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abstract

Using the findings from previous sensory research projects on predictive models, the current paper analyses whether, and how, the functional properties of acrylates can be imitated in cosmetic emulsions using biopolymers. It could be established that at a suitable concentration, a combination of two natural substances produced using biotechnology – gellan gum and xanthan gum – can replace an acrylic acid polymers and deliver the desired sensory properties and in some cases also the stabilisation. By taking rheological measurements in oscillation mode, a correlation to the sensory attribute of body could be established via the storage modulus G' and the plateau value. The quick break attribute also proved useful in evaluating a polyacrylate imitation. The measurement data of the rheology spectrum helped to establish the biopolymer combinations that were most similar to the polyacrylate. An after-sun cream-gel formulation was used to demonstrate that even a trained panel of sensory experts could not establish any significant sensory difference between the acrylate and gellan gum formulations.

Introduction

The demand for more sustainable cosmetics products has resulted in a more critical view of the ingredients used. In this context, the biodegradability and bioaccumulation potential of these ingredients are also evaluated. The focus is on substance groups from the field of acrylic acid polymers, which are widely used as a texture additive in gel and emulsion formulations (key word "liquid plastic"). In the course of a Bachelor's thesis at Zurich University of Applied Sciences (ZHAW Wädenswil, Switzerland), researchers investigated whether besides the gold-standard testing by a trained panel of experts [1], there was a suitable alternative measurement and evaluation method that presents and possibly predicts at least a selection of sensory attributes using analytical measurements [2, 3]. Findings from previous sensory research and development projects on predictive models for emulsions have also provided motivation to use this approach to focus on gel systems [4]. In particular, the sensory attributes quick break, body and long play have become especially important when evaluating the acrylate's sensory characteristics. A term paper written previously at the same university revealed that, based on its properties, a high-acyl gellan gum could be an interesting candidate for the above-mentioned sensory attributes. Accordingly, 0.1% and 0.2% gellan gum (Kelcogel CG-HA) were compared with 0.1% acrylates/C10-30 alkyl acrylate crosspolymer (Carbopol ETD 2020) in an after-sun cream-gel emulsion. To ensure the thermal stability of the emulsions (3 months at 3°C, 20°C and 40°C), 0.4% xanthan gum (Keltrol CG-SFT) was also added to all formulations. The rheological measurements were analysed accordingly. These results, together with the sensory feedback from trained and untrained panel tests, were compared and conclusions and findings drawn from this.

Materials and Methods

Test Formulation

The investigated standard formulation was a typical oil-water emulsion with an oil phase of just 20% and a starting viscosity of approx. 10,000 mPas. An emulsifier and xanthan gum were added as stabilisers. However, the main texture-relevant ingredients with regard to body and quick break, were the acrylates/C-10-30 alkyl acrylate crosspolymer or gellan gum. **Tab. 1** shows the basic formula used. As a comparison, the acrylate crosspolymer was replaced by gellan gum in different concentrations (0.1% and 0.2%). A placebo emulsion was also prepared that contained neither acrylate nor gellan gum. This showed the influence of the acrylate crosspolymer or gellan gum on the formulation. The percentage of xanthan gum was kept the same in all emulsions (0.4%). Sodium hydroxide was omitted from the gellan emulsions as gellan gum as a raw material forms a gel structure independently of the pH value.

Phase	Raw material	INCI	Content [%]
W1	Water demin.	Aqua	75.2
	Glycerin 99%	Glycerin	2.0
W2	Keltrol CG-SFT	Xanthan Gum	0.4
W3	Carbopol ETD 2020	Acrylates/C10-30 Alkyl Acrylate Crosspolymer	0.1
W4	NaOH 10%	Sodium Hydroxide	0.3
O	TEGO Care PSC 3	Polyglyceryl-3 Dicitrate/Stearate	2.0
	Dermofeel Sensolv	Isoamyl Laurate	3.0
	Coconut Oil organic	Cocos Nucifera Seed Oil	6.0
	Myritol 312	Caprylic/Capric Triglyceride	6.0
	Eldew SL-205	Isopropyl Lauroyl Sarcosinate	3.0
	Dermosoft MCAV	Caprylyl Glycol, Dicaprylyl Glycol, Glyceryl Caprylate	1.0
T	Perfume Vital N123	Parfum	0.2
	HydraSynol IDL	Isosorbide Disunflowerseedate	0.5
	Alpha-Lupaline	Lupinus Albus Seed Oil, Triticum Vulgare (Wheat) Germ Oil	0.3

W = aqueous phase, **O** = oil phase, **T** = excipients and active substances.
Green = consistent xanthan content. **Orange** = substituted portion of the different emulsions.

Tab. 1 Basic formula Acrylate 0.1-Emulsion.

Determination of Physical Measurements

The rheological measurements were taken using the Modular Compact Rheometer (MCR 2 00, Anton Paar) via a parallel-plate system (PP25) at a constant temperature of 22°C. The data were recorded using the Anton Paar RheoCompass 1.20 software. In addition to the conventional flow curve, the viscoelastic behaviour of the emulsions in oscillation mode was recorded, and the storage modulus G' [Pa], loss modulus G" [Pa], LVE region [Pa], plateau value [Pa], flow point G' = G" and loss factor (G'/G") determined.

Determination of Sensory Data

The prepared emulsions were evaluated via conventional profiling testing using a method based on the standard method according to ASTM (1997/2003) and adapted by ZHAW. The FIZZ Sensory Software 2.47B (Biosystemes) was used for sample coding and data collection. The panel of service experts trained in *leave-on* at the ZHAW assessed the attributes for pick-up, rub-out and after-feel phases such as density, spreadability or absorption. In addition, the protocol was supplemented to include specific gel attributes, which included body, quick break and long play. Body is perceived at the start of testing during shear application. It is limited by the quick break and marks the collapse of the internal gel structure from a creamy gel cushion into a more aqueous form. Long play is independent of body and can extend beyond the quick break point. Long play is observed as a perceptible gliding over the skin.

Triangle Testing

To assess whether substituting gellan gum for acrylate crosspolymer is perceived in the end product, a triangle test was conducted according to ISO 4120:2007 with a statistically required number of test runs to achieve the target significance level of 0.05. In a first test run, the reference emulsion (Acrylate 0.1-Emulsion) was compared with the Gellan 0.1-Emulsion. In a second run, the reference emulsion was compared with the Gellan 0.2-Emulsion.
The triangle test was also performed with laypeople, during which the reference emulsion (Acrylate 0.1-Emulsion) was compared with the Gellan 0.2-Emulsion. This was to establish whether untrained consumers would notice a reformulation.

Correlations between Physical and Sensory Data

All the raw data were processed using Excel Version 2013. The software XLStat Version 2019 was used to compare the data of the different investigation areas. The following applications were used: Tests for normal distribution, Pearson's correlation and linear regression. Analysing the correlation helps to identify potential links between two variables. Based on the regression analysis (linearisation), the dependency can be confirmed provided the R^2 value is close to value 1. In addition, the data distribution was reviewed for the confidence interval and only those models that achieved 95% were further considered.

Results and Discussion

The impact of the gellan proportion in emulsions is visible in the flow curves (**Fig. 1**). Increasing the gellan percentage increases the viscosity of the emulsions. The placebo emulsion has the lowest viscosity at the start as this contains no gel structure other than a xanthan gum component of 0.4%.

The increased viscosity of the Acrylate 0.1-Emulsion is striking. There is a positive correlation between the sensory attribute of density and the measured viscosity. Linearisation verified this link ($R^2 = 0.907$).

The means of the oscillatory measurements are presented in **Fig. 2**. Only at the flow point and plateau value are there significant differences between the emulsions. As expected, the placebo emulsion features the smallest storage modulus G'. This means that it contains the lowest elastic proportion, or the lowest gel structure. Acrylate 0.1-Emulsion and Gellan 0.2-Emulsion show the highest storage modulus values, which were also distinguished by higher body values.

At a lower proportion of gellan gum, the storage modulus G' values and consequently the body also decreases. This correlation can be evidenced by a linearisation between the storage modulus and body (rota) at $R^2 = 0.977$ and the body attribute (finger) $R^2 = 0.982$. The linear regression from measuring the storage modulus (x) can therefore be used to predict the body (y) of this emulsion according to the relationship $y = -39.83 + 11.83x$.

Comparing the measurements of the gellan emulsion with the acrylate emulsions shows that increasing gellan gum minimises the differences between the acrylate emulsion and the gellan emulsion. This means the higher the gellan content, the more similar the emulsions. However, this cannot be seen from the LVE region and plateau value results. For these values the deviation massively increases from 0.15% to 0.2% by

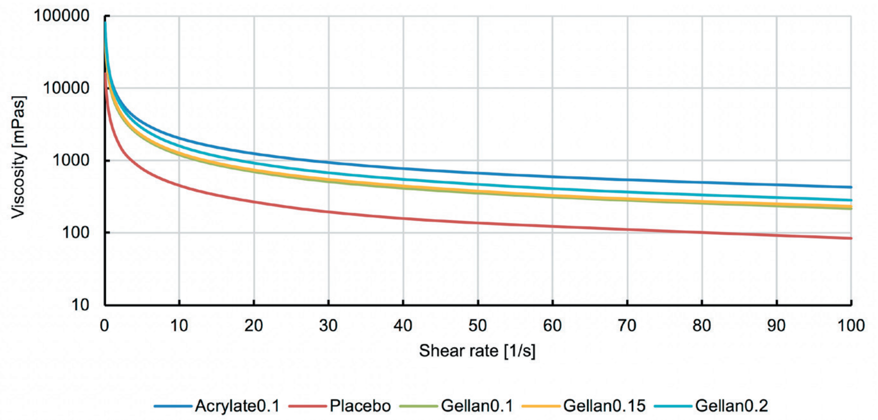


Fig. 1 Viscosity [mPas] and shear rate [1/s] of the emulsions (at 22°C, parallel-plate PP25). Rheometer: Anton Paar MCR 302.

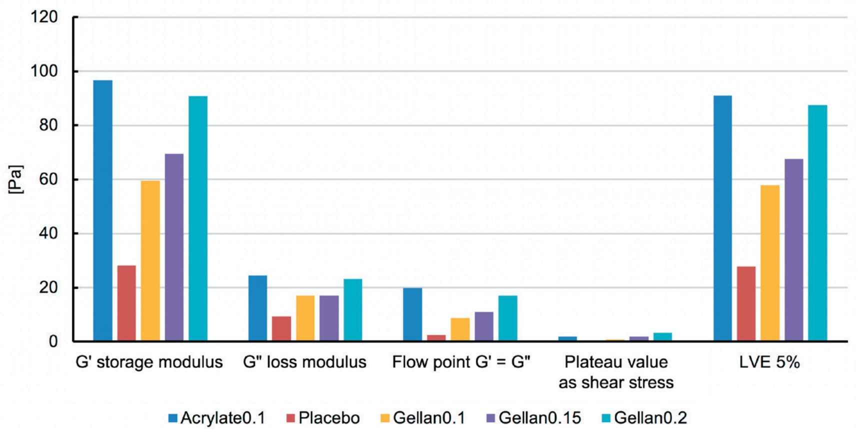
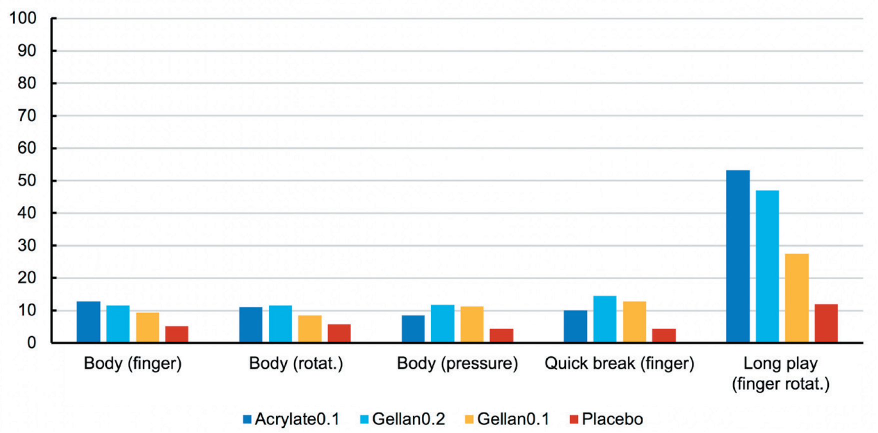


Fig. 2 Means of the oscillometric measurement (at 22°C, parallel-plate PP25). Rheometer: Anton Paar MCR 302.



Body (finger) = body perceived when rubbing between thumb and index finger.

Body (rotat.) = Number of rotations between thumb and index finger until a change in density.

Body (pressure) = assessment of the exertion required when rubbing a sample between thumb and index finger.

Quick break (finger) = Number of rotations between finger and thumb until the density/internal structure collapses.

Long play (finger rotat.) = Number of rotations until it is no longer possible to feel slip at constant motion between the thumb and index finger.

Fig. 3 Sensory evaluation of the attributes using the ZHAW manual "Gels", shown as means (arbitrary units).

increasing the gellan content. The quantity of gellan gum therefore needs to be carefully and specifically set as too high a dose could be detected from the sensory properties. This can be confirmed by the linearisation, which gave high correlations between the plateau value and body (rota) of $R^2 = 0.863$.

Fig. 3 shows how the emulsions differ significantly in their sensory properties, especially in the long play (finger rota) attribute. For instance, the expression of long play increases with increasing gellan gum content.

In this series of experiments it was also possible to establish a correlation of $R^2 = 1$ between long play and the physical measurement of flow point. For this type of formulation, a highly defined long play is associated with a high flow point.

The two emulsions Acrylate 0.1 and Gellan 0.1 were compared by means of triangle testing. At a significance level of 0.05, the trained expert panel could not identify any significant difference between the two emulsions. At 95% probability, the substitution of 0.1% acrylate crosspolymer with 0.1% gellan gum is not sensorially observed for this formulation.

The two emulsions Acrylate 0.1 and Gellan 0.2 were compared in a second experiment. In this case, a clear and significant difference was noted in the sensory properties between Acrylate 0.1 and Gellan 0.2 emulsions. Consequently, substitution of 0.1% acrylate crosspolymer by 0.2% gellan gum is detected by trained testers as a marked difference.

As already explained, it is striking that by increasing the gellan content, the plateau value rises rapidly. This, in turn, correlates strongly with the body attribute, which is described by a "creamy cushion" and also explains why substituting with 0.2% gellan gum is noted by the trained panel.

If differences are identified by a trained panel, this does not necessarily mean that consumers would notice sensory differences in a reformulated product. For this reason researchers also conducted triangle testing with consumers. In this case, only the Acrylate 0.1 and Gellan 0.2 emulsions were compared. The substitution of 0.2% gellan gum was not noted as a significant difference (0.05). It is therefore reasonable to speculate that consumers would not identify a reformulation of the formulations used at this concentration either.

Conclusion

It appears to be possible to substitute acrylate crosspolymer (0.1%) with gellan gum (0.1–0.2%) without major sensory impact. Substitution with 0.1% gellan gum was not identified by a trained panel. Substitution with 0.2% gellan gum was identified by a trained panel, however, not by an untrained panel. It can therefore be assumed that consumers will not notice a reformulation of the cream-gel formulation used in this study. The gellan gum must be specifically dosed as too high a concentration will be noticed, particularly by the change in body (creamy cushion).

On the basis of physical measurements it is possible to make informative statements on the selection of sensory expressions of hydrocolloids in emulsions. Specifically, the measurements of the storage modulus and plateau value in this project permit a statement to be made on the body. The flow point enables initial statements to be made on the expression of long play.

Acknowledgement:

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