J. Cosmet. Sci., 69, 67–75 (January/February 2018)

The Rheological and Skin Sensory Properties of Cosmetic Emulsions: Influence of Thickening Agents

YANAN LI, ZHAOQING ZHOU, XIAOMIN ZHAO, HUA ZHAO, and XIN QU, *ASI Shanghai Technical Centre, Ashland Inc., Shanghai 200233, China (Y.L., X.Z., X.Q.) and School of Science, Beijing Technology and Business University, Beijing 100048, China (Z.Z., H.Z.)*

Accepted for publication September 17, 2017.

Synopsis

Hydrophilic polymers are widely used in the cosmetics industry as thickening agents/rheology modifiers. These thickening agents have different chemical structures which affect the rheological properties, as well as the sensory attributes of the formula. Systematic study is important to determine the relationship among them. Six commonly used hydrophilic polymers, including cellulose derivatives and synthetic polymers, were used as thickening agents in a series of oil-in-water emulsions. The rheological properties were evaluated in relation to the thickening mechanism and polymer structures. Comprehensive skin sensory studies were carried out to test factors such as the pick-up, rub-in, and after-feel of these emulsions and the control sample. Results showed that all the samples demonstrated a non-Newtonian and shear-thinning behavior, and synthetic polymer-based formulas were more viscous than cellulose derivative-based ones. All eight attributes for the factors of appearance, pick-up, and rub-in showed statistically significant differences ($p \leq 0.05$), whereas all five attributes for the after-feel factor exhibited no statistically significant differences ($p > 0.05$) for different thickening agents. According to the results calculated using Pearson's correlation coefficients, four sensory attributes were mostly correlated with the rheological parameters.

INTRODUCTION

In recent years, the influence of specific raw materials on the rheological and sensorial properties of cosmetic formulas has become an important topic in the cosmetics industry. For example, Ozkan et al. (1) used steady flow and Large Amplitude Oscillatory Shear (LAOS) to characterize the yield stress and its correlation with sensory attributes. Lukic et al. (2) studied the effect of four emollients on the textural, sensorial, and *in vivo* skin performance of water-in-oil (w/o) hand creams. Tamburic et al. (3) investigated the application of thermo-rheology and textural analysis in the evaluation of w/o creams stabilized with a silicone emulsifier. Bekker et al. (4) studied mineral-based and wax-based cosmetic emulsions and jellies, relating their rheological measurement to their primary and secondary attributes when

Address all correspondence to Xin Qu at xqu@ashland.com.

applied to skin. Wang et al. (5) looked at the effect of the rheological properties of 12 moisturizing creams/lotions on their efficacy and attributes. Savary et al. (6) combined sensory and instrumental characterization to study the impact of emollients on the spreading properties of cosmetic products. The same authors (7) also conducted a large study on the impact of eight hydrophilic polymers on the textural properties of cosmetic emulsions. However, the aforementioned literature only evaluated limited sensory attributes, and few articles have correlated the skin sensory and rheological/mechanical properties of formulas with the chemical structure of raw materials.

Hydrophilic polymers are widely used in the cosmetics industry as thickening agents/rheology modifiers for gels, shampoos, emulsions, color cosmetics, etc. These thickening agents have completely different chemical structures, including natural and synthetic polymers, crosslinked and noncrosslinked polymers, homopolymers, copolymers, etc. The difference in polymer structure affects both the rheological properties and the sensory attributes of the formula. Systematic study is important to determine the relationship among them.

In this study, six commonly used hydrophilic polymers were used as thickening agents in a series of oil-in-water (o/w) emulsions. The rheological properties were evaluated and discussed in relation to the thickening mechanism and polymer structures. Comprehensive skin sensory studies were carried out, evaluating factors such as the appearance, pick-up, rub-in, and after-feel of these emulsions and the control sample. The results illuminated how, and to what extent, the polymer structure difference and rheological properties can affect the final skin sensory attributes of the emulsions.

EXPERIMENTAL SETUP

MATERIALS

Six commonly used rheological modifiers from Ashland were the object of this study. The International Nomenclature of Cosmetic Ingredients (INCI) names, codes, trade names, and chemical structures are illustrated in Table I.

Table I
INCI Names, Codes, Trade Names, and Chemical Structures of the Polymers Used

Code	INCI name	Trade name	Chemical structure
HEC	Hydroxyethyl Cellulose	Natrosol™ HEC 250 HHR	Graft, natural derivative, and nonionic
HPMC	Hydroxypropyl Methylcellulose	Benecel™ HPMCE10M	Graft, natural derivative, and nonionic
HMHEC	Cetyl Hydroxyethyl Cellulose	Natrosol Plus 330 HMHEC	Graft, natural derivative, long alkyl chains, and nonionic
PVP	Polyvinyl Pyrrolidone	FlexiThix™ polymer	Synthetic, crosslinked, and nonionic
PAA Na	Sodium Polyacrylate	RapiThix™ A-100 polymer	Synthetic, linear, anionic, and neutralized
PAA	Carbomer	Ashland™ 980 carbomer	Synthetic, crosslinked, anionic, and unneutralized

PREPARATION OF THE FORMULATIONS

Six emulsions containing the previously mentioned polymers were prepared. The emulsion formula is shown in Table II. To be consistent with practical use levels, the concentration for HEC, HMHEC, HPMC, and PAA Na was 1%; 5% for PVP; and 0.5% for PAA (adjusted to pH 6.5 with NaOH). One control sample containing no thickeners was also prepared for comparison.

RHEOLOGY

All rheological measurements were carried out with a MCR 101 (Anton Paar GmbH, Graz Austria) Rheometer, equipped with a cone plate (CP 50-1) at 25°C. A time of 5 min was set for all tests. Continuous flow tests were conducted at a shear rate range from 0.01 to 100 1/S. Amplitude sweeps scanned strain deformations from 0.1% to 100% at a constant frequency of 1 Hz for the emulsions.

SENSORY ANALYSIS

A panel of 10 college students (age 19–24) of both sexes was recruited from Beijing Technology and Business University. Sensory evaluation protocols based on well-accepted guidelines for the skin feel analysis of creams and lotions (ASTM, 2003) (8) were used to train the panelists. All of the sensory attributes evaluated in this study are shown in Table III. For each sensory attribute, four to five commercial products were used as standard reference points to define the scales (0–10) during the training.

STATISTICAL ANALYSIS

Several statistical analysis methods were applied using JMP 12.0.1 software (Cary, NC), with the confidence level set as 95%. For each sensory attribute, A one-way analysis of variance (ANOVA) of the Kruskal–Wallis tests was conducted to determine the overall differences among the seven emulsions, and the Tukey's honest significant difference (HSD) tests were conducted to compare the mean between each pair of the seven emulsions to categorize them.

Table II
Emulsion Formula Used in This Study

Trade name	INCI name	Supplier	% (w/w)
Distilled water	Water	Local	q.s. 100
Glycerin	Glycerin	Local	2
Hydrophilic polymers	Listed in the text	Ashland	0.5/1/5
GTCC	Caprylic (and) Capric Triglyceride	Local	4
Brij™ 72[a]	Steareth-2	Croda	2.55
Brij™ 721[a]	Steareth-21	Croda	1.65
Liquid Germall™ Plus preservative	Propylene glycol (and) diazolidinyl urea (and) iodopropynyl butylcarbamate	Ashland	0.5

[a]Trademark owned by a third party.

Table III
Sensory Attributes Evaluated in the Study

Factors	Sensory attributes	Definition
Appearance	Gloss	The degree of light reflected from the product
Pick-up	Firmness	Force required to fully compress the product between the forefinger and the back of the hand
	Ease of pick-up	The amount of product picked up by fingers
	Peak after pick-up	The degree to which products stands up after finger pick-up
Rub-in (after 15 circles)	Spreadability	The ease of spreading the product
	Hydration feel	The degree of hydration felt while rubbing in
	Oil feel	The degree of oiliness felt while rubbing in
	Absorbency[a]	Total circles used to disperse the samples until full absorbency is reached. Limit: 120 circles.
After-feel (after 5 m)	Gloss	The degree of gloss
	Slipperiness	The ease of sliding fingers across the skin
	Greasiness	The degree of feeling of greasiness/product residue
	Tackiness	The degree to which fingers adhere to residue product
	Moisture	The amount of moisture perceived when moving fingers across the skin

[a]Scales are defined by the equation: 10 − (total circles/12).

Principal component analysis (PCA) was used to analyze the relationships among samples, rheological parameters, and sensory attributes. Pearson's correlation coefficients (PCC) were calculated to analyze how the rheological properties influence the sensory attributes.

RESULTS AND DISCUSSION

THICKENING MECHANISM

As shown in Table I, three of the polymers, HEC, HPMC, and HMHEC are polysaccharides. They derive from a natural polymer—cellulose—and have the benefits of both natural and synthetic polymers. Celluloses are linear polymers consisting of (1-4) β-D-glucan with 1-4 glycosidic linkages. They can be substituted with hydroxyethyl and hydroxypropyl methyl to produce HEC and HPMC, respectively. HEC and HPMC thicken aqueous solutions mainly through H-bond interaction. HMHEC, which is hydrophobically-modified HEC, was also selected. Its thickening mechanism is through the combination of a hydrogen bond interaction (the same as traditional cellulosic derivatives) and a hydrophobic interaction of long alkyl chains. As synthetic polymers, slightly crosslinked PVPs thicken aqueous solutions mainly through interlinks among polymer chains and steric interactions. While PAA and PAA Na are polyacrylates with anionic groups, they thicken the systems mainly through electrostatic interactions—the polymer chain becomes uncoiled due to the rejections among the same electric charge groups.

RHEOLOGICAL PROPERTIES

The flow curves of six emulsions and the control sample are shown in Figure 1. All of the samples showed a non-Newtonian and shear-thinning behavior, with the viscosity

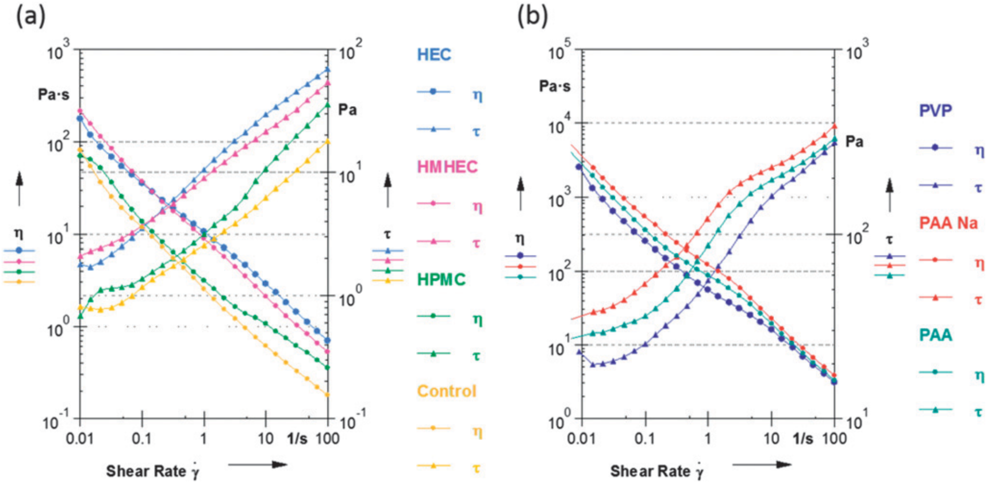

Figure 1. Flow curves of the six emulsions and the control sample.

depending strongly on the shear rate. Synthetic polymer-based formulas were more viscous than cellulose derivative-based ones. Under shaking, samples containing HEC, HPMC, and HMHEC could flow freely, whereas samples with PVP, PAA, and PAA Na could not flow.

Cellulose derivatives are linear polymers with modified side chains. The hydrogen bond interaction leads to a weak structure, which is subject to the influence of other ingredients in the formula. Conversely, synthetic polymers have a strong three-dimensional network, which is less subject to the influence of other ingredients in the formula. PAA and PAA Na polymers also have a strong anionic charge for electrostatic interactions for better thickening efficacy. In addition, the viscosity of the HMHEC sample increased significantly compared with the HMHEC aqueous solution. This is due to its unique thickening mechanism, a combination of the H bond and the synergetic thickening effect of long alkyl chains (9).

The amplitude sweep curves of these emulsions were also studied (figures not shown) and the typical rheological parameters are summarized in Table IV. Yield stress was obtained from the amplitude sweep curves as shear stress at the crossover point (10). The data

Table IV

Summary of the Typical Rheological Parameters of Seven Emulsions

Sample	Viscosity at 0.1 s^{-1} (Pa·S)	Viscosity at 1 s^{-1} (Pa·S)	Viscosity at 10 s^{-1} (Pa·S)	Viscosity at 100 s^{-1} (Pa·S)	G′ (Pa)	G″ (Pa)	Damping factor (1)	Shear stress at crossover point (Pa)
Control	11.6	2.6	0.6	0.2	21.3	9.2	0.4	2.7
HEC	34.9	10.5	2.9	0.7	47.4	33.3	0.7	13.1
HMHEC	36.8	8.9	2.1	0.5	47.3	29.6	0.6	8.4
HPMC	13.8	3.2	0.9	0.3	62.7	35.9	0.6	6.0
PVP	254.0	56.2	15.9	3.1	1,010.0	141.0	0.1	46.5
PAA Na	539.0	122.0	22.9	3.9	1,730.0	206.0	0.1	79.6
PAA	361.0	87.2	19.5	3.3	838.0	105.0	0.1	68.8

indicate that all the rheological parameters of synthetic polymers have much higher values than cellulose derivatives, except the damping factor. The difference in rheological properties definitely has an impact on the skin sensory attributes of the emulsions. For example, synthetic polymer-based emulsions have a richer skin feel than their cellulose-derived counter parts, whereas the latter are easier to spread into skin. Lower viscosity and yield stress indicate that the emulsion system has less resistance to flow, once the yield stress has been exceeded.

SENSORY ANALYSIS

Ten college students (age 19–24) of both sexes were recruited from Beijing Technology and Business University to participate in an evaluation of the sensory attributes of seven emulsions. The selection of the panellists was based on their interest, willingness, background, experience in using cosmetic products, and their ability to describe and rate the selected sensorial attributes. The panellists were systematically trained on the sensory evaluation protocols. For each sensory attribute, four to five commercial products were used as standard reference points to define the scales (0–10) used during the training. The panel's sensory evaluation results for the seven emulsions are shown in Table V. For each sensory attribute, a one-way ANOVA of the Kruskal–Wallist tests was conducted to determine the overall significant difference among the seven emulsions. The results are listed in the far-right column of Table V. The Tukey's HSD tests were used to compare the mean between each pair of the seven emulsions; the results are shown as letters A–C. The same letter in one row indicates that the corresponding emulsions are not significantly different for the attribute considered ($p \leq 0.05$).

The results showed that thickening agents play an important role in the sensory properties of the final formulas. All eight attributes for the factors of appearance, pick-up, and rub-in exhibited statistically significant differences ($p \leq 0.05$), whereas all five attributes of the after-feel factors showed no statistically significant differences ($p > 0.05$). As shown

Table V
Sensory Evaluation Results of Seven Emulsions[a]

Factors	Sensory attributes	Control	HEC	HMHEC	HPMC	PVP	PAA Na	PAA	Significance
Appearance	Gloss	6.8 ab	7.0 a	7.1 a	6.7 ab	4.7 c	5.9 b	6.4 ab	<0.0001
Pick-up	Ease of pick-up	4.3 b	4.5 b	4.3 b	3.8 b	6.2 a	5.8 a	4.3 b	<0.0001
	Peak after pick-up	2.6 c	3.6 b	3.4 bc	3.1 bc	5.5 a	5.1 a	4.6 a	<0.0001
	Firmness	2.0 c	3.3 b	3.1 bc	2.6 bc	6.6 a	6.1 a	5.6 a	<0.0001
Rub-in	Spreadability	6.7 a	5.5 ab	5.8 ab	5.8 ab	4.9 b	4.8 b	5.0 b	0.02
	Hydration feel	6.9 a	5.4 ab	5.5 ab	6.3 ab	4.8 b	4.9 b	5.5 ab	0.01
	Oil feel	4.2 ab	4.4 ab	4.1 b	4.3 ab	6.0 a	5.3 ab	4.4 ab	0.02
	Absorbency	5.9 a	6.1 a	7.2 a	6.6 a	7.5 a	7.8 a	7.4 a	0.03
After-feel	Tackiness	2.9 a	3.3 a	3.2 a	3.3 a	4.7 a	3.7 a	3.8 a	0.26
	Gloss (after-feel)	3.4 a	3.5 a	3.5 a	3.5 a	4.8 a	4.3 a	3.8 a	0.32
	Slipperiness	5.4 a	6.2 a	6.1 a	6.1 a	6.2 a	6.1 a	5.7 a	0.89
	Greasiness	3.3 a	2.8 a	3.3 a	3.5 a	3.8 a	4.0 a	3.4 a	0.62
	Moisture	4.5 a	4.6 a	4.8 a	4.4 a	5.1 a	4.6 a	4.7 a	0.26

[a]The same letter (a, b, c) in one row indicates that the corresponding emulsions are not significantly different for the attribute considered ($p \leq 0.05$).

in Table V, firmness was influenced most by thickening agents for all sensory attributes. The samples with cellulose derivatives had less firmness than the samples with synthetic polymers. This finding correlates well with the rheology results. Ease of pick-up and peak after pick-up were also highly influenced by the nature of the polymers, as the formulas with cellulose derivatives received lower scores due to lower viscosity. These samples flow easily, so a smaller quantity of these products could be picked up by fingers, and the peaks after pick-up were lower.

On the other hand, the formulas with cellulose derivatives scored higher than synthetic polymers for spreadability because of the lower viscosity and yield stress. It is well known that PAA-type thickening agents lead to a breakdown in contact with existing electrolytes on skin, which reduces the spreading force of a formulation. However, this breakdown is not as significant as the effect of their high viscosity and yield stress, which aligns with our spreadability prediction. The formulas with cellulose derivatives showed higher original gloss than the synthetic polymers ($p \leq 0.05$), which is also reported by Savary (7). Notably, the scores for gloss (after-feel) on skin tended to be higher for the synthetic polymers than for the cellulose derivatives, although no statistically significant difference was found.

Compared with synthetic polymers, cellulose derivatives tended to have more hydration, less oil feel, and slower absorbency. This could be explained by the nature of cellulose, which has more hydrophilic groups (hydroxyl groups) in its structure. These hydroxyl groups help the formula to retain water and give a greater hydration feel during the rub-in phase. However, this also leads to a lower absorbency of the formula because the absorbency is closely related to the moisture evaporation during the rub-in phase. In addition, of the synthetic polymers tested in this study, PAA has a relatively better gloss and hydration feel, which may be because of its chemical structure and process technology (Table V).

There were no statistically significant differences ($p > 0.05$) among the seven emulsions for the after-feel factor (tackiness, gloss, slipperiness, greasiness, and moisture). Similar results were reported by Wang et al. (5), who found that the efficacy of moisturizing was not necessarily linked to the hydrophilic polymers used in the formula.

PCA ANALYSIS

To illustrate the relationships among the eight rheological and 13 sensorial parameters, as well as the differences among the seven emulsions, PCA was conducted based on all the variables in Tables IV and V. As shown in Figure 2B, the first two principal components account for 86.3% of the total variance (component 1 = 75% and component 2 = 11.3%). Except for the damping factor, the positions of all the rheological parameters are close, which means they are related to one another. Regarding the sensorial attributes, absorbency, firmness, and peak after pick-up are closely related to the rheological parameters in the positive side of the Component 1 axis (PC1), whereas spreadability is closely related to the rheological parameters in the negative side of PC1. Based on the PCA results, the seven emulsions studied can be divided into two groups—cellulose-derivative & control and synthetic polymers(Figure 2A). The cellulose-derivative & control-based emulsions are on the negative axis of Component 1, and tend to have lower firmness, G', G'', yield stress and viscosity, more original gloss before use and less gloss on the skin after use, easier spread as lotions, more hydration feel and less oil feel during rub-in, and lower

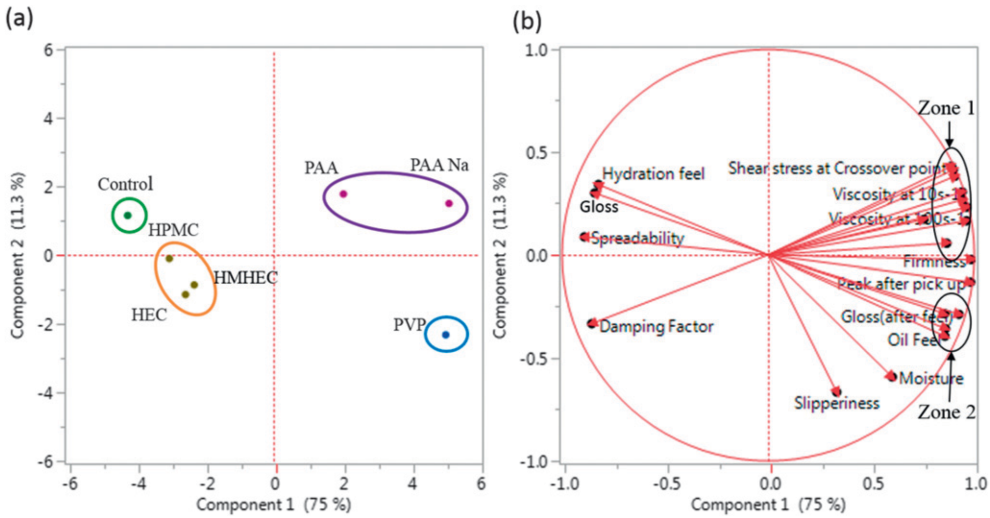

Figure 2. PCA results based on the rheology and sensory parameters. (Zone 1 from top to bottom: viscosity at 1 s^{-1}; viscosity at 0.1 s^{-1}; shear stress at crossover point; viscosity at 10 s^{-1}; G'; viscosity at 100 s^{-1}; greasiness; G''; absorbency. Zone 2 from top to bottom: gloss (after-feel); ease of pick-up; oil feel; and tackiness.)

absorbency. On the other hand, synthetic polymer-based emulsions are on the positive axis of Component 1, with the opposite rheological and sensorial properties from cellulose-derivative and control-based emulsions. Cellulose derivatives are closer to each other than to the control sample, with greater firmness, absorbency and slipperiness, and less spreadability; whereas PVP was distinct from the PAA and PAA Na group, with more moisture and oil feel in the synthetic polymer group.

PCC ANALYSIS

PCC were calculated to analyze how seven rheological parameters (except the damping factor) influenced 13 sensory attributes. Among them, four sensory attributes were mostly correlated with the rheological parameters studied; the PCC results are listed in Table VI. Firmness was most significantly correlated with the rheological parameters, with a significance of ≤0.01 and PCC of 0.87–0.97, followed by Absorbency and Peak after pick-up, with a significance of ≤0.03 and PCC of 0.80–0.84 and 0.83–0.93, respectively. The PCC of spreadability has a negative number, −0.80 to −0.87, which means the samples with higher viscosity have lower spreadability. The results showed that emulsions with high rheological parameters, such as viscosity and yield stress, tend to have higher firmness, peak after pick up, absorbency, and lower spreadability. But for the parameters of the after-feel factor such as tackiness or moisture, no significant PCC were shown. The PCC analysis suggests that a rheology test is more suitable for predicting primary skin feel parameters rather than after-feel parameters.

CONCLUSION

The purpose of this study was to illuminate how and to what extent polymer structure differences and rheological properties can affect the final skin sensory attributes of different