Real time monitoring of emulsions stability thanks to microrheology

Introduction

Emulsions are commonly used in food and cosmetic industries. Their shelf life is very important for the supplier and also for the customer. For many years, soluble polymers have been routinely added to emulsions and suspensions in order to improve their stability. These polymers enhance the stability by providing a gel like behaviour, leading to precise viscoelastic properties. These properties drive several end use properties such as physical stability or efficiency during use.

There are many interests in using an optical technique such as microrheology and Rheolaser® LAB6 to monitor viscoelastic properties with the aim of characterizing the stability: working without shear on weak gels, monitoring the rheology versus ageing time on the very same sample, thus simulating the behaviour of the emulsion in the packaging, and determining its stability completely at rest.

In this example, the purpose is to monitor the emulsions rheological properties and the effect of various polymer concentrations on the emulsion stability time. Four emulsions (20% v/v) with different xanthan concentrations (0.12 to 0.4%) are analysed in order to rank them depending on their stability.

Basics on the emulsion stabilization

Xanthan, considered such as a non-absorbing polymer, plays the role of a depletion flocculent and create a transient gel with the emulsion, a percolation network forms. The integrity of the gel persists for a given period of time, and local fractures appear, the structure collapses suddenly, then a denser creamed phase forms. This phenomenon is called delayed creaming.

Raw data: Particles Mean Square Displacement (MSD)

In microrheology, droplets probe the viscoelastic behaviour of an emulsion. Thus, particle Mean Square Displacement curve is the signature of the product rheology. The evolution of the MSD curves versus ageing time is then characteristic of the viscoelastic properties variations (Microrheology concept). Rheolaser® LAB enables to monitor rheology on a very same sample during ageing time.

Figure 1. Mean Square Displacement evolution of the emulsion (20% v/v) with 0.12% xanthan polymer
Rheolaser main assets:
- 1-click experiment & results;
- Measurement at rest;
- Non intrusive measurement;
- Ageing analysis on the very same sample.

The user can observe the evolution of the MSD curves from long to short displacement meaning an increase of elasticity and from short to long decorrelation time meaning an increase of viscosity (step 1). This step monitors the network flocculation and then stabilization. The network reaches an equilibrium and remains stable (step 2).

After 4 hours, the curves don’t move toward the bottom anymore (elasticity is constant), but the user can observe the curves moving back to the left, meaning a decrease of the viscosity, thus a physical destabilization of the samples. The structure is breaking (step 3). This is the beginning of microstructure evolution.

These changes can be quantified thanks to the following microrheological parameter: Macroscopic Viscosity Index (MVI) as shown below.

**Stability of the emulsions**

The macroscopic viscosity index (MVI) is directly obtained from the MSD curves (figure 1). Its evolution shows a first increase in step 1, then a plateau followed by a drop corresponding to step 3. So when the viscosity begins to decrease, the sample becomes unstable at the microscopic scale. The drop of the viscosity index appears later when the xanthan concentration increases. The more thickener is added to the emulsion, the more the creaming is delayed.

**Comparison with eye observation**

The figure 3 gives the destabilisation times measured with Rheolaser (corresponding to the drop of MVI) and macroscopic scale (visual observation). The microscopic scale detects destabilisation phenomenon much earlier meaning that the microstructure begins to destabilize before the sample changes at the macroscopic level, thus enabling the operator to rank quickly its formulations in terms of stability, contributing to decrease the time to market. The correlation between the two methods is good, the more structured is the sample (the higher is the xanthan concentration), the longer it is stable (the later is the viscosity drop time).

**Summary**

Monitoring the emulsion stability depending on the polymer concentration without external force and on the very same sample is one of the challenge of the industry. The use of Rheolaser allows the user to adjust its formulation and easily monitor the effect of the polymer concentration on the shelf-life of its formulated products.

Rheolaser® is a powerful tool, which can fully and easily characterize, in real time, the viscoelasticity of emulsion-gels versus ageing time. Measurement is done thanks a non-contact method which enables to analyse the sample without any external influence, on the very same sample.