# Assessing the effects of formulation variables on the water resistance, rheological and texture properties of O/W emulsions

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## Introduction

Water resistance is a desirable property across a range of cosmetic product categories. This work has focused on two formulation variables important for water resistance, 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.

## Materials and Methods

A simple O/W emulsion formulation (Table 1) was used in this study. The basic emulsifier system consisted of two non-ionic emulsifiers 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, from different polymer categories, were used (Table 2). Two groups of 8 emulsion samples, containing either basic or alternative emulsifier system (samples with + sign) and a non-polymer control, were tested.

**Table 1** Basic formulation (control)

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

**Table 2** 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 |

Rheological measurements were carried out on the RheoStress RS75 Rheometer (Haake, Germany, Fig.1a), using a 35-mm serrated parallel plate and the gap of 1 mm in both continuous flow and oscillatory mode. They were complemented by texture analysis, performed using a spreadability test (Fig. 1b). 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.

Briefly, each emulsion was evenly spread (drawn down) on a clean and weighted artificial skin substrate (Fig. 1c), dried in the oven, immersed in water twice for 20 min, with drying and weighting after each immersion. 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.



**Fig. 1 P**arallel plate rheological method (a), spreadability test (b) and preparation for the water resistance test (c)

## Results and Discussion

Fig. 2 presents typical curves obtained from the oscillatory shear stress tests, with rigidity (complex modulus G*) and elasticity (phase angle δ) as dependent variables. Each graph shows a corresponding emulsion pair, with + samples in black.

The control and the samples with VPE and SD have shown the same pattern of behaviour (lower rigidity and yield stress in the presence of ionic emulsifier), while the structure of the samples with PT was distinctly different, with little change imparted by ionic emulsifier.
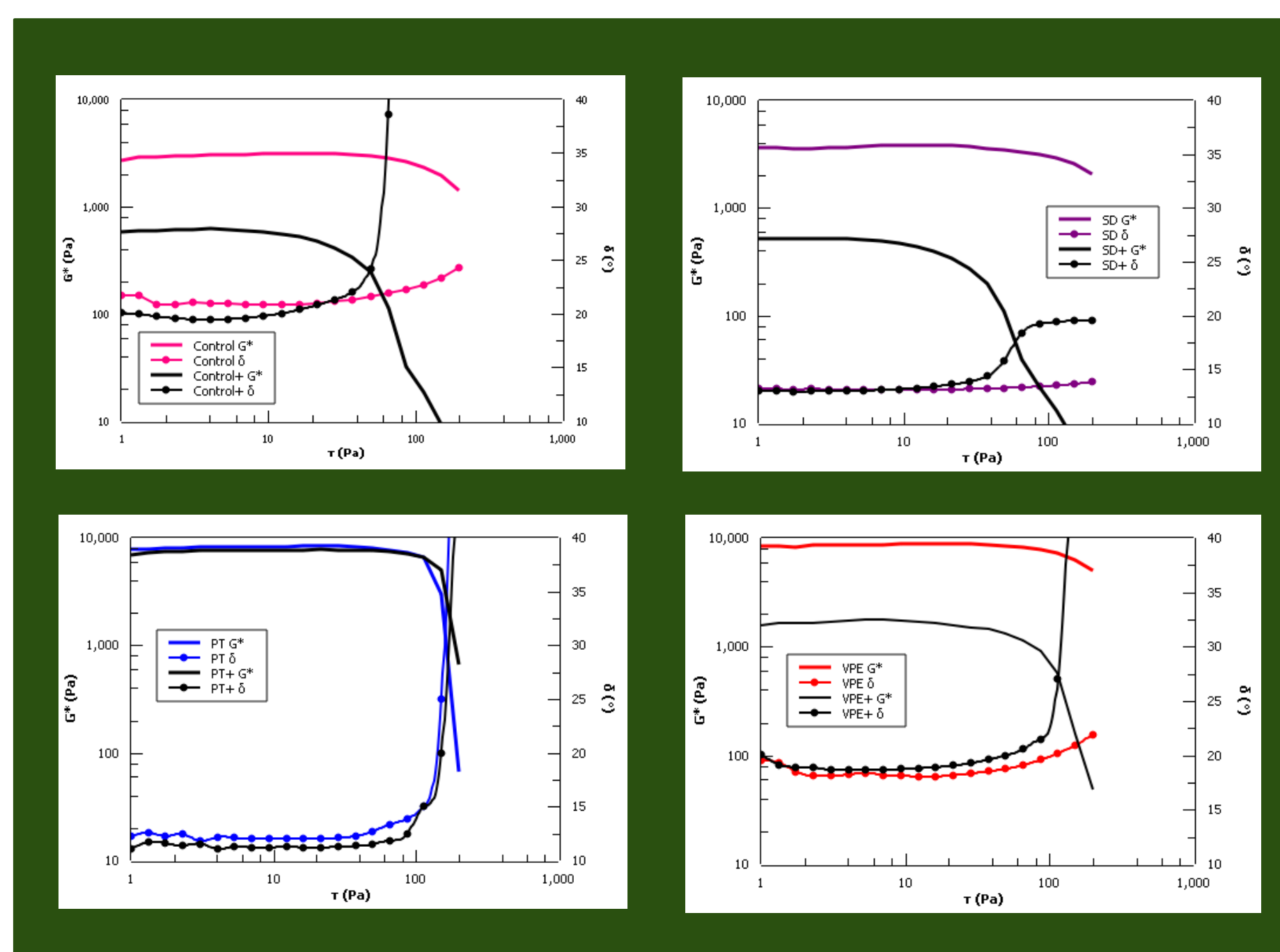


**Fig.2** Examples of oscillatory stress sweep curves, showing rigidity (G*) and phase angle (δ) as a function of shear stress

Typical examples of viscosity curves are shown in Fig.3. Interestingly, the curves obtained for the samples with PT, although different from others, are not exceptional. Hence, it is necessary to use a combination of oscillatory stress curves (Fig. 2), the viscoelasticity plot (Fig.4) and viscosity curves (Fig. 3) in order to obtain a complete rheological profile of semisolid samples.
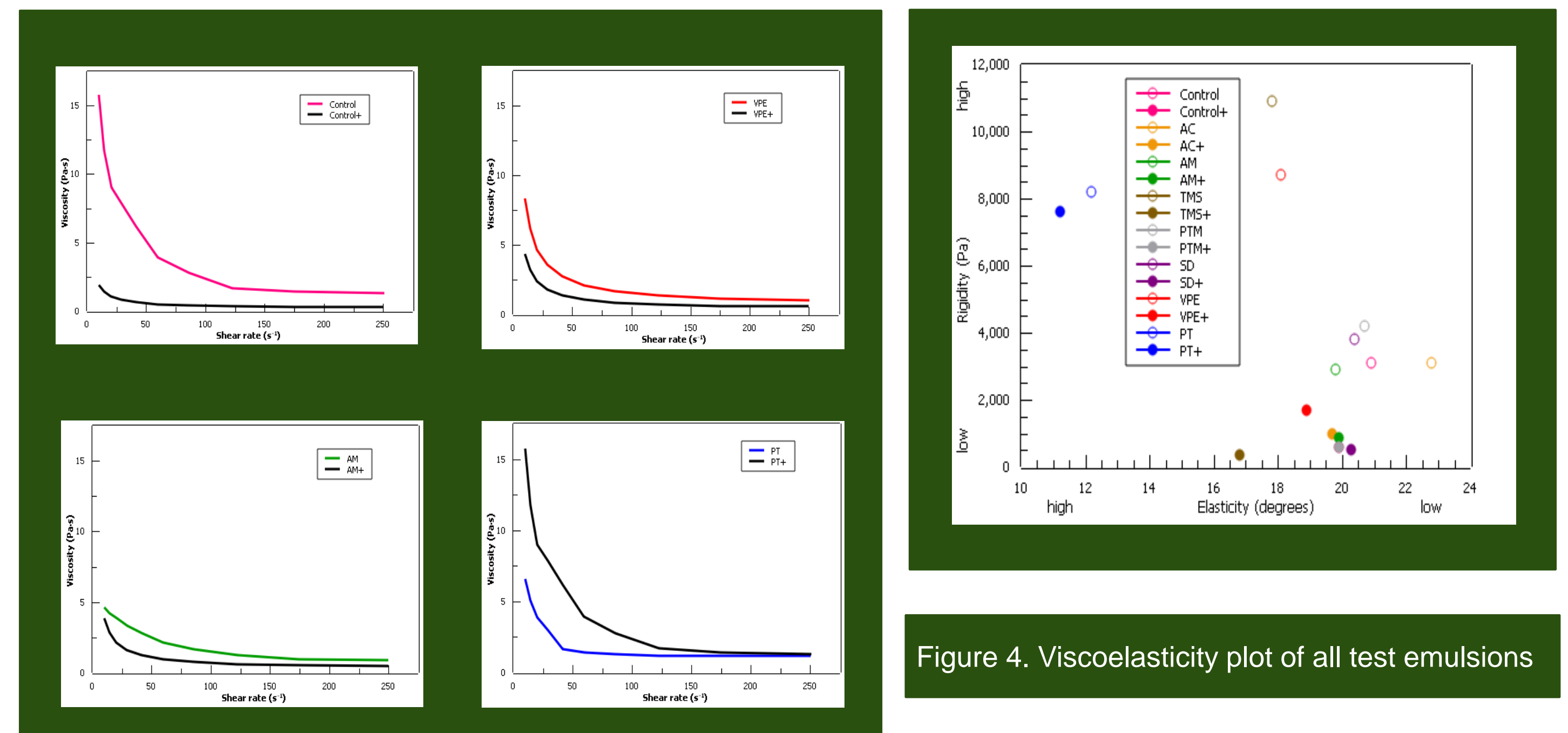


Figure 3. Examples of viscosity curves, showing the control, VPE, AM and PT emulsion pairs



Figure 4. Viscoelasticity plot of all test emulsions

The diagram obtained from the three-step thixotropy test of the VPE sample is shown in Fig. 5 (left). It shows the extent of instant thixotropic recovery (as the height of the viscosity curve in the third step as opposed to the first), which was lower for the + sample (54.2%) than for the basic sample (76.6%).

After introduction of ionic emulsifier, the texture parameters have decreased (Fig. 5, right), indicating that it had a profound effect on the lamellar phases of the original o/w emulsion, causing the weakening of its internal structure. This effect was magnified in the presence of all test polymers, except PT.
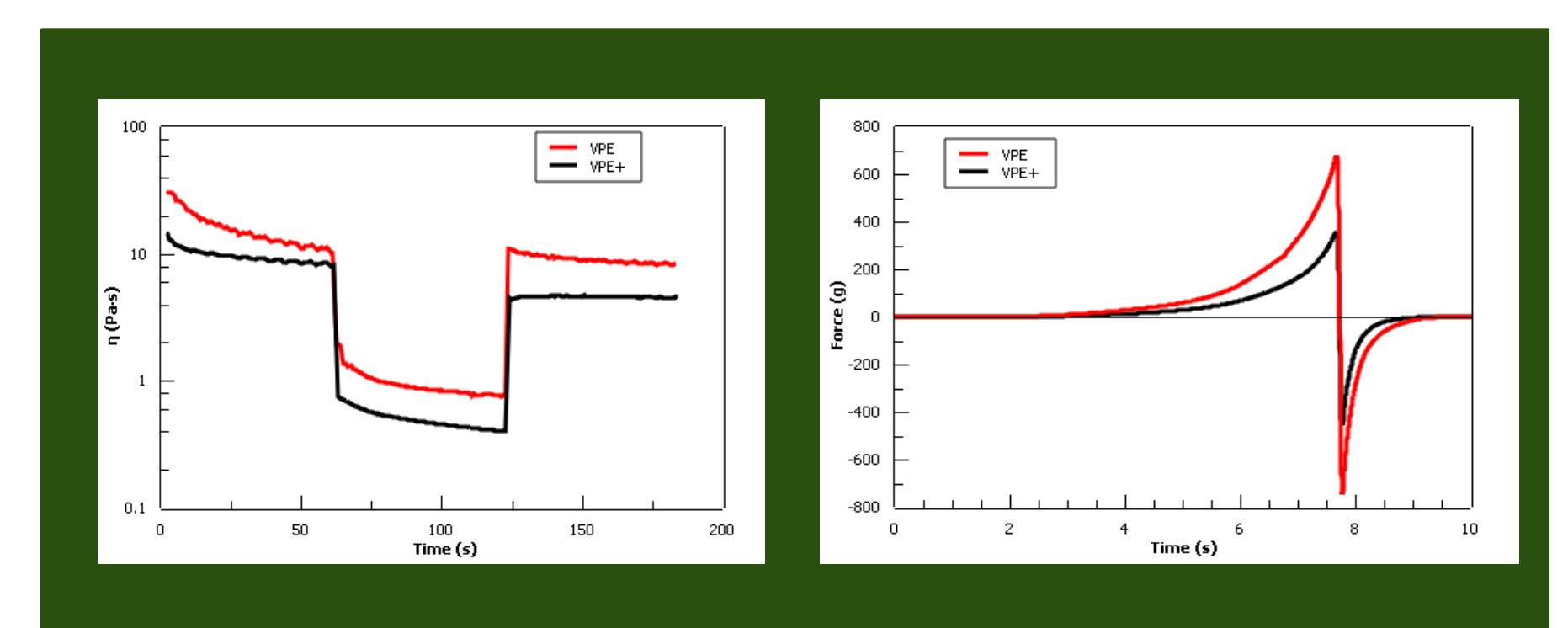


Figure 5. Three-step thixotropy curves (left) and spreadability curves (right) of VPE emulsion pairs

After the 1st immersion the samples with polymers AC, AM, SD and PTM have shown an increase in weight, indicating a significant absorption of water within the structure (Fig. 6). The control sample has performed in the same way, but with a smaller effect .



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 during the test, with average weight change of 11.1% after the first immersion and 12.9% after the second immersion. This means that the graft polymer VPE was the best performer in the water resistance study.
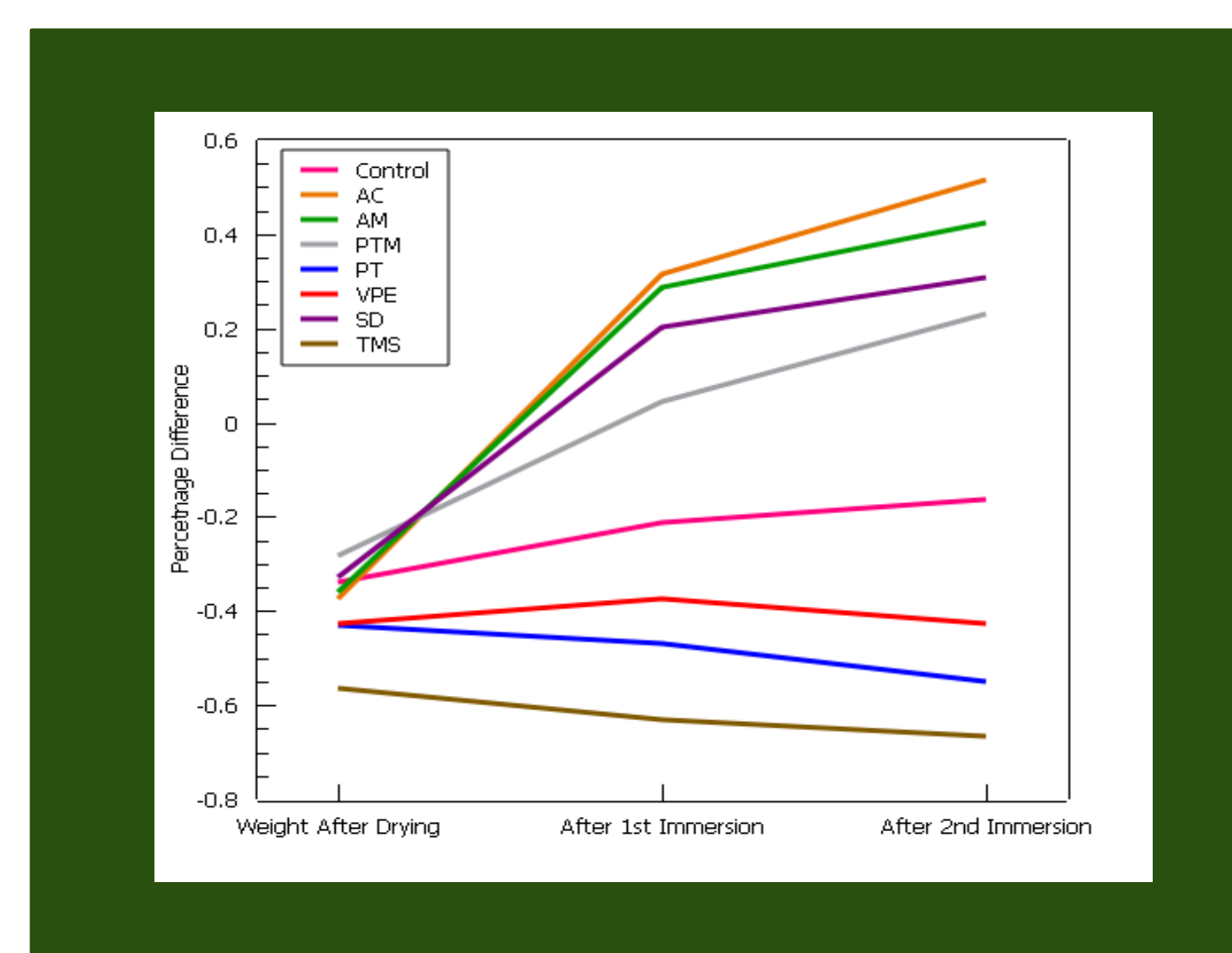
Figure 6. Differences in weight (in %) obtained during the water resistance test for the basic emulsion (control) and the basic emulsion with different polymers (n=3)

## Conclusion

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 polymer has changed the rheology and texture of all emulsion samples, but to a different degree and with different effects. The exception was block copolymer polyurethane-62 (and) trideceth-6, which has significantly increased all rheological parameters.

The best performer in the water resistance test 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.

## Acknowledgements

**References:**
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