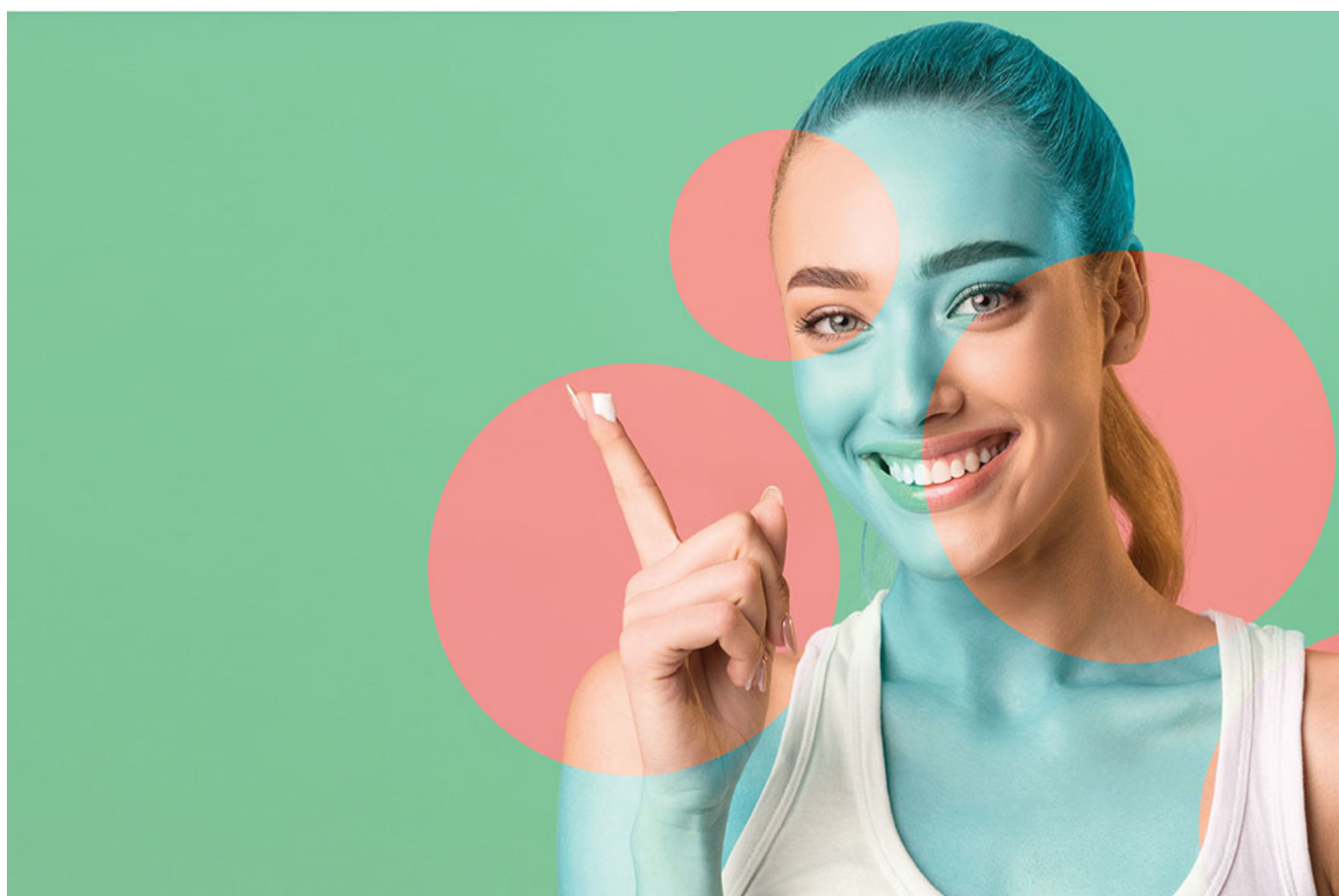


FORMULATING | C&T PEER-REVIEWED

Can Natural Polymers Replace Synthetic Carbomers?*

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**A portion of this paper was first presented during the IFSCC 2020 Congress.*



KEY POINTS

- Carbomers are versatile and stable rheology modifiers but are synthetic and cannot be formulated in a natural-claimed product.
- This study focused on replacing carbomers using combinations of natural polymers of the polysaccharide type.

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FROM THE VAULT

Garbage to Glamour: Recycling Food By-products for Skin Care



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There is pressure on cosmetic formulators to find suitable replacements for synthetic and semisynthetic cosmetic ingredients, and to develop products that could be marketed as natural. One of the most prominent examples is carbomer, a representative of an extensively used category of poly(acrylic acid) polymers.

The present study attempts to replicate the rheological and sensory properties of carbomer using natural polymers of the polysaccharide type. Polysaccharides are carbohydrate biopolymer structures formed by the condensation polymerization of repeating units of monosaccharides and disaccharides, and joined by glycosidic bonds. The terms *gums* or *hydrocolloids* are often used interchangeably when referring to polysaccharides of vegetable or biotechnological origin.¹ While all hydrocolloids have the property to form viscous dispersions in water, some of them also form gels. Hence, the food industry, and especially the cosmetic industry, make a distinction between thickeners and gelling agents.²

The mechanism of thickeners involves a non-specific entanglement of conformationally disordered polymer chains.² The viscosity of the dispersion is influenced by the polysaccharide hydrodynamic volume, which increases with molecular mass, chain rigidity and electrostatic charge density, and is greater for linear as opposed to a branched structure.³ Examples of natural thickening agents are xanthan gum, konjac gum, guar gum and cellulose derivatives.

In the gelling process, there is an additional step—the formation of junction zones. In the case of hydrocolloids, they are created by the physical association of their polymer chains through hydrogen and hydrophobic bonds and cation-mediated cross-linking.⁴ This process forms a three-dimensional network, which immobilizes water and creates a rigid structure resistant to flow. Examples of natural gelling agents include carrageenan, gellan gum, pectin and alginate. The textural properties (e.g., elastic or brittle) of a gel vary widely with the type of hydrocolloid used.

As opposed to the described physical gels, carbomer forms a more stable chemical gel at much lower concentrations due to the permanent cross-linking of its poly (acrylic acid) chains.⁵ Being a weak polymeric acid, carbomer requires the addition of a base to ionize the carboxylic acid groups, which causes the creation of negative charges along the polymer backbone and the uncoiling of the chains due to electrostatic repulsion.

The global carbomer market was valued at US \$722.9 million in 2018 and is expected to reach \$1.75 billion by 2028, expanding at a CAGR of 9.3%.

Source: AWS Marketplace



INCI	% w/w
A. Deionized Water (<i>aqua</i>)	70.0
Glycerin	2.0
Rheological Modifier	qs to target viscosity
B. <i>Butyrospermum Parkii</i> (Shea) Butter	7.5
Capryl/Caprylic Acid Triglyceride	7.5
Cetearyl Glucoside (and) Cetearyl Alcohol	4.0
C. Benzoic Acid	0.5
Sodium Hydroxide	qs to target pH
Citric Acid	qs to target pH
Deionized Water (<i>aqua</i>)	qs to 100.0

i

Considering the various mechanisms among these material types, as stated, the present study aimed to assess whether it is possible to replace a synthetic polymer carbomer with one or more natural hydrocolloids of the polysaccharide type in cosmetic emulsions. Rheological, textural and sensory methods were employed to evaluate the effectiveness of the replacement.

Materials and Methods

A simple COSMOS-approved o/w emulsion (see **Formula 1**) was used as a model base, with a variable quantity of rheological modifier. The benchmark was a commonly used poly(acrylic acid) polymer (INCI: Carbomer), alternatively used with six COSMOS-approved rheological modifiers of the polysaccharide type. They were classified as thickeners, i.e., xanthan gum, guar gum, konjac gum, cellulose gum; and gelling agents, i.e., gellan gum (high acyl and low acyl content) and carrageenan-*iota* type.

A series of hydrogels was initially formulated containing 0.3% carbomer and the various thickeners in concentrations required to achieve the same Brookfield viscosity as 0.3% carbomer (18.6 Pa•s \pm 10% at 200°C). These were characterized using continuous shear rate sweep and oscillatory shear stress sweep tests. This step was followed by producing and characterizing a range of corresponding emulsions (made according to **Formula 1**). Since no individual thickener produced the same rheological profile as carbomer, more than 20 combinations were evaluated, of which four were selected for further analysis. The number of polymers in each combination was limited to three.


Preparation of hydrogels: The preparation of single-polymer hydrogels followed a generic process of the dissolution and dispersion of the rheological modifier in water for 25 min, followed by the addition of the preservative and pH adjuster when required. The preparation of combination hydrogels followed the same process with modifications for carrageenan and gellan gum (high and low acyl content), where a higher temperature and the addition of calcium ions were necessary to achieve full hydration and gelation. Low acyl gellan gum also required the addition of 0.5% sodium citrate. Carrageenan and gellan gum were heated to 75°C and 85°C, respectively, held for 2 min at a constant temperature followed by the addition of calcium chloride, then cooled to 65-70°C for the addition of other rheological modifiers (if required).

Preparation of emulsions: The first step in the preparation of emulsions was the same as for hydrogels; the addition of glycerin. Following dispersion of the polymer(s), phases A and B were heated separately to 65-70°C, before combining them at high speed for 5 min. The emulsion was then taken off the heat and stirred at a low speed until it cooled to 40°C, at which point the preservative and pH adjuster were added as needed. The pH and Brookfield viscosity measurements were recorded.

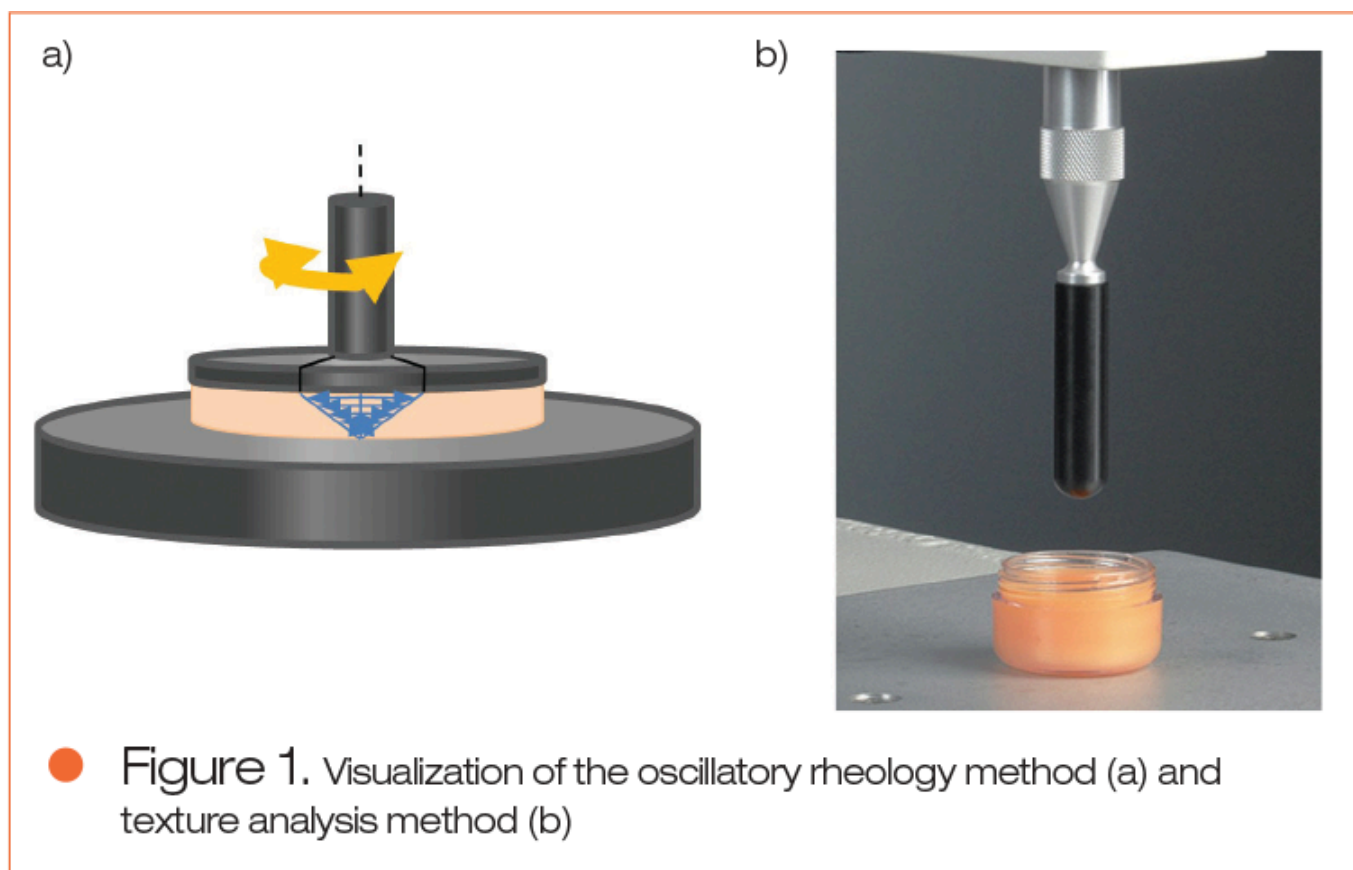
Rheological tests: Rheological measurements^a were carried out using a 35 mm serrated parallel plate and a gap of 1.0 mm. Dynamic (oscillatory) and continuous flow tests were used in conjunction to produce complete rheological profiles of the test samples. The oscillatory stress sweep was conducted by increasing the stress from 1 to 200 Pa at a constant frequency of 1 Hz. The maximum oscillatory stress of 200 Pa used for the hydrogels was increased to 400 Pa for the emulsions. 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.⁶

Two types of continuous flow tests were used: shear rate sweep and a three-step thixotropy test. In the shear rate sweep, the samples were sheared from 250 s⁻¹ to 10 s⁻¹ for 100 sec. The use of reverse order of shear rates (from high to low) has been shown to produce more repeatable data with less "noise."⁷ The three-step thixotropy test consisted of three phases, carried out at 10 s⁻¹, 250 s⁻¹ and 10 s⁻¹, with each step taking 60 sec. The results were expressed as the percentage recovery between the original viscosity measured at the first step, and the viscosity measured at the third step. **Figure 1a** shows a representation of the oscillatory method.

Texture analysis: Texture analysis was carried out using a texture analyzer^b with a 1/2" cylindrical probe, performing immersion/de-immersion tests to obtain a textural profile of the test samples. The positive (immersion) and negative (de-immersion) curves, based on the three replicas, were produced and analyzed by software^c. The parameters measured were: hardness (the highest force, measured in g) and compressibility (area under the curve, in g.sec) from the positive curve; and stringiness (g) and work of adhesiveness (g.sec) from the negative curve. **Figure 1b** shows the texture analysis method.

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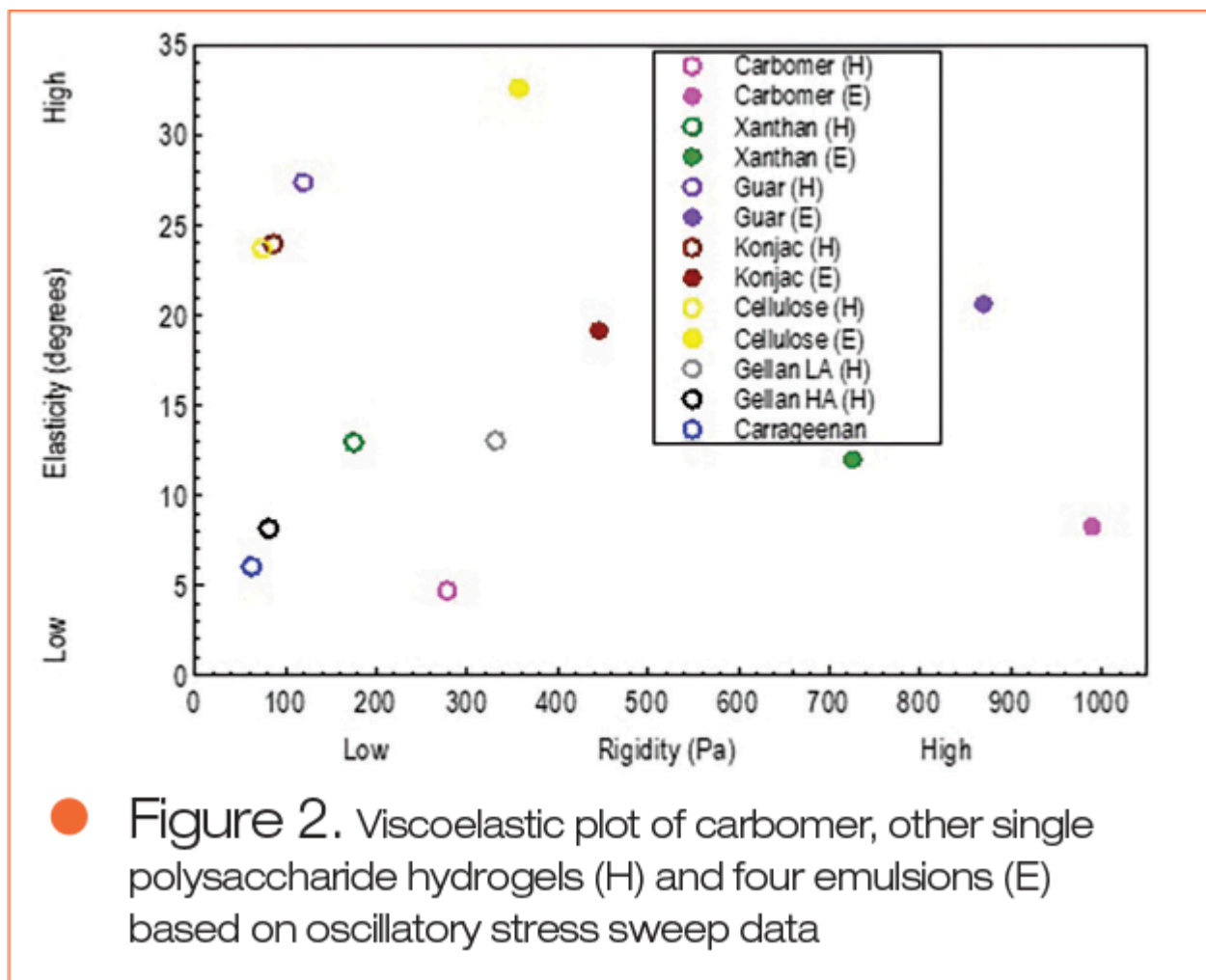
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Sensory analysis: The sensory assessment was performed on the four selected emulsion samples and consisted of two parts: sensory profiling and paired difference test, followed by the preference test. The sensory profiling test was performed by a semi-trained panel of eight assessors, who judged six emulsion attributes—firmness,

stickiness, wetness, spreadability, absorbance and integrity—with the view of identifying the closest match to the benchmark emulsion.

This was followed with a paired difference test by 40 naïve assessors to determine whether the representative emulsion was perceived as the same or different from the benchmark emulsion. The representative emulsion was selected from the sensory profiling test as the best-performing sample. The naïve panel was split into two groups: sighted and blinded (blindfolded), to eliminate any bias in their tactile judgment potentially caused by visual stimuli. The naïve assessors also performed the preference test under the same conditions (sighted or blindfolded).



● Table 1. Natural Rheological Modifier Combinations Tested

Name	Composition (% w/w)
CG	Carrageenan 1% + Gellan gum (high acyl) 0.2%
CGG	Carrageenan 0.6% + Gellan gum (high acyl) 0.3% + Gellan gum (low acyl) 0.2%
GX	Guar gum 0.8% + Xanthan gum 1.5%
CX	Carrageenan 1% + Xanthan gum 0.7%

Results and Discussion

Single polysaccharide tests: The results obtained from the oscillatory stress sweep of the hydrogels made by carbomer and seven potential replacement polysaccharides are summarized in a viscoelastic plot in **Figure 2**. In addition to the hydrogels, the plot shows the results of the four emulsions containing different rheological modifiers: carbomer, xanthan gum, guar gum and konjac gum. The viscoelasticity plot previously has been demonstrated⁸ as a useful tool for the visual analysis of viscoelastic data. It presents the relationship between two key viscoelastic parameters: elasticity and rigidity. Elasticity is expressed as the phase angle δ , also known as the lag phase, and indicates how much the movement of the sample is "lagging behind" the applied oscillatory stress.⁹ Lower phase angle indicates a more elastic sample. Rigidity is represented by the complex modulus G^* .



The analysis of **Figure 2** shows that both carbomer hydrogel (open pink circle) and the corresponding emulsion (closed pink circle) take distinct places in the plot, quite away from other hydrogels and emulsions. The carbomer hydrogel has the lowest phase angle (around 5 degrees), meaning it possesses the highest elasticity of all hydrogels. The closest are carrageenan and gellan with high acyl content (gellan HA), but both with notably lower rigidity than the carbomer sample (see **Figure 2**). This situation is mirrored by the carbomer emulsion, which is the most elastic and the most rigid of all emulsion samples, as well as significantly more rigid than the carbomer hydrogel. Cellulose gum and konjac gum were shown to be too far away from the desired viscoelastic profile of carbomer (see **Figure 2**), hence were omitted from further tests.

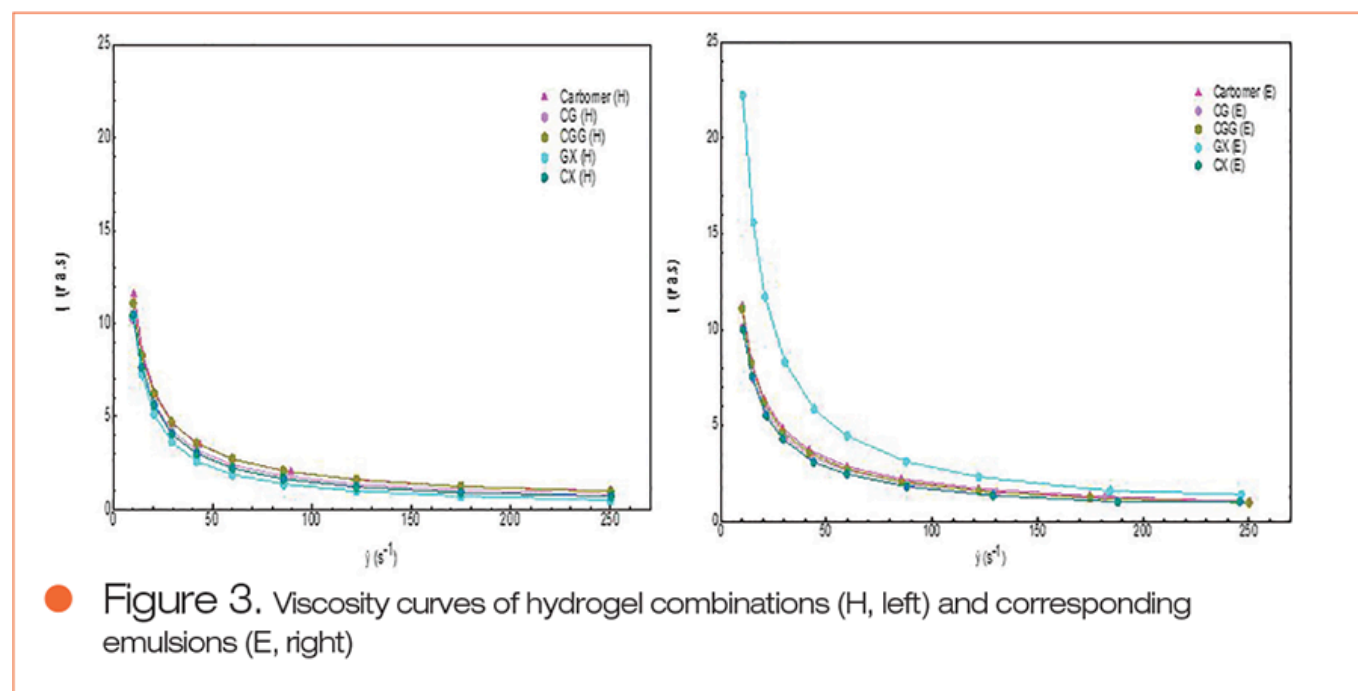
Combination polysaccharide tests: Analysis of the viscoelastic plot leads to the conclusion that the replacement cannot be a single polysaccharide polymer, but rather a combination. And as stated, the number of polymers in a combination was limited to three, which was for practical reasons. Thus, based on the preliminary testing of more than 20 polymer combinations, four combinations of three or fewer polymers were selected for further study (see **Table 1**). Using terminology from food science,² the combinations consisted of: two gelling agents (CG), three gelling agents (CGG), two thickeners (GX) and one gelling agent and one thickener (CX).

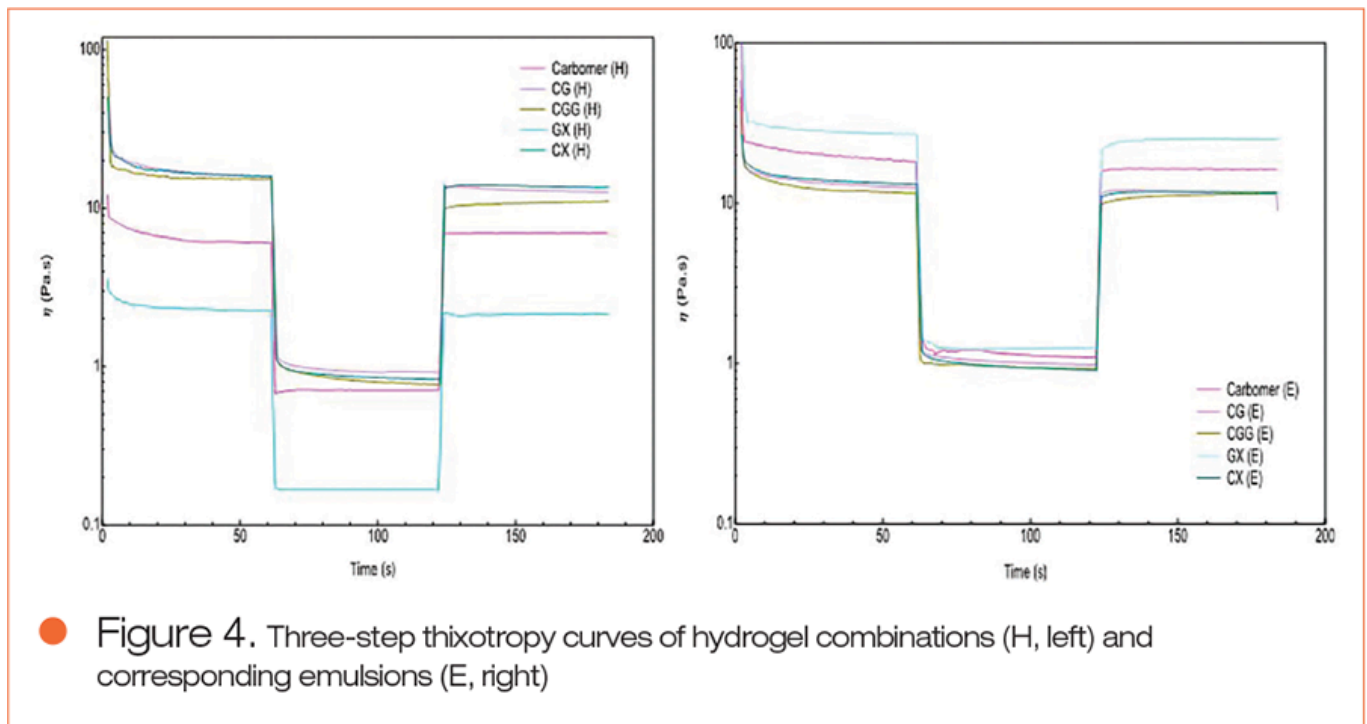
The hydrogels and emulsions obtained by these combinations were tested using a range of continuous flow and oscillatory methods. The continuous flow tests gave the viscosity profile of each polymer combination, in comparison with carbomer. The results of the flow measurements for the hydrogels and the corresponding emulsions are shown in **Figure 3**. The viscosity curves for all hydrogels look remarkably similar. As expected, they show a shear-thinning behavior, probably of the plastic type, although the existence of the yield point cannot be determined from the viscosity curve (see **Figure 3**, left). Based on the viscosity curves only, it would be possible to miss the distinct difference in the carbomer hydrogel structure in comparison with other samples—and to make a wrong conclusion that any of the tested combinations would be suitable as its replacement.

The viscosity curves of the emulsions are also quite similar, except for the combination GX (guar gum + xanthan gum). The GX emulsion showed a considerably higher starting viscosity, which decreased faster than the rest of the samples, reaching a similar value to others at the final shear rate of 250 s^{-1} (see **Figure 3**, right). The range of shear rates used was chosen to reflect common processes products are subjected to, such as pouring and spreading on the surface.⁷

The pronounced shear-thinning behavior of the GX sample indicates the existence of the internal network of entangled polymer chains (in addition to the lamellar gel structure formed by the emulsifier system), which forms a high-viscosity structure at rest.¹⁰ However, under the influence of increasing external force, the network consisting of two thickeners with no junction points⁴ easily yields and loses its resistance, i.e., viscosity.

Three-step thixotropy test: To detect further differences in the structures of the test samples, they were subjected to the three-step thixotropy test. This continuous flow test assesses changes in viscosity as the function of time and is divided into three sections (steps), usually of the same length; namely subjecting the sample to low, high, and again low shear rates, which are constant for the duration of each step. The diagrams obtained from the three-step thixotropy tests are shown in **Figure 4**. They visually present not only the extent of an instant thixotropic recovery (the height of the viscosity curve in the third step as opposed to the first), but also the extent of shear-thinning (the slope of viscosity curves) under different conditions of shear.⁶

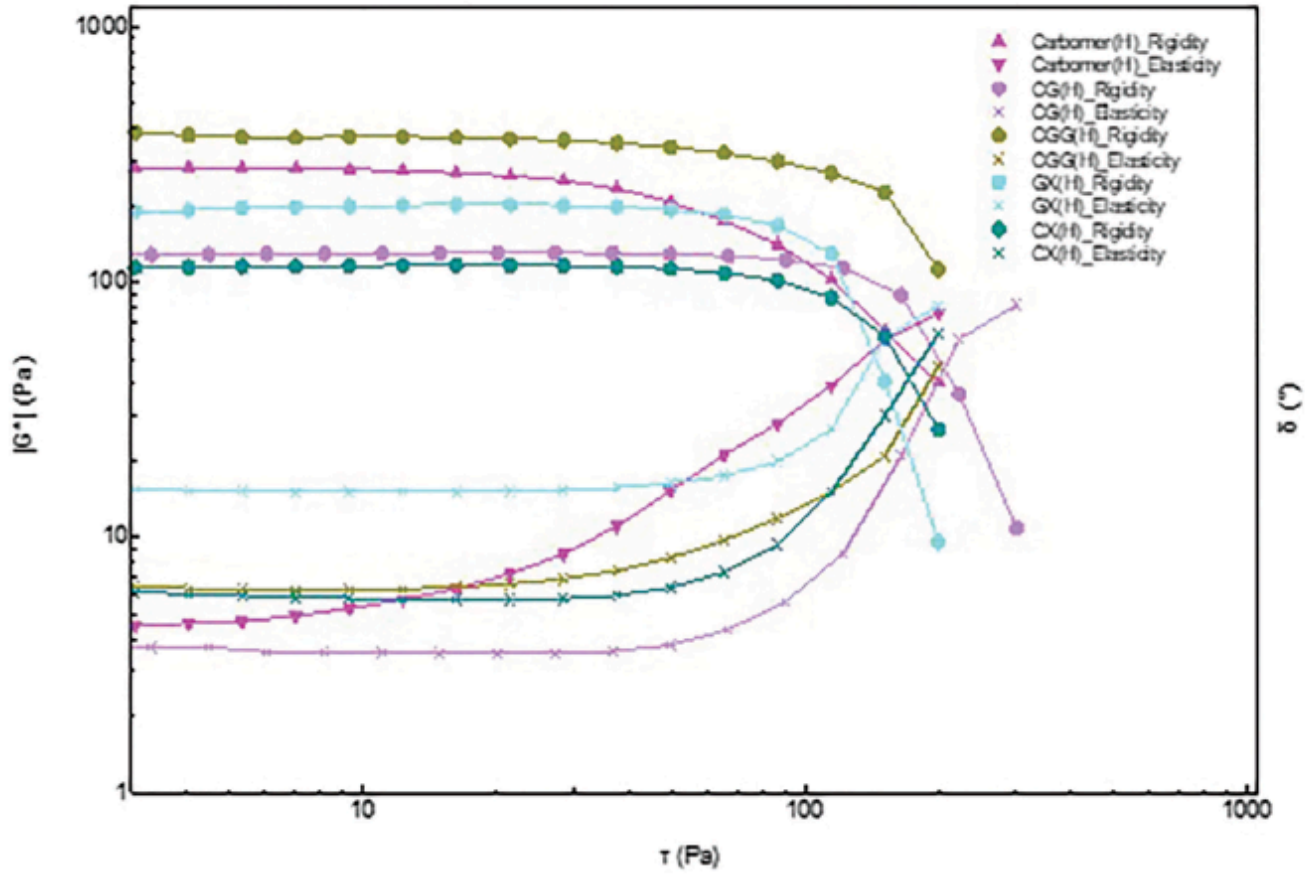




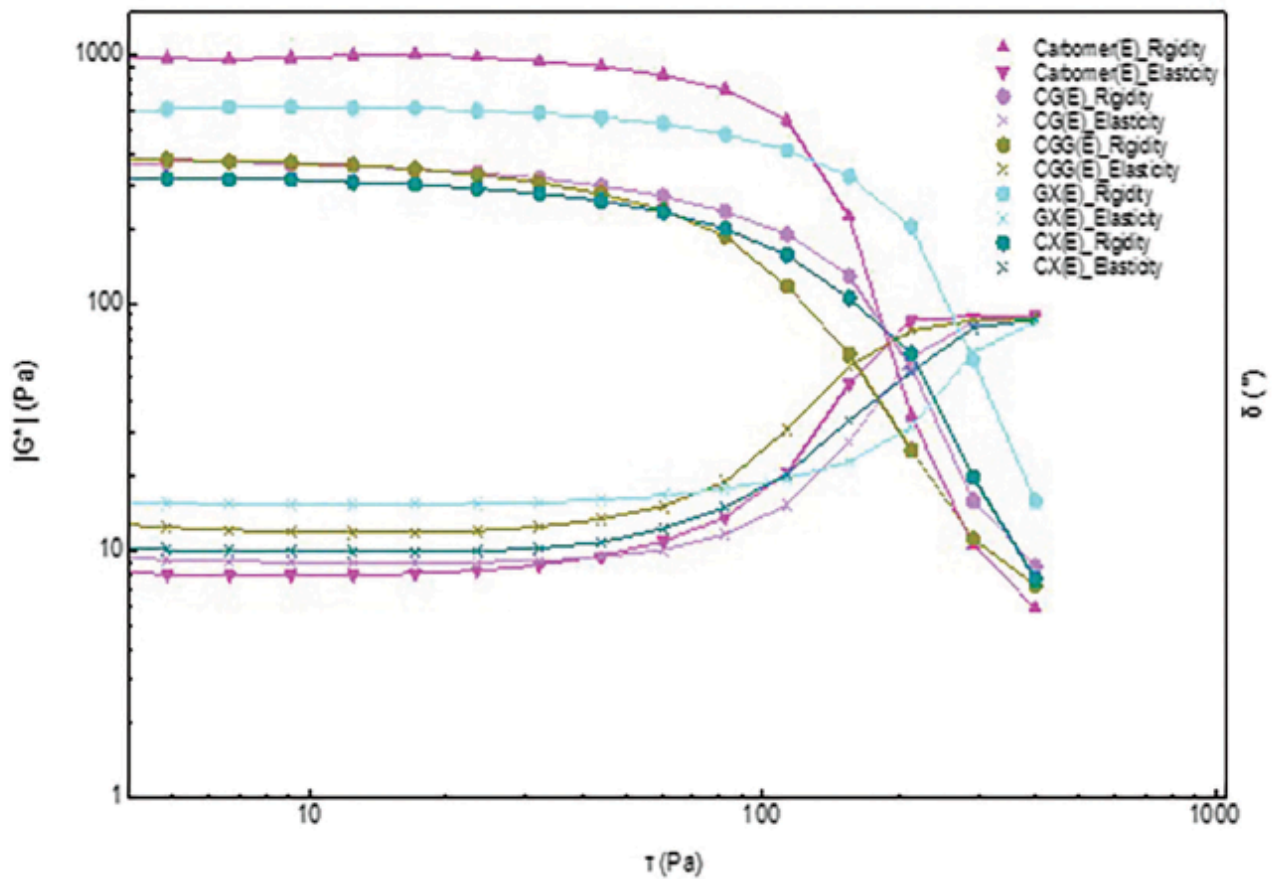
The analysis of **Figure 4** reveals some clear differences in the thixotropic behavior of the samples. In terms of hydrogels, the combination GX showed the lowest level of viscosity in all three steps, but specifically in the second step (at 250 s^{-1}), revealing the weakest polymer network. There seems to be a much more dramatic difference in the structure between this and the other samples than indicated by their viscosity curves (see **Figure 3**, left). The same combination had the highest viscosity values when incorporated into the emulsion (see **Figure 4**, right), which is consistent with the viscosity curves graph. This points to the interaction between the structures formed by the emulsifier and the thickener systems.

The samples containing carbomer were in the middle, between the sample GX and the others, in both cases. All hydrogels and emulsions showed a nearly 100% recovery in their internal structure immediately after the removal of high external force (step 3), with the carbomer hydrogel achieving more than 105%. This phenomenon has been observed previously⁸ and could be attributed to the formation of new points of contact under the effect of strong shearing force.

Oscillatory stress sweep test: The curves obtained by the oscillatory stress sweep (see **Figures 5** and **6**) present the two key viscoelastic parameters of semisolids: rigidity, expressed as complex modulus G^* , and elasticity, expressed as the phase angle δ . Combined with the viscosity and three-step thixotropy diagrams, they allow a complete rheological profile to be considered when characterizing semisolid samples.



● Figure 5. Results of oscillatory stress sweep tests of hydrogels

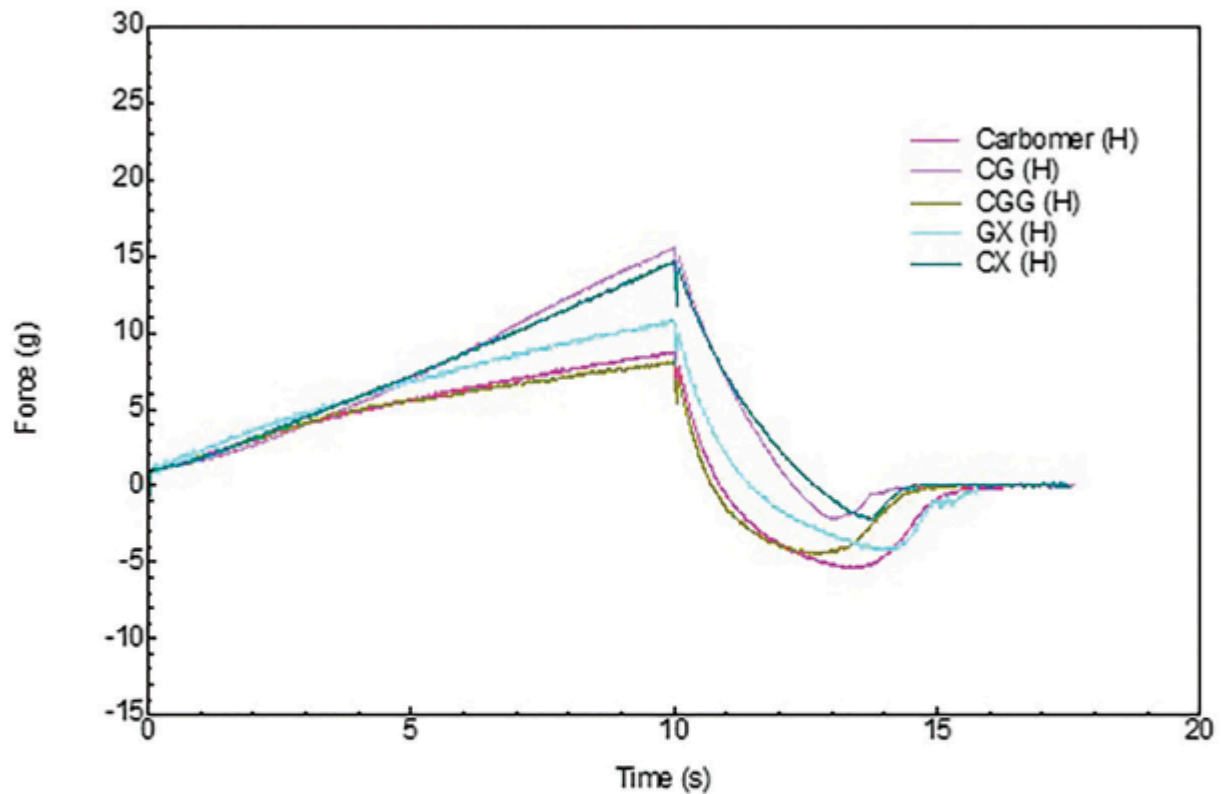


● Figure 6. Results of oscillatory stress sweep tests of emulsions

Figure 5 presents the oscillatory stress curves for the range of hydrogels, mirrored by the same data for the corresponding emulsions in **Figure 6**. The first Y-axes show the complex modulus (rigidity) as a flat line while the sample is in the linear viscoelastic region. The line curves downwards when the structure of the system starts yielding, which is used to calculate the yield stress of the sample. This is the same region where the second Y-axes, the phase angle, starts increasing.

Figure 5 shows that the hydrogel with carbomer had a relatively high rigidity, surpassed only by the sample CGG, but that it had a lower yield stress value than all combination hydrogels. This is known to be significant for the sensory characteristics of topical semisolids.¹¹

The carbomer sample also showed high elasticity (low phase angle δ), second only to the sample CG, the combination of the two gelling agents carrageenan and gellan gum HA. However, since the linear viscoelastic region was the shortest of all hydrogels tested, this revealed a higher loss of elasticity, as the stress was increased in comparison with the other hydrogels (see **Figure 5**), which is consistent with the lower yield stress.⁶



● Figure 7. Texture analysis (immersion/de-immersion curves) for hydrogels containing carbomer or polysaccharide combinations

● Table 2. Texture Analysis Values of Selected Hydrogel Combinations

Hydrogel combination	Positive curve		Negative curve	
	Hardness (g)	Compressibility (g.s)	Stringiness (g)	Adhesiveness (g.s)
Carbomer	8.792	56.611	5.456	15.348
CG	15.094	55.803	2.17	2.188
CGG	8.098	53.99	4.545	11.273
GX	10.816	18.437	4.305	10.279
CX	14.724	54.126	2.239	2.011

The viscoelastic profiles of the corresponding emulsions, however, revealed slightly different trends. The carbomer-containing emulsion showed the highest rigidity, as well as the highest elasticity, and comparable values of yield stress with other emulsion samples (see **Figure 6**). The emulsion containing the combination GX has had notably higher yield stress than the rest, accompanied by the lowest elasticity (the highest phase angle), which is a reflection of the different rheological profile of the combination containing xanthan gum. This information complemented the findings obtained from the continuous flow methods (see **Figures 3 and 4**).



Texture tests: It has been shown previously that there is a good correlation between certain texture and flow rheology parameters of semisolids.¹² Another study¹¹ also established multiple statistical correlations between sensory and rheological properties; for example, between texture and level of thixotropy, yield stress and firmness, slipperiness and elastic and viscous moduli. Therefore, it was of interest to test the texture parameters of the two series of samples (combination hydrogels and their corresponding emulsions) in relation to the carbomer benchmark.

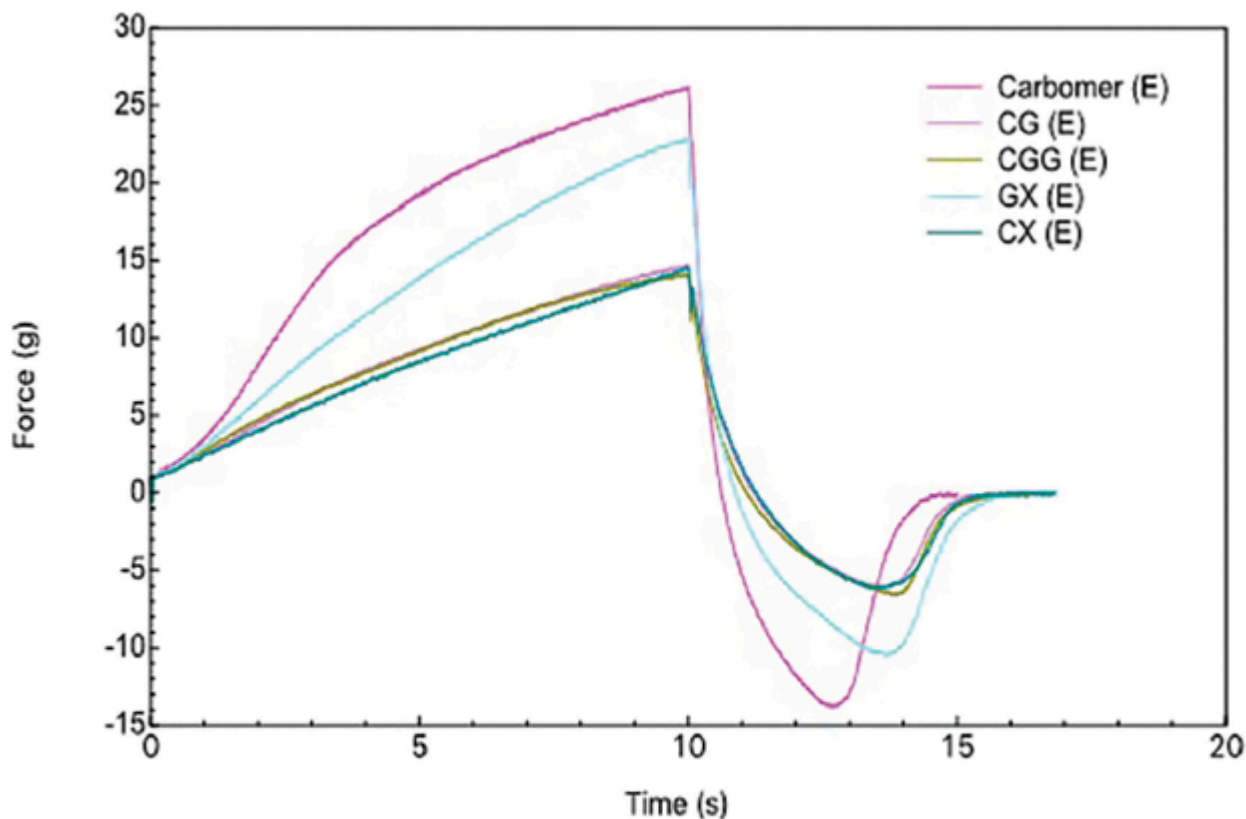
The immersion/de-immersion tests have provided four texture parameters (see **Table 2**). These were the maximum force and the area under the curve, from the positive and negative parts of the curve, respectively. **Figure 7** shows a graphical representation of the immersion/de-immersion results of the carbomer and the combination hydrogels, while **Table 2** presents numerical values of the parameters hardness, compressibility, stringiness and adhesiveness.

As expected, the texture analyses revealed the differences in hydrogels' responses to the penetration and withdrawal of the cylindrical probe. Since the forces are different (vertical pressure as opposed to shear), the responses are not identical, but they are complementary. For example, the hardness of carbomer hydrogel was among the lowest (see **Figure 7, Table 2**), while the hardness of the corresponding emulsion was the highest (see **Figure 8**), which is in line with the rigidity of its hydrogel (see **Figure 5**) and emulsion (see **Figure 6**). This is confirmation that the carbomer interacts with the lamellar phases of the emulsion based on the nonionic

system cetearyl glucoside/cetearyl alcohol, causing the significant strengthening of its internal three-dimensional structure.¹⁰

Sensory profiling: The sensory profiling test was performed in order to select the carbomer replacement emulsion with the most similar textural properties to the benchmark. The results provided by the panel of eight assessors are presented in the form of a spider diagram in **Figure 9** (left). The analysis by the non-parametric Friedman means rankings test has established that the combination CG was the best match to carbomer. This test was followed by the paired difference and preference tests using 40 naïve assessors, of which half were sighted and half blindfolded. The paired difference test revealed a perceivable difference between the carbomer and the CG sample.

Interestingly, when asked which sample they would prefer, the blinded panel pointed to the CG cream as opposed to the sighted panel, which preferred the carbomer benchmark (see **Figure 9**, right). This is probably due to the white residue left on the skin by the CG sample during the rub-out stage. This residue was subsequently absorbed but it led the sighted panel to assess the CG sample as "slow absorbing" and judge it as less preferred. It has been reported that physical gels, as opposed to chemical gels, tend to leave a residue on the treated surface due to the lack of strong cohesive forces in their structure.¹¹ It was suggested that the use of highly elastic systems could minimize the amount of residue, which could be one of the approaches to solve this issue. With additional formulation work, it appears it would be possible to produce the exact tactile and visual match to the carbomer-containing emulsions.



● Figure 8. Texture analysis (immersion/de-immersion curves) for emulsions containing carbomer or polysaccharide combinations

