

Rheological and Texture Analysis Methods for the Assessment of Viscoelasticity

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abstract

The purpose of this study was to compare the dynamic (oscillatory) rheological method with a novel texture analysis (TA) method for the assessment of viscoelastic properties of cosmetic semisolids.

The instruments used in this study were an air-bearing controlled-stress rheometer (RheoStress RS75, Haake, Germany) and a texture analyser (TA.XT Plus, Stable Micro Systems, UK). The model formulation was a standard semisolid emulsion, containing increasing concentrations of carbomer and xanthan gum, respectively. The rheological methods used were stress sweep (0.5–500 Pa at 1 Hz) and frequency sweep (0.01–10 Hz at 10 Pa). The texture analysis method used was an immersion/de-immersion test with cylindrical probe.

The results were analysed for their consistency with theoretical predictions and the presence any correlations between the methods. The analysis revealed consistent trends related to two novel TA parameters, stringiness (which decreased with the increase in thickener concentration) and resilience (which has shown a mild increasing trend). Elastic modulus G' and viscous modulus G'' (both at 1 Hz) were positively correlated to resilience and negatively correlated to stringiness, indicating that those TA parameters reflect the viscoelastic status of the sample.

Introduction

All semisolid cosmetic products belong to the group of viscoelastic materials, having both liquid-like (viscous) and solid-like (elastic) characteristics [1]. It is of practical, as well as theoretical interest, to determine the position of a particular product on the viscoelastic scale. Dynamic (oscillatory) rheology is a standard method used to assess viscoelasticity, whereby an oscillating shear stress is applied to the sample and the resulting strain measured as its response [2]. There are two principal approaches used in oscillatory rheology: a) stress sweep (an increase in the oscillatory stress under the constant frequency) and b) frequency sweep (an increase in the frequency of oscillation under the constant stress, which is low enough to keep the sample within its viscoelastic range).

Viscoelastic behaviour is a complex phenomenon, commonly measured by placing a sample between two parallel plates. The bottom plate is stationary, while the top one oscillates in the clockwise/anticlockwise manner at a given frequency, applying a certain level of shear stress, which causes a certain level of deformation (strain) within a sample (Fig. 1a). A range of rheological parameters is being used to describe the level of material's viscoelasticity. The most frequently used are: elastic modulus G' (the measure of energy stored and recovered), viscous modulus G'' (the measure of energy lost as flow), phase angle δ (how much the resulting deformation

lags behind the applied stress) and complex modulus G^* (the measure of sample rigidity).

In addition to rheological methods, texture analysis presents a useful approach to assess many aspects of semisolid behaviour. The immersion/de-immersion (penetration) test using a cylindrical probe, represented in Fig. 1b, is one of the most commonly used due to its versatility [3]. It consists of the immersion of the probe into the sample using a pre-determined speed and depth, and the withdrawal (de-immersion) of the

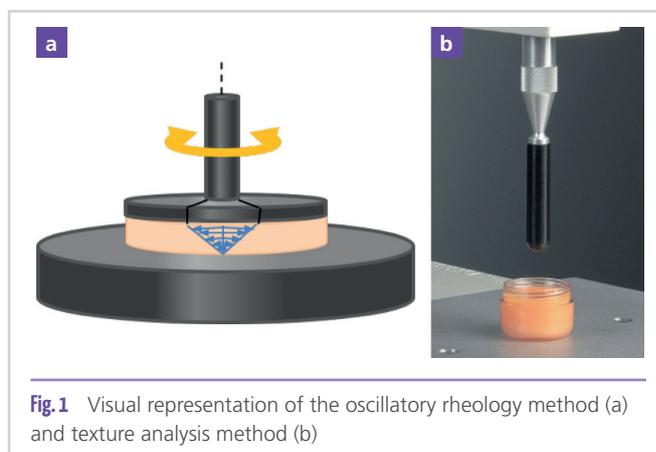


Fig. 1 Visual representation of the oscillatory rheology method (a) and texture analysis method (b)

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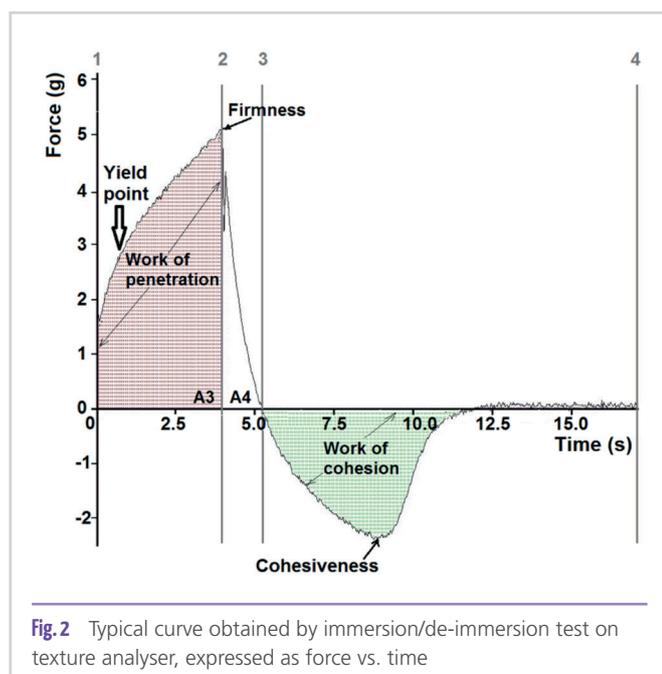


Fig. 2 Typical curve obtained by immersion/de-immersion test on texture analyser, expressed as force vs. time

probe. A typical response of a semisolid sample, shown in **Fig. 2**, consists of the positive and negative curve, with the following standard parameters: firmness (maximum on the positive curve), consistency (area under the positive curve), cohesiveness (maximum on the negative curve) and work of cohesion (area under the negative curve) [3].

It has been indicated by *Tai et al.* [4] that TA could be successfully employed to quantify certain rheological properties, as well as some aspects of sample viscoelasticity. Indeed, our recent study [5] has revealed that the results obtained from the TA penetration test can also be used to identify the yield value (an inflection on the positive curve, **Fig. 2**) and to measure the level of thixotropy (the difference in TA parameters between the initial and repeated probe immersions). The current study was concerned with assessing the two novel TA parameters [4]: stringiness (the distance at which the sample ruptures when the probe rises over the surface) and resilience (the ratio between two areas that make the positive curve, A3 and A4) and to compare them with well-established parameters obtained using oscillatory rheology.

Materials and Methods

Taking the same approach as in the previous study [5], a simple o/w emulsion (**Tab. 1**) was used as a model formulation. Two series of samples, each containing a different rheological modifier, were used: with neutralised carbomer (0.1 %, 0.2 %, 0.3 %, 0.4 % and 0.5 % w/w) and with xanthan gum (1.5 %, 2.0 %, 2.5 %, 3.0 % and 3.5 % w/w).

The instruments used in this study were an air-bearing controlled-stress rheometer (RheoStress RS75, Haake, Germany) and a texture analyser (TA.XT Plus, Stable Micro Systems, UK). Rheological measurements were carried out using a 35-mm serrated parallel plate, with the gap of 0.5 mm. The methods used were stress sweep (0.5–500 Pa at 1 Hz) and frequency sweep (0.01–10 Hz at 10 Pa).

The texture analysis method used in this study was the immersion/de-immersion test, with a one-inch diameter cylindrical probe made of perspex. The pre-test speed was 1 mm/s, both test and post-test speed 2 mm/s, the immersion distance 8 mm and the trigger force 1 g. All measurements were carried out in triplicate, at a constant temperature of 22°C.

Results and Discussion

Oscillatory (dynamic) rheological testing involves the application of a sinusoidally-oscillating (i.e. clockwise/counterclockwise) shear stress to a sample and the subsequent measurement of the shear strain. Either shear stress or oscillating frequency can be varied and the resulting viscoelastic response of the sample observed. If the shear stress is kept constant and frequency changes, the test is known as a frequency sweep. Conversely, if the frequency stays fixed and the stress changes, the test is known as the oscillatory stress sweep (to distinguish it from the flow stress sweep used in continuous flow rheology). Dynamic tests are performed at very low shear stresses, normally below the yield point, allowing an insight into the internal structure of a semisolid without destroying it [6]. They could distinguish between elastic and viscous rheological properties of the material (e.g. elastic and viscous modulus, respectively), and could provide a range of complex parameters that explain the viscoelastic balance within the sample (e.g. phase angle, complex modulus).

Phase	INCI name	Concentration %w/w
A	Glyceryl Stearate, Ceteareth-20, Ceteareth-12, Cetearyl Alcohol and Cetyl Palmitate	4.0
	Butyrospermum Parkii	4.0
	Ethyl Hexyl Palmitate	20.0
	Propylparaben	0.2
B	Glycerol	3.0
	Methylparaben	0.2
	Carbomer	0.1–0.5
	Xanthan Gum	1.5–3.5
	Triethanolamine	q.s. up to pH 6.0
	Aqua	up to 100.0

Tab. 1 The formulation of the semisolid w/o emulsion used in the study

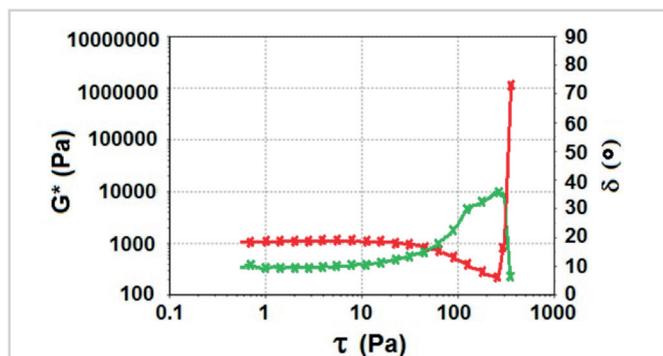


Fig. 3 Oscillatory stress sweep results for 0.1% carbomer, showing a decrease in the complex modulus (G^* – red line) and an increase in the phase angle (δ - green line) at stress levels above 20 Pa

Since most oscillatory rheology is performed below the yield value [7], it was important to detect the limits of the “viscoelastic range” for each sample, i.e. the stress levels at which its internal structure stays intact. Oscillatory stress sweep tests from 0.5 to 500 Pa at the constant frequency of 1 Hz were carried out on all samples. A typical example, shown in **Fig. 3**, presents the response of the emulsion with 0.1% carbomer.

From the graph in **Fig. 3** it could be seen that the values of both complex modulus G^* and phase angle δ are constant in the lower stress region, but that both start changing when shear stress reaches a certain level, i.e. enters the yield region. Complex modulus, the measure of sample rigidity, starts to decrease, while phase angle or lag phase starts to increase. Since phase angle ranges between 0 and 90° (or an ideal elastic solid and ideal viscous liquid, respectively), its increase indicates the change towards more dominant viscous component [6].

On the basis of these tests, the shear stress of 10 Pa was shown to be below the yield value in all test samples, hence it was selected as the constant stress in all frequency sweep

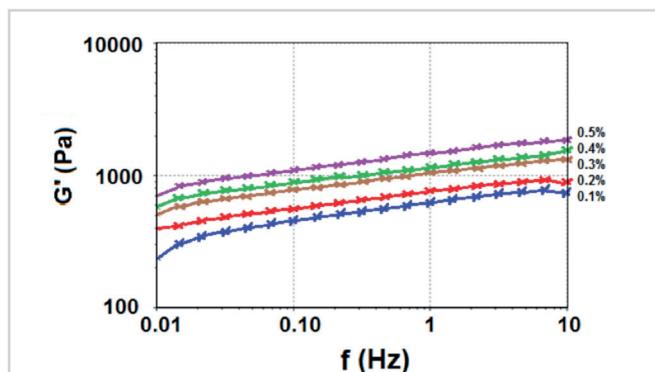


Fig. 4 Elastic moduli for the emulsion samples with increasing carbomer concentrations

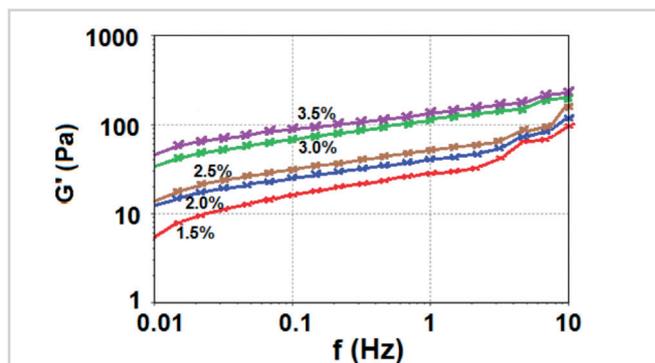


Fig. 5 Elastic moduli for the emulsion samples with increasing xanthan gum concentrations

tests. **Figs. 4** and **5** show the results expressed as elastic modulus vs. frequency for the samples with carbomer and xanthan gum, respectively. Numerical values of both moduli are presented in **Tab. 2**, showing, as expected, an increasing trend with the increase in polymer concentration for both series of emulsions.

Texture analyses is a well-established method for the evaluation of textural properties of semisolid cosmetic products, for example firmness, consistency, cohesiveness, and spreadability [3,8,9,10]. Standard TA deformation tests also provide information about product fracturability and stringiness, the latter one defined as the distance that the product is extended during decompression before separating from the probe [4]. It was of interest to establish, using a typical cosmetic product, whether some of the TA parameters relate to the viscoelastic properties of the semisolids. The use of resilience and stringiness as useful additional TA parameters was recently suggested [4]. Resilience is a derivative parameter, calculated from the two areas of the positive curve, as $A4/A3$ ratio (**Fig. 2**), while stringiness is a directly measured parameter.

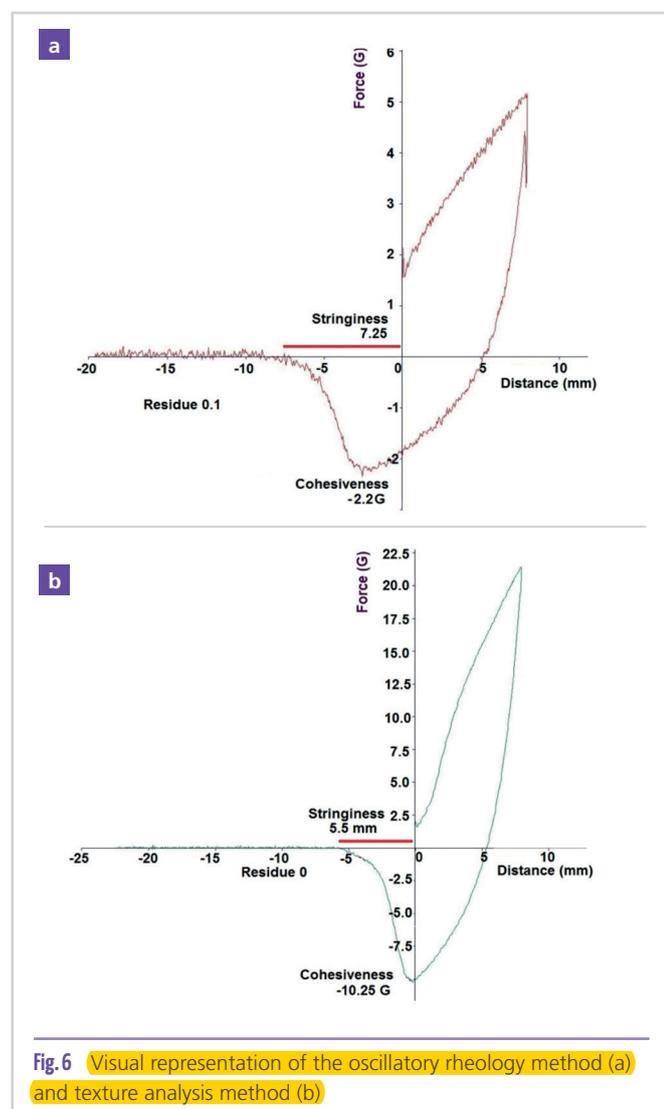
In order to detect stringiness, a different type of graph is needed, i.e. the one that shows the relationship between the force of resistance exerted

Polymer (% w/w)	Elastic modulus G' (Pa)	Viscous modulus G'' (Pa)
Carbomer		
0.1 %	619.3	127.9
0.2 %	755.9	141.4
0.3 %	1034.0	192.4
0.4 %	1139.0	209.7
0.5 %	1463.0	275.6
Xanthan gum		
1.5 %	28.0	13.9
2.0 %	39.9	16.6
2.5 %	51.3	21.4
3.0 %	112.5	46.9
3.5 %	133.2	45.9

Tab. 2 Oscillatory rheology parameters obtained at the frequency of 1 Hz for the emulsion samples stabilised with carbomer and xanthan gum. All values represent the mean of 3 measurements, with the coefficient of variation below 5%.

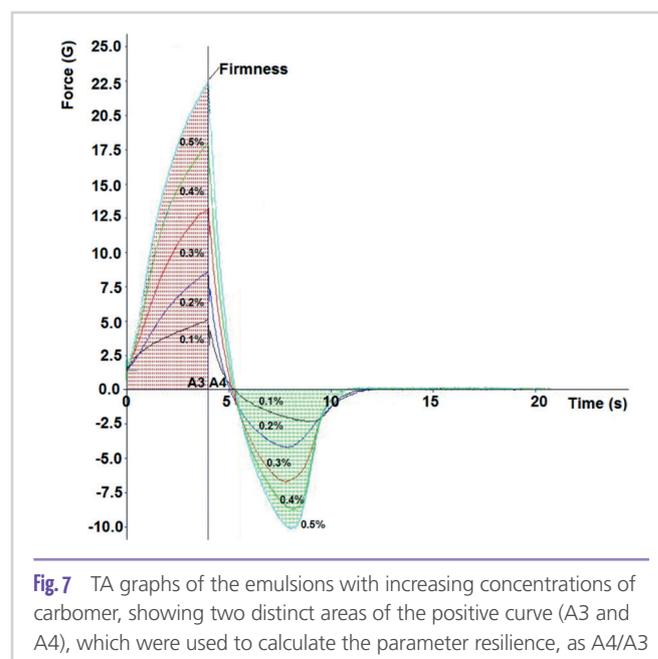
by the sample as a function of the distance of the probe from the sample surface. **Figs. 6a** and **b** show the examples of such curves for the samples with 0.1% and 0.5% carbomer, respectively. It is notable that stringiness has decreased with the increase in the polymer concentration in the emulsion. This is consistent with the sensorial expressions of “long flow” and “short flow”, respectively, used in the formulation practice.

It is known that the internal structuring of most cosmetic semisolid emulsions is due to the effect of complex emulsifiers, present in excess to what is needed to cover the o/w interfaces. This excess stabilises emulsion by simultaneously increasing its viscosity and immobilising the dispersed oil droplets. The emulsifier used in this formulation contains a mixture of low and high HLB components, combined with emulsifying waxes, which provides a tight packing of molecules at the interface. It is well established that co-emulsifiers



(fatty amphiphiles), promote the formation of crystalline gel (in some cases liquid crystalline) structures, which directly affect the sample rheology [11]. Therefore, the properties of the existing three-dimensional crystalline gel network change dramatically when combined with the three-dimensional structure of xanthan gum or the complex cross-link network of carbomer. In principle, the addition of rheological modifiers increases the overall rigidity of the gel/liquid crystal bilayers [12], which manifests itself as a decrease in stringiness.

Fig. 7 shows the results of the immersion/de-immersion tests for all five emulsions stabilised with carbomer. Each TA trace is an average of 3 measurements, with the coefficient of variation of below 2.5%. Apart from the consistent change of TA parameters with increasing polymer concentration, it is interesting to note that there are some visible trends in the shape of curves obtained. For example, there is a shift in the peak of the negative curve towards shorter time as the concentration of carbomer increases, until it reaches certain concentration, at which it appears to stabilise (**Fig. 7**). However, all negative curves obtained for the test emulsions show smooth appearance, as opposed to a discontinuous one, detected in the cases of some hydrogels at higher concentrations, e.g. acrylates/C10-30 alkyl acrylate crosspolymer gels [4]. The presence of the negative curve discontinuity, referred as material being “choppy”, indicates that the withdrawal of the probe from the sample consists of several steps, which is probably related to the micro-gel structure formed by the polymer. “Choppiness” is a negative sensorial property which indicates a difficulty in product application.



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Fig. 6 Typical curve obtained by immersion/de-immersion test on texture analyser, expressed as force vs. distance. Stringiness is defined as the distance that the product is extended during de-immersion stage before separating from the probe; a) emulsion with 0.1 % carbomer; b) emulsion with 0.5 % carbomer.

Tab. 3 presents all TA parameters of interest, including resilience and stringiness. Parameter stringiness has shown a consistent decreasing trend with an increase in polymer concentration, while resilience has mildly increased. According to a standard definition, resilience is an ability of the material to return to its original form after being bent, stretched or compressed. A completely resilient liquid should have the resilience value of 1, which is in line with the results found for water, glycerol and low concentration SLES using the TA method, while gels, creams and shampoos have revealed much lower values of resilience [4]. In this study, a good linear regression fit between resilience and the two oscillatory moduli (elastic modulus G' and viscous modulus G'') at 1 Hz was obtained for the emulsions with carbomer (**Fig. 8**).

The emulsions with xanthan gum have shown lower a correlation coefficient (R^2) for resilience, but better for stringiness, than those with carbomer. The graph showing the linear regression fit between stringiness and G' and G'' is presented in **Fig. 9**. Clearly, a larger range of samples should be tested to get the confirmation of any mathematical relationship, but the existence of trends is detectable in the cases of both series of emulsions.

It is interesting to note that the results for stringiness for the emulsion samples evaluated in this study contradict the results obtained for the shampoo formulations with SLES. *Tai et al.* [4] have found an increase in stringiness with increasing concentrations of SLES, which is due to the changes in surfactant structuring. However, their results concerning the stringi-

ness of acrylates/C10-30 alkyl acrylate crosspolymer gels in the concentration range 0.1–0.75 % have shown the same trend as in this study [4].

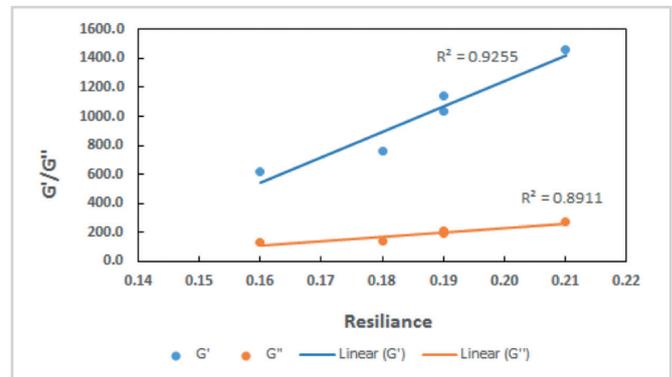


Fig. 8 Linear regression fit between a TA parameter resilience and two oscillatory parameters, elastic modulus G' and viscous modulus G'' , for the series of emulsions with carbomer

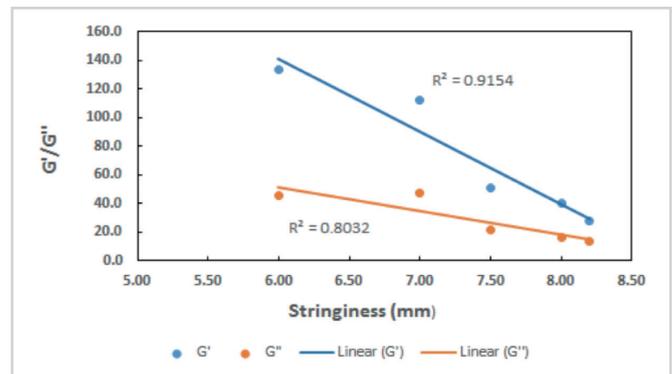


Fig. 9 Linear regression fit between a TA parameter stringiness and two oscillatory parameters, elastic modulus G' and viscous modulus G'' , for the series of emulsions with xanthan gum

Polymer (% w/w)	TA parameters of the test emulsions					
	Firmness (g)	Consistency (g.s)	Cohesiveness (g)	Work of Cohesion (g.s)	Resilience (A4/A3)	Stringiness (mm)
Carbomer						
0.1 %	5.13	17.17	-2.39	-8.33	0.16	7.25
0.2 %	8.67	25.53	-4.28	-15.04	0.18	6.50
0.3 %	13.57	40.14	-6.78	-21.07	0.19	6.00
0.4 %	18.06	54.66	-8.80	-25.27	0.19	5.75
0.5 %	22.56	67.43	-10.20	-28.67	0.21	5.50
Xanthan gum						
1.5 %	3.45	12.61	-1.45	-4.69	0.18	8.20
2.0 %	4.93	17.48	-2.22	-7.80	0.19	8.00
2.5 %	5.56	19.64	-2.60	-8.98	0.21	7.50
3.0 %	7.29	24.30	-3.34	-10.98	0.20	7.00
3.5 %	9.06	29.86	-3.47	-11.92	0.22	6.00

Tab. 3 Texture analysis parameters of the emulsion samples stabilised with carbomer and xanthan gum

Conclusion

The results obtained by the application of oscillatory rheology and texture analysis on the two series of semisolid emulsion samples have revealed some practically useful correlations. Specifically, TA parameters resilience and stringiness were analysed alongside oscillatory parameters elastic modulus (G') and viscous modulus (G''). The study has found that resilience mildly increases with the increase in polymer concentration for both carbomer and xanthan gum-stabilised emulsions. Stringiness has shown the opposite trend, i.e. negative correlation with both G' and G'' . In conclusion, if carefully interpreted, TA parameters resilience and stringiness could be used to assess the level of viscoelasticity of cosmetic semisolids.

Acknowledgements

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Note

Shorter version of this paper was presented as a poster at the 24th IFSCC Conference in Seoul, South Korea on 23–25 October 2017. The poster was commended as one of the “top 10 posters” at the conference.

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