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Water Resistance vs. Rheology Control: An Exploration

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Key words: emulsions, water resistance, rheological profile, texture analysis, film-forming polymers

Abstract

Water resistance is a desirable property across a range of cosmetic product categories, including decorative cosmetics, leave-on hair products, sun protection and skin care (e.g. hand barrier creams). This work has focused on two formulation variables, the type of emulsifier system and the choice of film-forming polymer, both known to change the rheological profiles of semisolid systems. The aim of this study was to assess the effects of these two factors on the rheological and texture profiles, as well as the water resistance characteristics, of semisolid O/W emulsions.

A simple O/W emulsion formulation, containing glycerol, mineral oil, water, preservative and emulsifier system was used in this study. The basic emulsifier system consisted of two non-ionic emulsifiers (sorbitan stearate and polysorbate 60) in combination with a co-emulsifier cetearyl alcohol. The alternative emulsifier system had an anionic emulsifier sodium cetearyl sulphate added to the above emulsifier mixture.

A range of seven film-forming polymers were used in the study, representing acrylates, silicones, graft copolymers and block copolymers. Two groups of 8 emulsion samples, containing either basic or alternative emulsifier system and including a non-polymer control, were tested. Rheological measurements were carried out in both continuous flow and oscillatory mode and were complemented with texture analysis, performed using a spreadability test. In the absence of universally accepted *in vitro* water resistance test, a gravimetric method for measuring water resistance was developed and applied to all test samples.

The results have shown a variety of rheological profiles, which were both emulsifier- and polymer-dependent. The addition of sodium cetearyl sulphate have resulted in softer (lower complex modulus) and more spreadable formulations (lower firmness), which coincided with lower water resistance scores. The block copolymer polyurethane-62 (and) trideceth-6 has produced specific rheological profiles, characterised by high internal resistance and high elasticity. The graft copolymer vinyl pyrrolidone/ eicosene was the best performer in terms of water resistance, showing the lowest weight change of 11.1% after the first 20-min immersion in water and 12.9% after the second immersion. The non-ionic emulsifier mixture based on sorbitan stearate and polysorbate 60 has provided superior performance in comparison to its combination with the ionic emulsifier sodium cetearyl sulphate.

Introduction

Water resistance is not only required for most sun protection products but is also a desirable property across other product categories, including decorative cosmetics, leave-on hair products and skin care (e.g. hand barrier creams). It could be achieved using one or more of the following formulation approaches: high concentration of non-polar emollients, specific combinations of waxes and resins, latex-based water-dispersible polymers, specific combinations of emulsifiers, as well as oil- and water-soluble film-forming polymers. This work has focused on two formulation variables, the type of emulsifier system and the choice of film-forming polymer, both known to change the rheological profiles of semisolid systems in addition to influencing their water resistance.

Currently, there is no globally accepted *in vitro* water resistance method in any cosmetic category. According to Cosmetic Europe [1], an *in vivo* water resistance test is under development. Table 1 shows a variety of water resistance testing standards that exist across the world. The unifying factor for all tests is the maximum water resistance time of 80 minutes.

Table 1. A review of standards used across the world regarding water resistance

Region	Standard
ASEAN (Brunei Darussalam, Cambodia, Indonesia, Laos, Malaysia, Myanmar, Philippines, Singapore, Thailand, Vietnam) ^a	ISO 24444:2010
Australia and New Zealand ^b	AS/NZS 2604:2012
Canada ^c	Colipa 2006 or FDA 2011 or ISO 24444:2010
China ^d	ISO 24444:2010
European Union ^e	Colipa 2006
Japan ^f	ISO 24444:2010
Korea ^g	ISO 24444:2010
South Africa ^h	Colipa 2006
Taiwan ⁱ	ISO 24444:2010
USA ^j	FDA 2011
^a (ASEAN, 2015); ^b (Therapeutic Goods Administration, 2016); ^c (Health Canada, 2013); ^d (China Food and Drug Administration, 2013); ^e (European Commission, 2006); ^f (Ministry of Health and Welfare, 2000); ^g (Ministry of Food and Drug Safety, 2016); ^h (SABS Standard Division, 2014); ⁱ (Taiwan Food and Drug Administration, 2016); ^j (FDA, 2011)	

The International Organisation for Standardisation (ISO) has set up a technical committee to develop the ISO/TC 217/WG 7 test methods for sun protection products, including an *in vitro* water resistance method [2]. While this work is still in progress, the list of parameters proposed to be controlled during the test is available (Table 2).

Table 2. Parameters and requirements proposed by ISO for *in vitro* water resistance testing

Parameter	Requirement
Flow rate	0.02 - 0.5 m/s
Water temperature	28 – 32 °C
Water conductivity	800 – 1000 µS/cm
Water pH	6.5 - 7.5
Bromine/Chlorine for sanitisation	To be controlled, if used
Reference Sunscreen	One selected so far

Polymers of various chemical classes and with variety of structures have been used to impart the water resistance property to cosmetic products, for example acrylates, silicones, latex-based, graft and block copolymers. Most of them are multifunctional, acting as film formers and rheological additives, therefore necessitating the need to assess their multiple effects on the product.

This study has focused on two formulation variables of the water-resistant products: the type of film forming polymer and the type of emulsifier system. One of the study aims was to evaluate the effects of these variables on the rheological and texture profiles of O/W emulsions. In addition, the study aimed to develop a water resistance method and use it to assess the effects of both variables on the test emulsions.

Materials and Methods

Materials

A range of seven film-forming polymers, belonging to four chemical groups, have been used, as follows: acrylates copolymer, acrylates/C12-22 alkylmethacrylate copolymer, trimethylsiloxysilicate, phenyl trimethicone, stearyl dimethicone, vinyl pyrrolidone/eicosene copolymer and polyurethane-62 (and) trideceth-6. The acronyms used in further text, alongside their chemical category, are presented in Table 3.

Table 3. Film-forming polymers used in the study

INCI name	Acronym	Category
Acrylates copolymer	AC	Acrylates
Acrylates/C12-22 Alkylmethacrylate copolymer	AM	Acrylates
Trimethylsiloxysilicate	TMS	Silicones
Phenyl trimethicone	PTM	Silicones
Stearyl dimethicone	SD	Silicones
Vinyl pyrrolidone/eicosene copolymer	VPE	Graft copolymer
Polyurethane-62 (and) trideceth-6	PT	Block copolymer

The samples in each group consisted of one base formulation without added polymer (control) and seven test formulations, each containing one of the polymers tested. The concentration of each polymer in the emulsion was 1%w/w, which was suggested in the literature as sufficient to exert water resistance. The second group of samples mirrored the first, except that each contained an additional emulsifier, sodium cetearyl sulphate. All samples from the second group were labelled with a + sign (e.g. AC+).

Table 4. Formulations of test emulsions: basic and alternative (with additional ionic emulsifier)

INCI Name	Basic formulation % (w/w)	Alternative formulation % (w/w)
Paraffinum Liquidum	15.0	15.0
Glycerine	3.0	3.0
Firm-forming polymer	1.0	1.0
Sorbitan Stearate	3.5	3.5
Polysorbate 60	1.5	1.5
Sodium Cetearyl Sulphate	-	2.5
Cetearyl Alcohol	5.0	5.0
Methylparaben	0.4	0.4
Propylparaben	0.2	0.2
Aqua	Up to 100.0	Up to 100.0

Methods

Preparation of emulsions

A standard hot emulsification process at 80°C was used in the preparation of all test emulsions. If additional emulsifier was used, it was added to the oil phase at the beginning of the process. The polymers were dispersed in the water phase before emulsification.

Rheological tests

Rheological measurements were carried out on the RheoStress RS75 rheometer (Haake, Germany), using a 35-mm serrated parallel plate and the gap of 1.0 mm. Dynamic (oscillatory) and continuous flow tests were used in conjunction to produce complete rheological profiles of the test samples [3]. The oscillatory stress sweep was conducted by increasing the stress from 1 to 200 Pa at the frequency of 1 Hz. The maximum oscillatory stress of 200 Pa was used in most cases, but it was increased if required by a high sample rigidity. A reduction in the complex modulus of 10% was used as the measure of yield stress, i.e. the point at which the sample yields and starts flowing [4].

Two types of continuous flow tests were used: shear rate sweep and three-step thixotropy test. In the shear rate sweep, the samples were sheared from 250 s⁻¹ to 10 s⁻¹ for 300 sec. The use of reverse order of shear rates (from high to low) has been shown to produce less 'noisy' and more repeatable data [5]. The three-step thixotropy test consisted of three phases, carried out at the shear rate of 10, 250 and 10 s⁻¹ respectively, each step taking 60 seconds [5]. The results were expressed as % recovery, i.e. the difference in the original viscosity, measured at the first step, and the one measured at the third step.

Texture analysis

Texture analysis was performed on the TA.XT Plus instrument (Stable Micro Systems, UK), using a standard spreadability method. The spreadability fixture consisted of a female and male 45° perspex cone probes, whereby the female probe was filled with the sample and the male immersed into the sample at the predetermined speed and distance (Fig. 1). The positive (immersion) and negative (de-immersion) curves, based on three replicas, were produced and analysed by the Texture Exponent software. The parameters measured were firmness (the highest force, measured in g) and work of shear (area under the curve, in g.s) from the positive curve, and stickiness (g) and work of adhesion (g.s) from the negative curve [6].

Water resistance test

In the absence of universally accepted *in vitro* water resistance test (WRT), a gravimetric method for measuring water resistance was developed and applied to all test samples. The method is presented in the stepwise manner in Table 5. Each emulsion was evenly spread (drawn down) on a clean and weighted artificial skin substrate (Fig. 2), dried in the oven, immersed in water twice for 20 min, with drying and weighting after each immersion..

Table 5. In-house *in vitro* water resistance method (WRM). All measurements were performed on a three-decimal place analytical balance

Step 1	Clean substrate under warm running water with 2 g 23% SLES and allow to air dry
Step 2	Weigh substrate
Step 3	Attach substrate to an impression bed, apply 2 ±0.5g of sample onto the top edge of the substrate in a rough line
Step 4	Using a 300 µm open wound draw down bar, spread down firmly and consistently the sample to the free bottom edge to create an even film
Step 5	Measure the size of the film in terms of width and length
Step 6	Weigh substrate
Step 7	Put onto the middle shelf of a 35 °C oven for 15 minutes
Step 8	Remove from oven and weigh substrate
Step 9	1 st immersion: Immerse the substrate, bottom edge first, into 500 ml of distilled still water at the RT (22 °C) for 20 minutes
Step 10	Remove from water, top edge first, and hold vertically for 5 seconds to allow excess water to run off
Step 11	Leave to sit horizontally for 1 minute at RT
Step 12	Put onto the middle shelf of a 35°C oven for 20 minutes
Step 13	Remove from oven, allow to cool and weigh substrate
Step 14	2 nd immersion: repeat steps 9-12
Step 15	Remove from oven, allow to cool and weigh substrate



Figure 1. Spreadability test

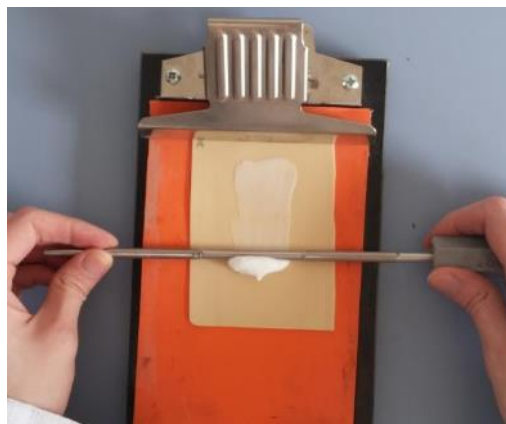


Figure 2. Example of a draw-down of the sample on the artificial skin substrate, in preparation for the water resistance test (WRT)

Because of the slightly different film dimensions and weights of polymer films, the comparisons were made on the basis of the 'percentage change' calculated between the initial dry sample weight and the dry sample weight after the 1st and 2nd immersion.

Statistical analysis

Statistical analyses were conducted using software SPSS Statistics (IBM, USA). The tests used were Paired Sample *t*-Test and One-way Repeated Measures Analysis of Variance (One-way RM ANOVA). Paired Sample *t*-Tests were conducted on all emulsion samples, comparing their weight after application on the substrate and drying (WAD) with the weight after the 1st water immersion and drying, as well as WAD and the weight after the 2nd water immersion and drying. This analysis was performed on both basic and alternative formulations. A One-way RM ANOVA was used to compare the change in weight over time for all formulations. The probability threshold was set at 0.05.

Results and Discussion

The results of different rheological tests are summarised in Table 6. Since all samples have shown a shear thinning behaviour, the viscosity values at both low and high shear rate were presented. It is apparent that the addition of ionic emulsifier (samples marked with +) has caused a decrease in viscosity, except in the case of block copolymer polyurethane-62 (and) trideceth-6 (PT). The rigidity of all samples, expressed as the complex modulus G^* , has decreased in all cases, although for the sample with PT much less than for the others. The % recovery after high shear did not follow the same pattern, in some cases being markedly better (e.g. AC+ and PT+), in most cases similar, but for stearyl dimethicone (SD) it was considerably lower (from 96% to 39%) after the addition of ionic emulsifier.

The yield stress has decreased in the case of the alternative control formulation and most of the polymers (Table 6), while two polymers have increased it (AC and particularly PT). A higher yield value indicates a better internal structuring which could withstand a higher shear force before it starts flowing [7]. The phase angle, also known as lag phase, indicates how much is the movement of the sample 'lagging behind' the applied oscillatory stress. It is used as a measure of material's elasticity [8], where the lower angle means the more elastic sample. The results in Table 6 show that the control and all polymer-containing samples, except PT, have similar level of elasticity, irrespective of the addition of ionic emulsifier. The elasticity values, as well as the whole rheological profile, of the emulsion samples with a block-copolymer PT are different from the rest of the range. This points out at the specific chemical structure of the polymer, causing stronger internal interactions with water and the components of the emulsion system.

Table 6. Rheological characterisation of the test samples, including flow (viscosity and yield stress), thixotropy (% recovery) and oscillatory parameters (complex modulus - rigidity and phase angle –elasticity)

Sample	Viscosity at 10s ⁻¹ (mPa.s)	Viscosity at 250s ⁻¹ (mPa.s)	% viscosity recovered in 3-step test	Yield stress (Pa)	Complex modulus (Pa)	Phase angle (degree)
Control	7.1	0.7	41.8	65.55	3100	20.9
Control+	1.9	0.3	52.9	12.30	600	19.9
AC	7.4	1.0	58.4	16.26	3100	22.8
AC+	4.9	0.7	70.3	21.49	1000	19.7
AM	4.0	0.9	66.0	37.53	2900	19.8
AM+	3.8	0.5	71.1	16.26	850	19.9
TMS	8.6	0.9	55.2	16.26	10900	17.8
TMS+	1.5	0.2	47.1	9.31	340	16.8
PTM	8.6	0.7	31.7	37.53	4200	20.7
PTM+	1.4	0.3	42.0	16.26	600	19.9
SD	3.6	1.2	96.0	49.60	3800	20.4
SD+	1.3	0.3	38.9	9.31	520	20.3
VPE	8.3	1.0	76.6	86.64	8700	18.1
VPE+	4.3	0.6	54.2	21.49	1700	18.9
PT	2.3	0.7	20.8	233.60	8200	12.2
PT+	8.4	1.7	48.9	336.00	7600	11.2

The viscoelasticity plot (showing rigidity vs. elasticity) presents a useful tool for the visual analysis of viscoelastic data. Fig. 3 shows the viscoelastic coordinates of all 16 test emulsions, whereby the alternative formulations are represented by full circles.

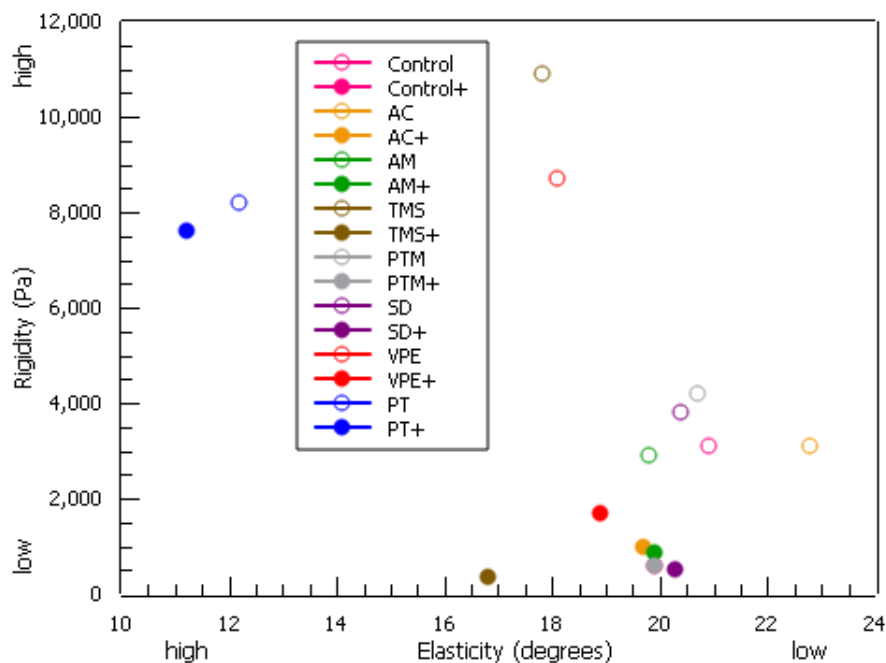


Figure 3. Viscoelasticity plot of all test emulsions. The control+ sample occupies the same position as the TMS+, resulting in it being 'hidden' behind the TMS+.

The viscoelastic plot brings about the same conclusions, i.e. that the samples with PT are different from others, and that the addition of ionic emulsifier reduces the rigidity of all samples, but it also allows for simultaneous observations of multiple relationships amongst the samples.

The graphs on Fig. 4 represent some typical curves obtained from the oscillatory shear stress tests for the pairs of emulsions (basic and alternative formulation) with different polymers. The samples with additional emulsifier are shown as black lines in all cases. The first Y axes shows the complex modulus (rigidity), which tends to be a flat line while the sample is in the linear viscoelastic region. The line curves downwards when the structure of the system starts yielding [4], which is used to calculate the yield stress presented in Table 6. The examples show the same pattern of behaviour for the control and the samples with VPE and SD (lower yield stress in the presence of ionic emulsifier), while the structure of both samples with PT looks distinctly different.

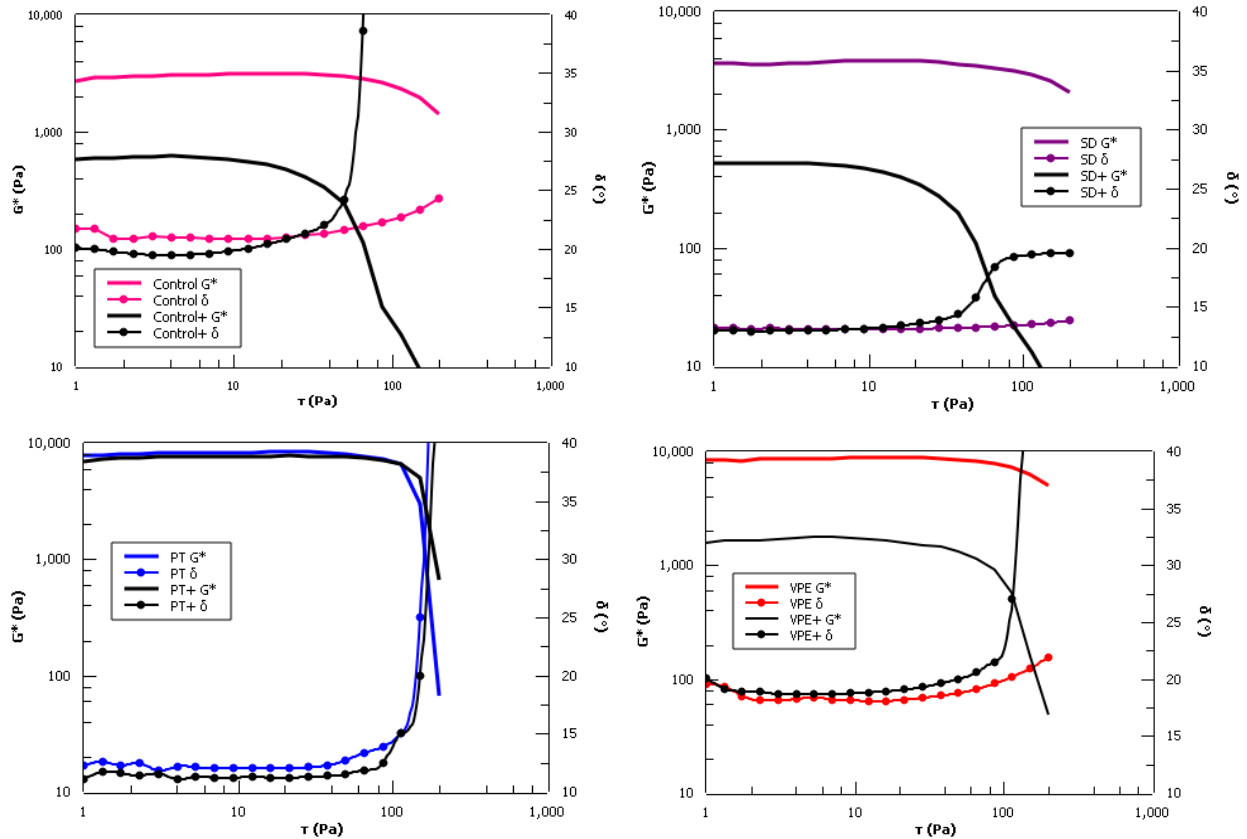


Figure 4. Examples of oscillatory stress sweep curves, showing rigidity (G^*) and phase angle (δ) as a function of shear stress

Two examples of diagrams obtained from the three-step thixotropy tests are shown in Fig. 5. They visually present the extent of an instant thixotropic recovery (as the height of the viscosity curve in the third step as opposed to the first), expressed in numerical terms in Table 6. In addition, the curves are useful in assessing other aspects of rheological behaviour, for example the extent of shear-thinning (as the slope of viscosity curves) and the overall difference in structure between the sample pairs.

One of the reasons for introducing the ionic emulsifier sodium cetearyl sulphate, beside an increased emulsion stability, was to improve product sensory properties. The difference in the homogeneity of internal structure (smoothness) is clearly illustrated in the three-step thixotropy graphs. Comparing the smoothness of viscosity curves obtained at constant low shear (10 s^{-1}), it is apparent that the addition of ionic emulsifier has made a desired effect of stabilising the lamellar structure formed by the non-ionic emulsifier pair and a co-emulsifier cetearyl alcohol [9]. However, in most cases it has also weakened the product's response to external forces (Table 6).

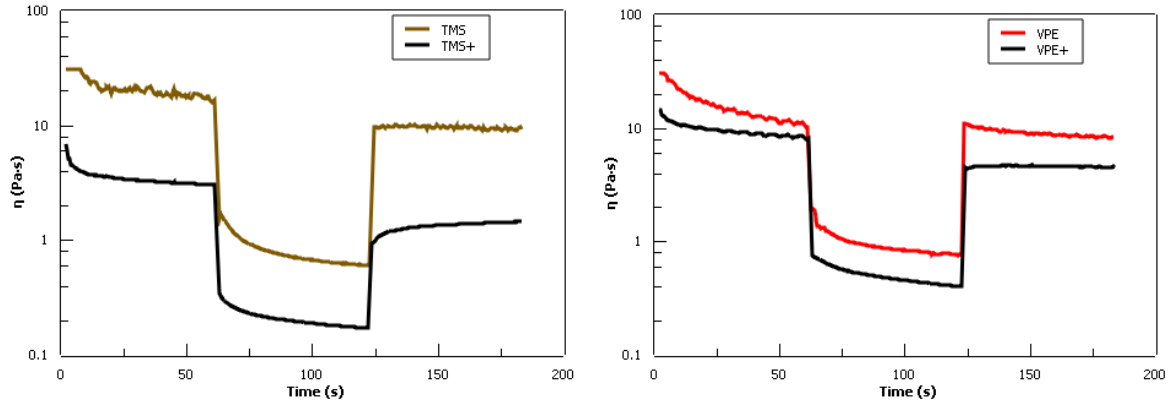


Figure 5. Examples of three-step thixotropy curves, showing the TMS and VPE emulsion pairs

The continuous flow tests have resulted in the viscosity curves, the selection of which is shown in Fig.6. It is interesting to note that the viscosity curves of the samples with PT, although different from others, are not exceptional. Hence, it would be possible to miss the distinct difference in their structure in comparison to other samples should they be analysed only from the point of view of their viscosities. The oscillatory stress curves (Fig. 4) and the viscoelastic plot (Fig.3), in addition to viscosity curves (Fig. 6) allow a complete rheological profile to be considered when characterising semisolid samples. This full picture could make a crucial difference in understanding the product performance and customer sensory experience.

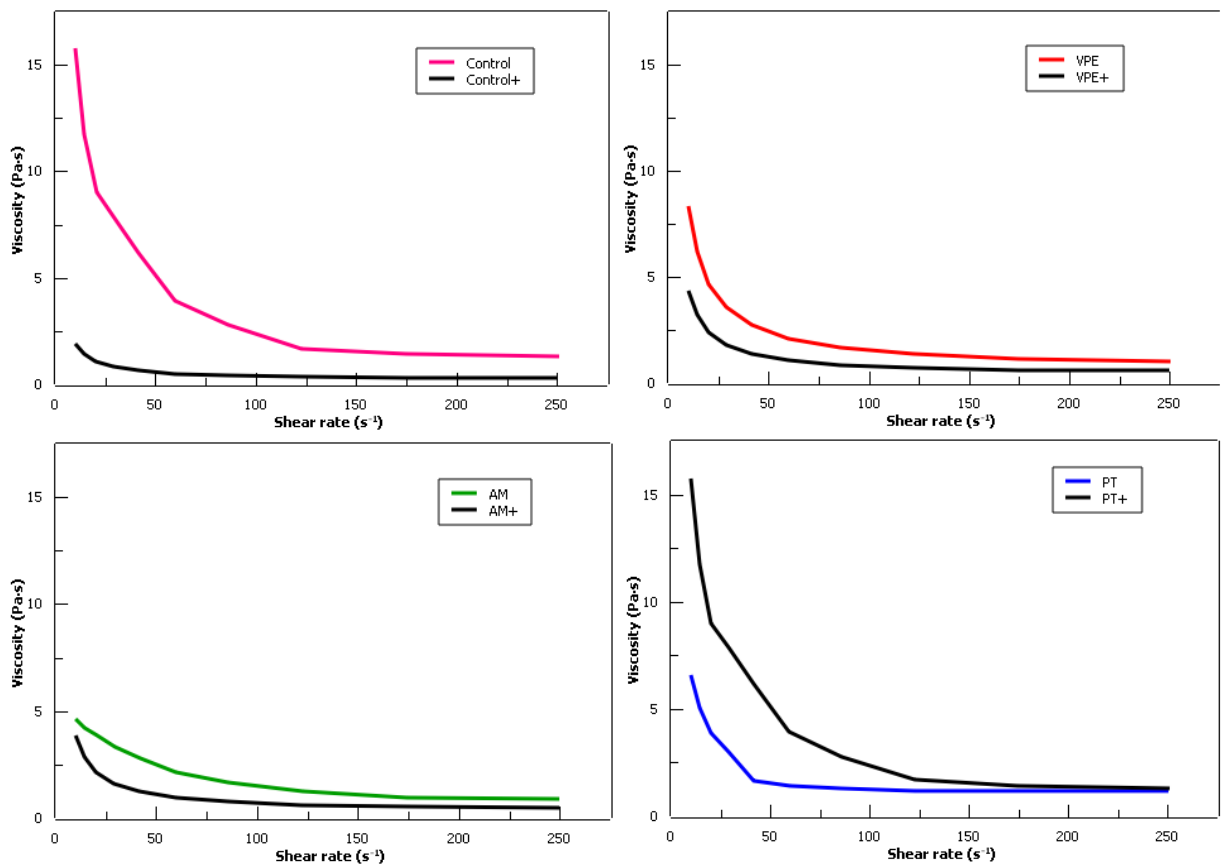


Figure 6. Examples of viscosity curves, showing the control, VPE, AM and PT emulsion pairs

Two examples of spreadability curves obtained from the texture analyser are shown in Fig. 7. It has been shown previously that there is a good correlation between some texture and rheology parameters of semisolids [10]. In line with those findings, both samples have shown lower values for both force parameters (firmness and stickiness) and area parameters (work of shear and work of adhesion) after the

introduction of ionic emulsifier. It is clear that the anionic nature of this material has a profound effect on the lamellar phases of the original o/w emulsion, causing the weakening of its internal three-dimensional structure. This effect is magnified in the presence of all test polymers, except PT, in the presence of which the viscosity and elasticity increase, but rigidity stays almost the same (Figs. 3, 4 and 6).

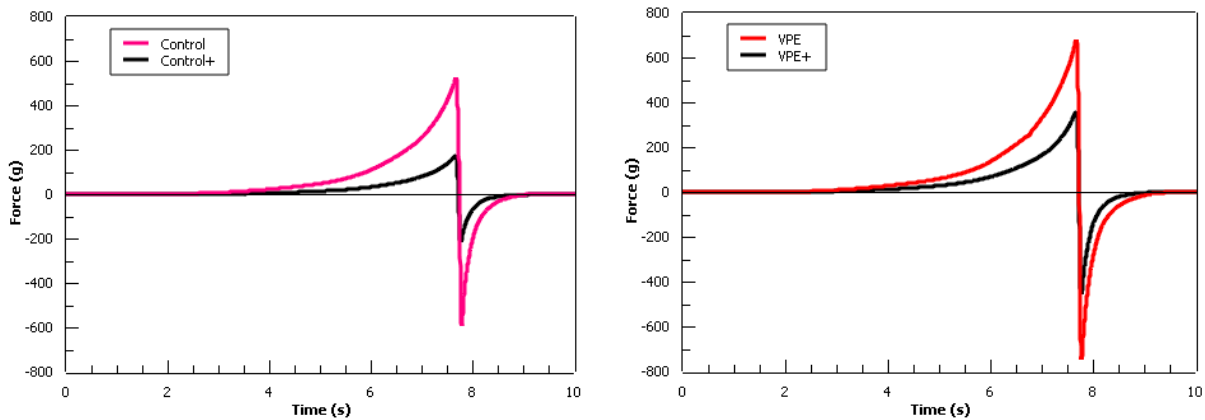


Figure 7. Examples of texture analyser curves, showing the control and VPE emulsion pairs

With distinct differences in the structure of basic and alternative emulsions detected with rheology and texture analysis, it was of interest to assess whether and to which extent those differences affect water resistance property of the test samples. In addition, it was important to detect any variations in the water resistant efficacy between seven polymers used in this study.

Based on the literature sources [11,12] and existing test protocols, an in-house method for the water resistance test (WRM) of skin products was developed (Table 5) and carried out. It has become apparent during the testing that all emulsions with the ionic emulsifier have performed worse than their counterparts, some not going through the 2nd immersion due to a large loss of material after the 1st immersion. This confirms the assumption that ionic emulsifiers contribute to large water absorption, hence should be avoided in the formulation of water resistant cosmetic products.

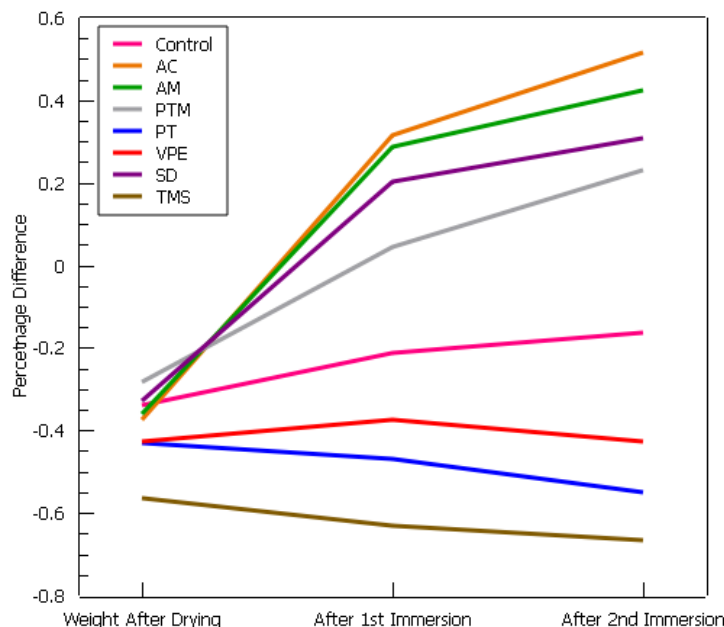


Figure 8. Differences in weight (in %) obtained during the water resistance test for the basic emulsion (control) and the basic emulsion with different polymers (n=3)

One important observation during the testing was that the drying time of 20 minutes at 35 °C was not sufficient to completely remove the absorbed water from all samples, resulting in the increase in their weight after the immersion/drying cycle.

The summary of the WRM results for the samples with different polymers in the basic emulsion is shown in Fig. 8. The % difference in weight was negative after the initial drying for all the samples, as expected. However, after the 1st immersion the samples with polymers AC, AM, SD and PTM have shown an increase in weight, indicating a considerable absorption of water within the structure. The changes were statistically significant ($p < 0.05$) for all four polymers, continuing to be significant between the 1st and 2nd immersion (One-way RM ANOVA, followed by Paired t Test). The control sample has performed in the same way, but with a smaller effect size. This finding indicates that the absorbed water was sufficiently strongly bonded to the components of the emulsion, most probably within the lamellar by-layers, to resist evaporation during a 20-minute drying at increased temperature. In addition, the absorbed water was in some cases masking the loss of product from the surface of the artificial skin, making the product performance appear better than it was.

Contrary to the above, the samples with polymers PT and TMS have revealed a net loss of their weight, which was significant in both cases. Only the sample with VPE has not shown a significant change in weight all the way through the test (i.e. between the original dry state and the 1st and 2nd immersion, respectively, as well as between the two immersions). Its average weight change was 11.1% after the first immersion in water and 12.9% after the second immersion. This means that the graft polymer vinyl pyrrolidone/ eicosene copolymer was the best performer in the WRM analysis.

Conclusions

The results of this study have demonstrated that the addition of anionic emulsifier sodium cetearyl sulphate to a non-ionic emulsion has an effect of decreasing the strength of internal emulsion structure, making it less viscous, less rigid and with a lower yield stress.

The addition of a polymer has changed the rheology and texture of all emulsion samples, but to a different degree and with different effects. In most cases, the polymer has increased rigidity and decreased yield stress, although the changes in different parameters should be analysed separately for each polymer. The exception of the general trend was block copolymer polyurethane-62 (and) trideceth-6, which has increased all the above mentioned parameters, and doubled emulsion elasticity.

The results of the tests using in-house water resistance method have shown that excessive water absorption was the problem for half of the polymer tested, with the loss of material during the 1st and 2nd 20-minute immersion being the problem for most. The best performer was the sample with the graft polymer vinyl pyrrolidone/ eicosene copolymer, which did not show a significant change in weight during the test. Therefore, it is recommended for use in the formulation of skin products with water resistant properties.

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