Leveraging synergy between Guar and Xanthan gums A modern formulation tool

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Abstract:
Rheological properties play an important role in beauty and personal care formulations. Natural polymers have long been used as rheology, sensory, and texture modifiers. Guar gum is a natural polymer extracted from the endosperm of the Guar bean. It is commonly used as a rheology modifier in the food industry. In this article, we discuss its rheological behaviour and application as a thickener in different types of cosmetic formulations. We also investigate how the synergistic combination of Guar gum and Xanthan gum results in enhanced viscosity. The wide pH range and cationic components compatibility, together with its unique sensory profile, make the underused guar gum a very promising ingredient for the thickening of various beauty and personal-care products.

Keywords:
- Guar Gum
- Xanthan Gum
- Rheology
- Tribology
- Personal care
- Galactomannan
- Synergy
- Peer Reviewed

INTRODUCTION

Rheology modifiers are essential ingredients used in formulating beauty and personal care products.
They alter the rheological behaviour of a finished product to deliver technical and application benefits, including enhanced sensorial and texture properties that improve the consumer experience.

The correlation between rheology modification and aesthetics has been the object of complex studies for decades (1) (2), with the multidisciplinary science of rheology playing a fundamental role in determining key parameters that govern product behaviour. Besides deepening the understanding of such mechanisms and behaviours, the results of these studies show that human touch – specifically via the fingerstips – remains one of the most sophisticated and multi-functional sensory instruments that consumers use to decide which products they like and would repurchase (3).

The term 'rheology', originating from the Greek words *rhéō* ("flow") and *logia* ("study of"), was invented by Eugene C. Bingham in the 1920s and is the study of the deformation and flow of matter (4).

Flow is the continuous deformation of a material under the influence of external forces. When a force is applied to a liquid, the latter will flow to relieve the strain from that force. Different systems resist this flow in different ways, and the measurement of this resistance gives us one of the most frequently used rheological parameters: viscosity (4).

Viscosity is easy to understand and relates to everyday experience. It is common, for example, to 'perceive' that honey is thicker than water. However, viscosity alone cannot describe the complex behaviour of rheology modifiers and finished products.
More complex parameters are needed to explain the molecular mechanisms of rheology modification, with G' (elastic or storage modulus) and G" (viscous or loss modulus) being fundamentally important (5).

Polymers are an essential class of ingredients used as rheology modifiers in the beauty and personal care industry and they can be broadly divided into synthetic and natural categories (6, 7).

Consumers' demand for more sustainable formulations using natural and renewable ingredients have also accelerated. This has prompted more investigation into the use of polysaccharides – also known as gums – as rheology modifiers, with the ultimate goal of replacing existing ingredients with more natural alternatives that nevertheless lend products highly appealing sensory characteristics.

Ingredient (INCI Name)	Number of launches
Xanthan Gum	66525
Carrageenan	2847
Cyamopsis Tetragonoloba (Guar) Gum	1081

Figure 1. Some natural rheology modifiers used in personal care product launches in the last five years (Mintel, updated 10th October 2022, excluding colour cosmetics, deodorants, and fragrances).

THE SYNERGY BETWEEN GUAR GUM AND XANTHAN GUM

Xanthan gum is a polysaccharide commercially produced by precipitation of the broth isolated from the exocellular coating on bacterial cell walls after fermentation.
It has a complex structure comprising a backbone of β-D-(1,4)-glucose with branching trisaccharide side chains of β-D-(1,2)-mannose and β-D-(1,4)-glucuronic acid.The comb-like trisaccharide side chains found on the primary chain confer water soluble properties.

The anionic charge of Xanthan gum is due to carboxylic acid residues on D-glucuronic acid and pyruvic acid moiety on the terminal D-mannose.Its thickening and gelation mechanisms require the formation of junction zones, hypothesised to occur through hydrophobic interactions on the helix (8).

Guar gum is a polygalactomannan found in the endosperm of the seeds of the Cyamopsis Tetragonolobus plant. It is a hydrophilic heteropolysaccharide of mannose and galactose monomer units, where the mannose constitutes the main linear chain of the polymer and the galactose forms the pendant branches. The mannose units are linked together by β-1,4 glycosidic bonds, and the galactose units are linked to mannose through α-1,6 glycosidic bonds. The mannose-to-galactose ratio of Guar gum is approximately 2:1 (9).

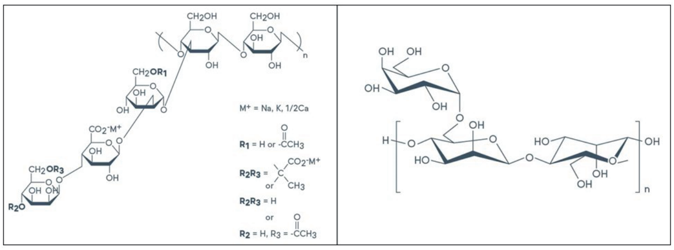

Figure 2. Chemical structure of Xanthan Gum (left) and Guar Gum (right).

Rheological properties of Guar and Xanthan gum have been thoroughly studied and described in literature (10). Findings include the fact that a synergistic interaction between the two gums can occur and both are often used in food technology (11).

We designed various tests to investigate the potential benefits of applying synergistic mixtures of Guar and Xanthan gum to the formulation of beauty and personal care products. Aqueous systems made of a 1.0% (w/w) total polymer concentration were prepared with Guar-to-Xanthan ratios of 100:0, 90:10, 80:20, 60:40, 50:50, 40:60, 20:80, 10:90, and 0:100. The gums were mixed in deionised water at 20°C for two hours under a high-speed, three-blade, over-head propeller stirrer.

Measurement of Brookfield Viscosity and Brookfield Yield Value

A Brookfield RVDVI+ viscometer was used to measure the viscosity of the samples 24 hours after their preparation. While it is widely recognised that Brookfield viscosity has little 'rheological significance', most application scientists across various disciplines (e.g. food, cosmetics, etc.) make use of this quick and relatively inexpensive technique. Brookfield viscosity results are generally easily correlated with the everyday experience of various materials. Brookfield viscosity results are shown in Figure 3.

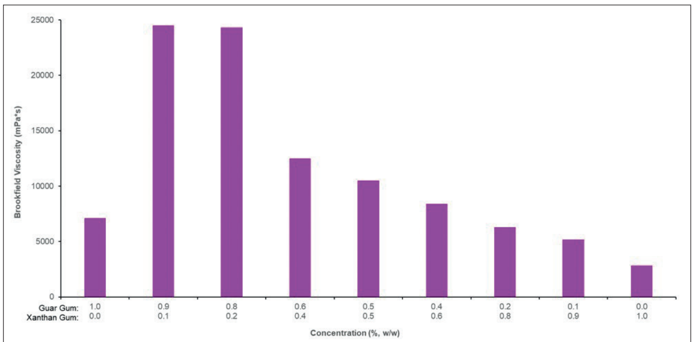

Figure 3. Brookfield Viscosity of various mixtures of Guar gum and Xanthan gum (20°C, 10 rpm).

This plot shows that the interaction between Guar and Xanthan gums results in synergistically-enhanced viscosity, which appears to reach its maximum value where Guar-to-Xanthan ratios are in the region between 90:10 and 80:20, as the food science literature also describes (12).

The term "synergistically-enhanced viscosity" means that the viscosity of aqueous systems containing mixtures of the two gums is greater than that obtained when each gum is used individually at the same total concentration.

Though interesting, viscosity alone is insufficient to describe and understand phenomena occurring within complex systems. For instance, the Weissenberg effect observed while preparing some samples hinted at potentially increased elastic behaviour (13), which prompted us to further investigate this aspect by measuring the yield value of the systems.

Because the Yield Value is a zero-shear-rate property, an approximation of it can be obtained from the Brookfield Yield Value (BYV), as described by the following equation (14):

$$BYV = \frac{(Brookfield\ Viscosity\ at\ 0.5\ rpm) - (Brookfield\ Viscosity\ at\ 1\ rpm)}{1000}$$

Although not as sophisticated and precise as more complex rotational and oscillatory techniques, using a Brookfield viscometer is a simple and quick way to evaluate the yield value of a sample.

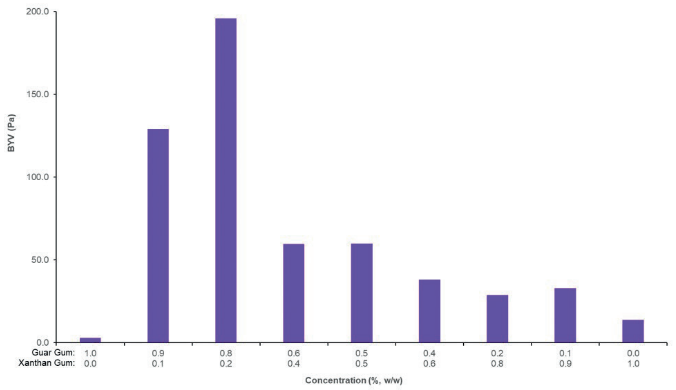

Figure 4. Brookfield Yield Value (BYV) of various mixtures of Guar gum and Xanthan gum (Brookfield Viscosity measured at 20°C, 0.5, and 1 rpm).

Figure 4 shows that the results obtained for Guar gum and Xanthan gum used alone correlate well with everyday formulation practice. In other words, Guar gum cannot form suspending systems, while Xanthan gum can (compatibly with the physical characteristics of the particles to suspend).

Moreover, the synergistic interaction between the two polymers appears to positively affect the suspending properties of the mixtures.

Further investigations were conducted to gain a better understanding of the behaviour of these systems at a more intimate level.

Rheology Measurements in Oscillatory Regime

A research rheometer (MCR302e CC27, Anton Paar) was used to perform a more comprehensive rheological characterisation in oscillatory regime to better understand the inter- and intra-molecular interactions taking place between Guar and Xanthan gum.

Samples previously prepared with Guar gum alone, Xanthan gum alone and the 80:20 mixture underwent a preliminary Strain Sweep to determine the Linear Viscoelastic Region (LVER, results not shown). Subsequently, we conducted frequency sweeps within the LVER at Angular Frequencies between 0.1 and 100 Hz, and measured the elastic (G') and viscous (G") moduli. Results are shown in Figure 5.

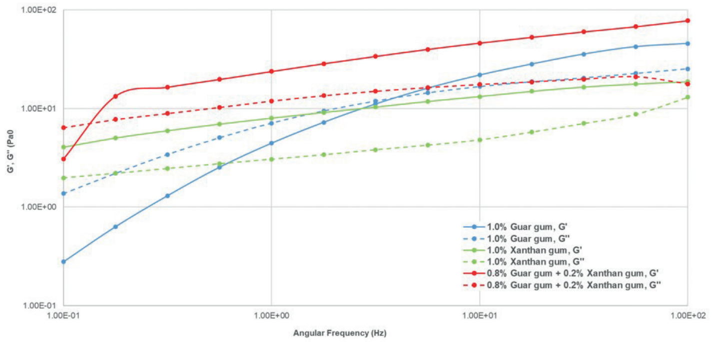

Figure 5. Frequency Sweeps of aqueous systems made with 1.0% of Guar gum alone, Xanthan gum alone, or a Guar-to-Xanthan 80:20 mixture (LVER, 20°C).

The sample made with 1.0% of Xanthan gum alone shows G' above G" across the Frequency range, hinting at a predominantly elastic structure.

The sample made with 1.0% of Guar gum alone shows a Cross-Over point at approximately 6 Hz, with the system displaying more elastic behaviour above this point and more viscous behaviour below it.

The inherent rheological characteristics described above correlate well with what is shown in Fig. 4. Generally speaking, systems with predominantly elastic behaviour tend to have better suspending properties than those with more viscous behaviour.

Interestingly, the synergistic mixture of Guar and Xanthan gum assumes a predominantly elastic behaviour across the Angular Frequency range investigated. Moreover, G' and G" for this system are shifted upwards, suggesting that these variables and the real-life effects they describe are greater than those of samples using Xanthan gum alone.

Apart from offering technical value, these results can also serve as rigorous support for the more simplistic data generated from Brookfield measurements.

CASE STUDY: APPLICATION OF SYNERGISTIC MIXTURES TO PRACTICAL FORMULATION

Four water-based cosmetic products were formulated to evaluate the benefits of employing synergistic interactions of Guar and Xanthan gum in practical applications.

The formulae were designed to be representative of similar finished products found in the market.
They featured commonly-used ingredients such as humectants (e.g. Glycerin, Propanediol), pH adjusters (e.g. Lactic Acid), preservatives (e.g. Sodium Benzoate, Potassium Sorbate), and chelating agents (e.g. Sodium Gluconate), etc.

The only differentiation between the four products was the rheology modifier used, as detailed below:

- Formula FX: 1.0% Xanthan gum alone.
- Formula FXG1: 0.8% Guar gum and 0.2% Xanthan gum.
- Formula FXG2: 0.4% Guar gum and 0.1% Xanthan gum.
- Formula FG: 1.0% Guar gum alone.

Brookfield Viscosity of the four products was measured 24 hours after preparation and the results are shown in Figure 6.

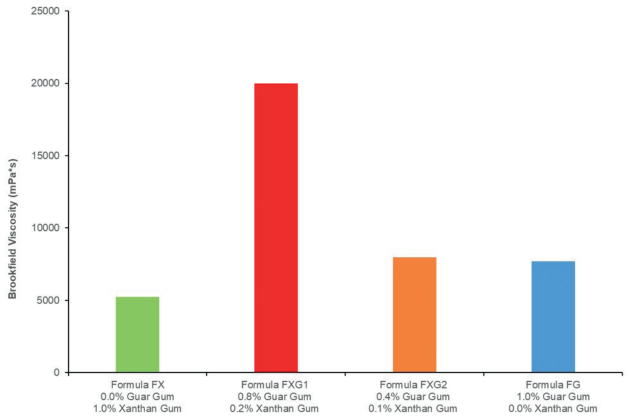

Figure 6. Brookfield Viscosity of four products prepared with different mixtures of Guar and Xanthan gum (20°C, 10 rpm).

Formula FXG1 displays the strong synergistic viscosity increase previously seen in much simpler systems.
Maintaining the Guar-to-Xanthan ratio of 80:20 but decreasing the total concentration of gums from 1.0 to 0.5% results in FXG2 exhibiting a viscosity that is very close to that of FG (Guar gum alone at 1.0%), but greater than FX (Xanthan gum alone at 1.0%).

Products FX and FXG2 were selected to undergo tribological and sensory evaluations. Three points supported this choice:

- FX features Xanthan gum alone. It serves as a suitable benchmark because it is a generally much more well-known and widely used ingredient than Guar gum.
- FXG2 shows that leveraging the synergy between both gums makes it possible to significantly reduce the total use level of the rheology modifier while retaining good viscosity.
- Based on previous evaluations in this paper, synergistic mixtures of the two gums have enhanced elastic properties compared to Guar gum alone.

	CONCENTRATION (%w/w)			
INCI NAME	**FX**	**FXG1**	**FXG2**	**FG**
Cyamopsis Tetragonoloba (Guar) Gum	0,00	0,80	0,40	1,00
Xanthan Gum	1,00	0,20	0,10	0,00
Betaine	1,00	1,00	1,00	1,00
Glycerin	15,00	15,00	15,00	15,00
Propanediol	15,00	15,00	15,00	15,00
Sodium Benzoate	0,20	0,20	0,20	0,20
Potassium Lactate	0,30	0,30	0,30	0,30
Lactic Acid	QS to pH4	QS to pH4	QS to pH4	QS to pH4
Aqua/Water/Eau	Up to 100	Up to 100	Up to 100	Up to 100

Table 1. Concentration in (%w/w) of the four formulae FX, FXG1, FXG2, and FG presented in the case study.

Tribology

The term ‘tribology’, originating from the Greek words *tribos* (“to rub”) and *logia* (“study of”), is the study of friction, wear and lubrication. Friction and wear are generated at the interface of contacting bodies in relative motion and occur in components such as bearings, gears, and screws (15).

Friction is generated between materials that interact or are in close contact with each other. It can also occur when body parts have occasional or repeated skin-on-skin or skin-on-clothing contact. For instance, spreading a cream onto the face, contact between the inner thighs and clothing during jogging, and intimate skin contact during sexual activity all generate friction.

It is interesting to note that the fingertips – through the complex human nervous system – perform complex tribo-rheological assessments in a matter of few seconds when applying a facial cream, for example.

In simple terms, we may quickly perceive a product that “opposes friction” to be sticky, and one that “decreases friction” to be lubricious or slippery. Tribology testing of samples FX and FXG2 was performed on a research rheometer (DHR2, TA Instruments) fitted with a custom three-ball-on-plate measuring system. This was brought into contact with a soft silicone substrate onto which the sample was positioned.

An axial load of 1N was applied, and the Angular Velocity was varied between 0.05 to 20 rad/s.
The Coefficient of Friction was calculated as the ratio of torque to load and plotted as a function of the calculated Sliding Speed expressed in linear velocity. The test was performed at 37°C to simulate the average skin temperature. The plot generated is called a Stribeck curve (Figure 7).

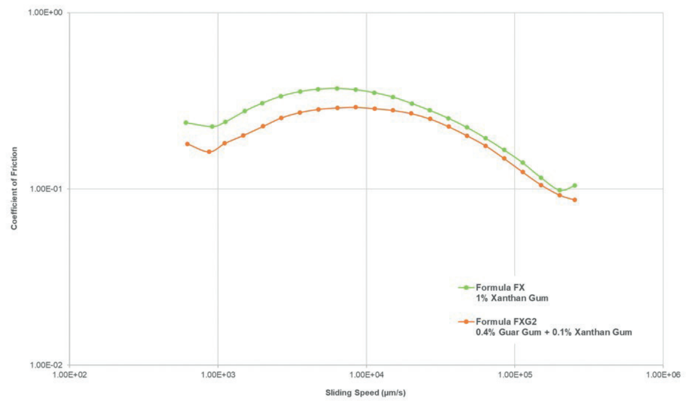

Figure 7. Stribeck curves of samples FX and FXG2.

In general terms, sample FXG2 consistently generates lower friction than FX across the spectrum of sliding speeds under analysis. In other words, product FXG2 is more lubricating or less sticky than FX.

Sensory Assessment

Stickiness at various time points and after-application skin feel were evaluated (Figure 8) by subjecting FXG2 and FX to a sensory assessment performed by nine trained panellists.

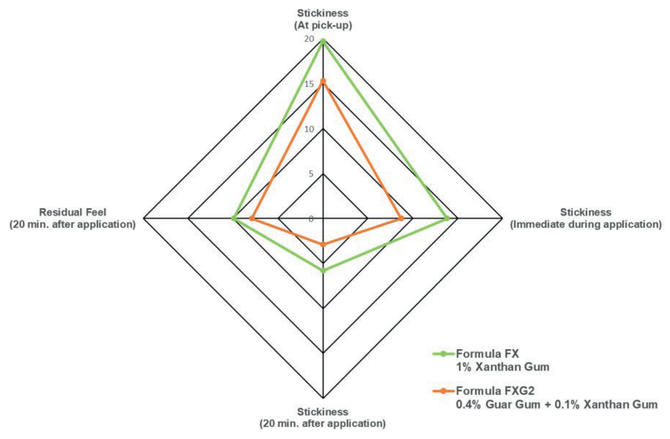

Figure 8. Spider Graph generated from the sensory assessment of FX and FXG2.

The results of the sensory assessment correlate with the tribological evaluation, demonstrating that product FXG2 was perceived as less sticky than FX at all time points.

CONCLUSIONS

We have presented a collection of tests to deepen the understanding of the rheological and sensory properties of synergistic mixtures of Guar and Xanthan gum.
This study was driven by the fact that Guar gum is not widely used in the beauty and personal care industry. This is arguably due to the lack of understanding within the industry of the beneficial properties Guar gum when used alone or in combination with Xanthan gum.

Beyond relevant gains in viscosity, our study findings have shown that using synergistic mixtures of Guar and Xanthan gum makes it possible to reduce the total use level of rheology modifiers in the formulation of beauty and personal care products, while enhancing performance, e.g. boosting lubricity and reducing stickiness.

Though preliminary, these results align with modern formulation trends, such as the use of more sustainable ingredients that are effective in meeting consumer needs.

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