

The Impact of Use Level and Activation on the Interfacial Rheological Properties of NUTRAVA® Citrus Fiber Peak at the Water-oil Interface

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ABSTRACT

The interfacial rheology data reveals that NUTRAVA® Citrus Fiber peak stabilizes water-oil interface through providing structure at the interface.

It is shown that the structure level is highly dependent on the level of activation of the NUTRAVA® Citrus Fiber peak and the more activated it is the more structure evolves at the interface, whereas the use level of NUTRAVA® Citrus Fiber peak has minor impact for the structure at the interface. Whereas when looking at the bulk rheological properties both use level and activation level impact the rheological properties.

INTRODUCTION

Food producers are looking for clean label possibilities¹, including “good for you” benefits, lower number of ingredients, simpler, more consumer-friendly and sustainably sourced ingredients for their products, while still getting the required functionalities like stabilization, suspension, texture/mouthfeel, taste and flavour perception.

NUTRAVA® Citrus Fiber peak (CF) can be used as a clean-label friendly ingredient and the combination of soluble and insoluble dietary fibers fits into the market trend of functional ingredients for use in clean-label friendly food products. One of the food applications in which CF can be used successfully is oil-in-water systems².

CF consists of ~40% insoluble fiber, primarily cellulose, and ~40% soluble fiber, pectin, which is retained during our patented process.

Stabilizing emulsions can be done in different ways, and this investigation focus on the oil-water interface, where interfacial rheology is used to monitor the interaction between CF, oil and water. CF require an activation step to ensure optimal functionality, this investigation elucidate different levels of activation and the use level of CF.

METHODS AND MATERIALS

DOE, Design of experiments, MODDE (version 13 from Sartorius Stedim Biotech, Goettingen, Germany):

The factors investigated: Concentration; 0.1, 0.3 and 0.5% CF and activation level ranging from low-speed mixing (LSM), high-speed mixing (HSM) to homogenization (HOM).

Oil interface: Rapeseed oil (kokkens catering, DK)

Preparing CF dispersions:

Low activation (LSM): Add CF (NUTRAVA[®] Citrus Fiber peak (CP Kelco ApS, Lille Skensved, Denmark)) to water while mixing with a magnet for 5 minutes at 500 rpm. Continue mixing at 300 rpm for an additional 5 minutes, while adjusting pH to 4.2 (+/- 0.2), using 50% w/v citric acid (CAS no. 5949-29-1) solution. Continue mixing for 6min at 700 rpm.

Intermediate activation (HSM): Add CF to water while mixing with a magnet for 5 minutes at 500 rpm. Continue mixing at 300 rpm an additional 5 minutes, while adjusting pH to 4.2 (+/- 0.2), using 50% w/v citric acid (CAS no. 5949-29-1) solution. Move the beaker to Silverson L5M-a (Silverson Machines, Inc., MA, USA) shear at 7500 rpm for 6 minutes.

High activation (HOM): Add CF to water while mixing with a magnet for 5 minutes at 500 rpm. Continue mixing at 300 rpm an additional 5 minutes, while adjusting pH to 4.2 (+/- 0.2), using 50% w/v citric acid (CAS no. 5949-29-1) solution. De-aerate, by use propeller mixer at 200rpm for 2min and remove air bubbles with a disposal pipette. Then homogenize on APV2000 (Grundfos, Hungary) running at 200/50, run on re-circulation for 5min, ensuring all sample have passed through at least three times.

Rheological test:

Structure (G' & G'') and viscosity of the samples were measured at 23°C with an Anton Paar MCR 302 rheometer (Anton Paar GmbH, 8054 Graz, Austria) equipped with a cylindrical geometry (CC27). After loading the sample into the rheometer allow 2 minutes of waiting time before measurement is started.

Time sweep: time = 300s, strain = 0.3%, frequency = 0.1Hz (10 measuring points, measuring point duration = 30s), G' after 300s is extracted. Strain sweep: Strain amplitude 0.1 ... 100% (log distributed).

Interfacial rheology test:

Using the double wall ring³ (DWR) for TA instrument DHR3 rheometer (TA instruments, New Castle, DE 19720, USA), **Fig. 1**. Set the interface: Add the bottom layer, fill it up to the marker in the bottom geometry. Move the ring down to ~13000 μ m. To ensure that the ring is placed in the middle of the interface monitor the axial force and stop the program when a sudden drop is observed, this is the gap where the top of the ring hit the interface, subtract further 500 μ m from the reading and this is the interface gap. Cover the surface with rapeseed oil, measurement conducted at T = 23°C.

In sequence: Time sweep: Time = 30000 s, frequency 0.1 Hz, strain 0.3%. Frequency sweep: Frequency 100 – 0.001rad/s, strain 0.3%. Wait 1800s no data collected, Strain sweep: 0.001 – 100%, 7 points / decade, frequency 0.1Hz. Wait 1800s no data, then Flow curve: Shear rate 0.1 – 300s⁻¹, 10 points / decade.

RESULTS

Measuring interfacial structure may be challenging as the structure of the CF dispersion already has structure when activated by HSM or even more when activated by HOM, this structure of the dispersion causes the surface to be slightly uneven making it difficult to place the ring directly at the interface between oil and water as illustrated in **Fig. 1**. This may result in larger standard deviation between measurements.

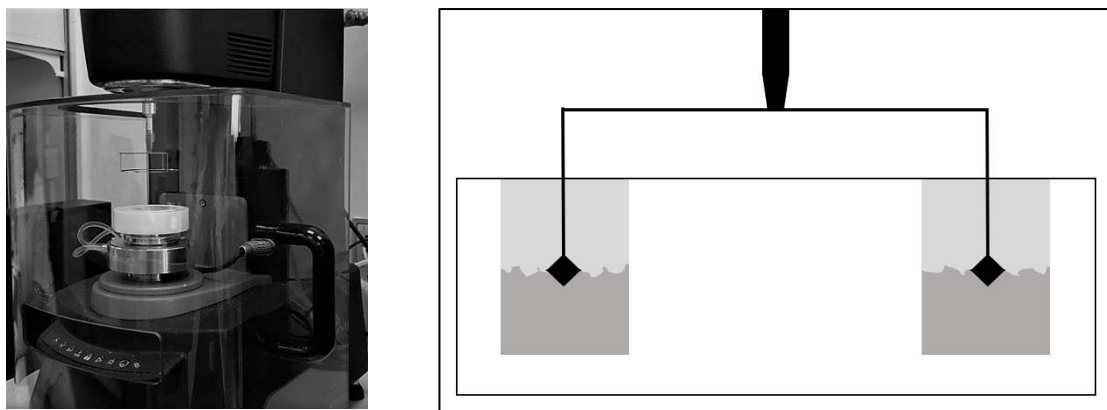


FIGURE 1: TA instrument DHR3 rheometer equipped with a Double Wall Ring (DWR) system, and illustration of uneven surface at the interface between oil and CF dispersion resulting in difficulties in placing the ring in the DWR geometry

The CF dispersions were prepared according to the DOE, listed in **Tab. 1**, and both the interfacial and well as the bulk rheology were measured. The collected responses for structure were G'_I (Interfacial modulus) after 30000s, G'_B (Bulk modulus) after 300s. The summary of fit of the models is shown in **Fig. 2**, R^2 = Shows the model fit and Q^2 = Shows an estimate of the future prediction precision future more the difference between R^2 and Q^2 should be smaller than 0.3 for a good model. The coefficients for the scaled and centered factors with error bars and the observed response versus the predicted response are plotted.

TABLE 1 (right): DOE – Factors: CF% and CF dispersion activation level (LSM, HSM, HOM)

Exp No	Exp Name	Concentration (%)	Activation level
1	N1	0.1	LSM
2	N3	0.1	HSM
3	N5	0.1	HOM
4	N7	0.3	LSM
5	N8	0.3	HSM
6	N9	0.3	HOM
7	N10	0.3	HSM
8	N2	0.5	LSM
9	N4	0.5	HSM
10	N6	0.5	HOM

The interfacial structure (G'_I) can be predicted very well as the model fit $R^2 = 0.90$ and robustness $Q^2 = 0.85$ is high. It is seen that the concentration is not a significant factor, but the level of activation is significantly changing the structure at the interface. LSM providing the lowest structure and HOM the highest structure at the interface. Whereas for the structure in the bulk rheology (G'_B) both the concentration and level of activation is significant factors. The G'_B can be predicted very well as the model fit $R^2 = 0.98$ and the robustness $Q^2 = 0.94$.

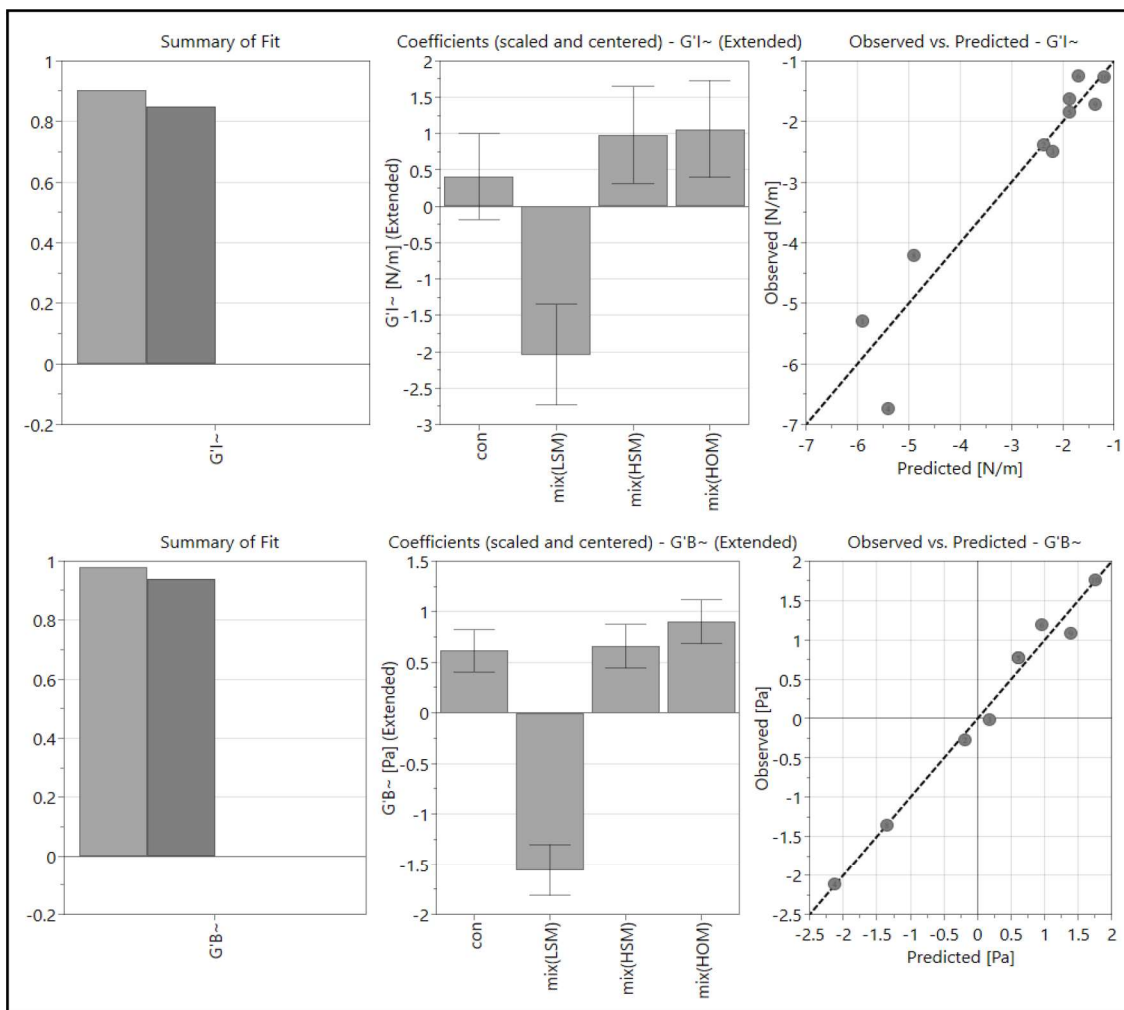


FIGURE 2: Summary of Fit of the model, showing R2 and Q2 of the model, coefficients (scaled and centered factors with error bars) and the observed response and predicted response are plotted for the interfacial structure (G'_I) Model fit R2 = 0.90; robustness Q2 = 0.85, top plots, and the bulk structure (G'_B) Model fit R2 = 0.98; robustness Q2 = 0.94, bottom plots ($c = 0.1\%$ LSM excl. as an outlier)

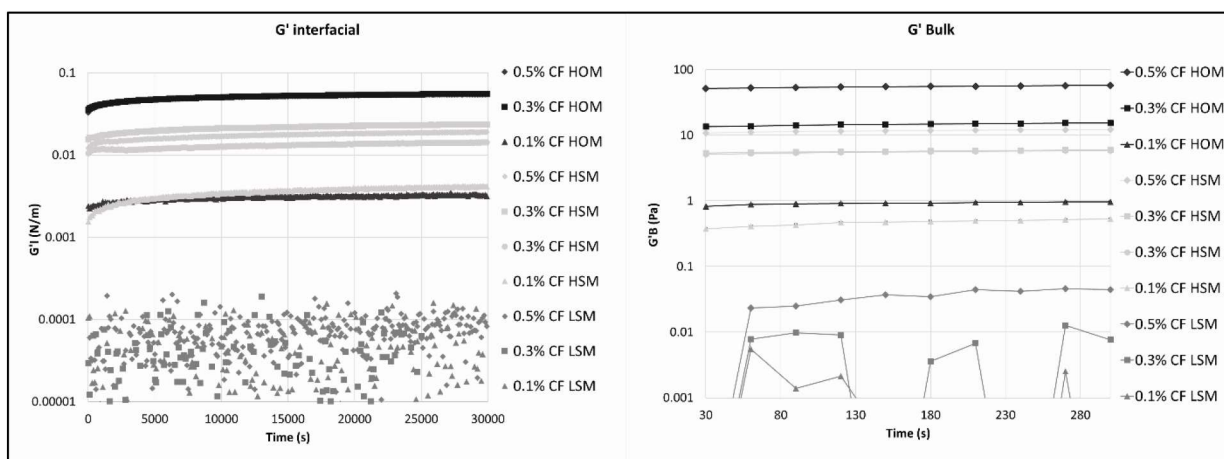


FIGURE 3: The structure G'_I (Interfacial rheology, left plot) and the structure G'_B (Bulk rheology) as a function of time for different CF concentrations and level of activation, the 2 repeated 0.3% CF activated with HSM indicates the repeatability

The development of structure as function of time is seen in **Fig. 3**, the structure at the interface builds is already there at the beginning of the measurement and still builds up over time and reaches a plateau after at least 10000s, although at low activation levels does not provide structure at the interface nor does it build up over time. From the bulk measurements it is seen that there is structure in the CF dispersions from the beginning and it does not change in time, also for the bulk rheology the low activated CF does not have a lot of structure and increasing CF concentration result in increased $G'B$.

Extracting the structure after the time sweep and comparing $G'I$ and $G'B$ shows that there is a clear trend that increasing concentration as well as increasing level of activation increases the bulk rheology properties, whereas it is not as clear for the interfacial properties, **Fig. 4**.

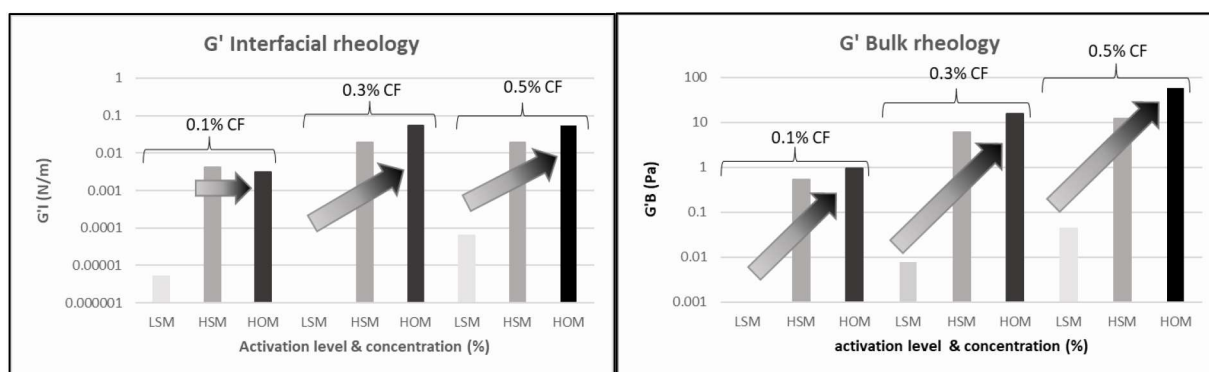


FIGURE 4: The structure $G'I$ (Interfacial rheology, left plot) and the structure $G'B$ (Bulk rheology) as a function of time for different CF concentrations and level of activation

CONCLUSION

The interfacial rheology data reveals that one of the mechanisms, that NUTRAVA[®] Citrus Fiber peak can stabilize water-oil interface is through providing structure at the interface.

It is shown that the structure level is highly dependent on the level of activation of the NUTRAVA[®] Citrus Fiber peak and the more activated it is, the more structure evolves at the interface, whereas the use level of NUTRAVA[®] Citrus Fiber peak has minor impact for the structure at the interface.

Looking at the bulk rheology both use level and activation level impacted the rheological properties. Increasing use level result in increased Structure ($G'B$) as expected, and it was seen that level of activation also increase the structure $G'B$ $LSM < G'B HSM < G'B HOM$.

REFERENCES

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