 and 0.1, and the Yield stress is 178, 74 and 3.4 Pa, for A, B and C, respectively. It can be seen that the reduction in viscosity from samples A to C is much greater than the reduction in the yield stress.

Let us now consider the composition of each sample and the possible "colloidal" interactions present. Sample A is a hand cream[d]. It is considered an O/W emulsion that is "structured" using liquid crystalline phases. The latter are made from a mixture of sodium cetearyl sulfate (C16/C18 sulfate anionic surfactant), cetearyl alcohol (C16/C18 alcohol) and stearic acid (C18 carboxylic acid). This combination produces lamellar liquid crystalline phases that extend into the continuous phase producing a three-dimensional "gel network" structure. The liquid crystalline structure is also enhanced by incorporation of electrolyte (Na_2SO_4) in the system. The gel network is expected to have high "cohesive" structure and hence it should give a high yield value (178 Pa) and high dynamic viscosity (69 Pa.s).

Sample B is an aloe vera gel[e], simply an aqueous natural extract. The extract is "gelled" using carbomer[f] that is neutralized by triethanolamine. The carbomer is cross-linked polyacrylic acid, which on neutralization produces "microgel" particles. The latter are produced by dissociation of the COOH groups forming COO- groups,
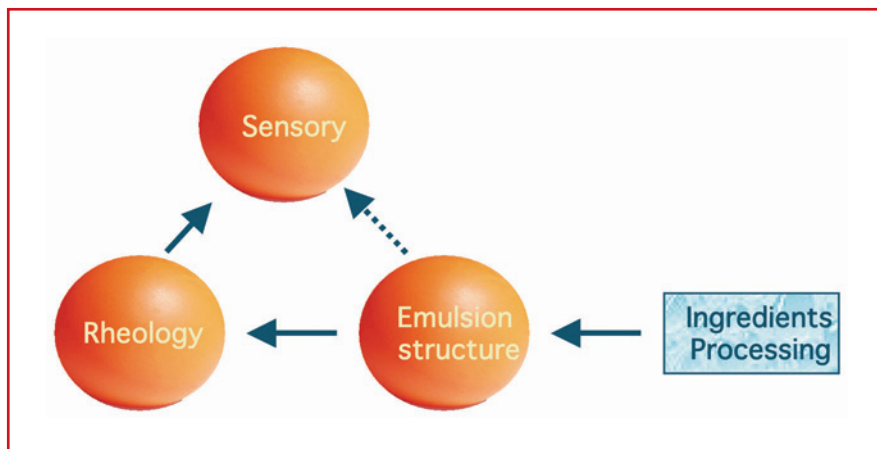
Figure 6. A model to link emulsion structure with sensory attributes via rheology

and this causes swelling by expansion of the double layers. The microgel particles will have a high charge and an extended double layer. This gel structure is expected to be less "cohesive" than the three dimensional "gel network" structure produced using lamellar liquid crystalline phases. As a result, the yield value (74 Pa) and the dynamic viscosity (2.6 Pa.s) are lowered.

Sample C is an in house formulation prepared using an emulsifier/biopolymer system[g] (1%) and 10% oil phase (triethylhexanoin). The emulsifier/biopolymer system consists of a surfactant mixture of steareth-100, steareth-2, glyceryl stearate citrate and sucrose, and a stabilizer (thickener) system consisting of mannan (konjac) and xanthan gums. The most likely mechanism of stabilization is based on adsorption of the emulsifier system at the oil/water interface (with the possible adsorption of some hydrocolloid system). The excess emulsifier/biopolymer system remains in bulk solution. This emulsion produces a relatively low yield value (3.4 Pa) and low dynamic viscosity (0.1 Pa.s). These low values are due to the low oil volume fraction in the system and hence droplet/droplet interaction is relatively weak. However, the biopolymer system can produce a weak "gel" structure and hence a low yield stress.

Ultimately, the fundamental knowledge obtained from the rheology-sensory relationship is actually only the first step in a process to modify specific properties of a formulation. The relationship between emulsion structure

and sensory will be difficult to extract. A correlation between rheology and sensory could therefore help to obtain the desired skin sensory properties. Figure 6 is a visualization of this concept.

The discussion above shows that colloidal models can be used to explain the relationship between rheology and emulsion structure of a personal care formulation. The next challenge will be to obtain sensory attributes from the combination of the sensory-rheology relationships and the colloid models. Finally, once such a relationship has been established, it should be possible to correlate the ingredients used and the process involved to the ultimate sensory attributes of the personal care products. Then, the formulation chemist may choose the optimum ingredients and optimum process to achieve the required goal of the sensory attributes.

This knowledge should therefore facilitate the development of innovative cosmetic formulations. This study, however, has clearly shown that the relation between rheology and sensory can be found by the use of multivariate techniques.

Conclusion

The first part of the study shows that many rheological properties are highly correlated. For some properties this is very logical and for others it is unexpected. PCA might help to get a better understanding of several rheological properties on a specific set of samples.

Cohesiveness has been used as a typical example for a sensory attribute. Univariate calibration method does

not show good correlations, but multivariate calibration methods proved to be successful. The regression model in this study shows that cohesiveness can be described by yield stress and dynamic viscosity. The validation of the model shows that the error in the test set is approximately the same as the error in the calibrations model, therefore these models are reliable. Further work is in progress to build a direct link between sensory and emulsion structure and possibly to ingredients and processing condition.

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