



STATIC MULTIPLE LIGHT SCATTERING TO PREDICT LONG TERM STABILITY OF EMULSIONS WITH POLYMERS

INTRODUCTION AND LITERATURE MICROSCOPIC APPROACH

Polymers are widely used in the industry to control viscosity, provide end use properties and enhance the shelf life. At high concentration, the polymer stabilizes the emulsion forming a percolated network, which can persist for a very long period of time (months), but ended always to collapse and giving two separated phases. This kind of emulsions is very problematic for industry as no method exists to predict the breaking of the emulsions, samples can be qualified stables in QC-tests and break after during commercialization.

Teece & al. show from confocal microscopy measurements that for O/W emulsions with xanthan, droplets form a network with strands of thickness l_s and mesh size ξ depending on polymer concentration (see figure hereunder). They correlate this size properties with visual observation of destabilization. The smaller the cages and the thinner the strands, the longest the delayed collapse. This method with confocal microscopy detection is powerful but not ready to use for industry, requires to add fluorescent agent, to have experience to fix parameters and obtain good quality images.

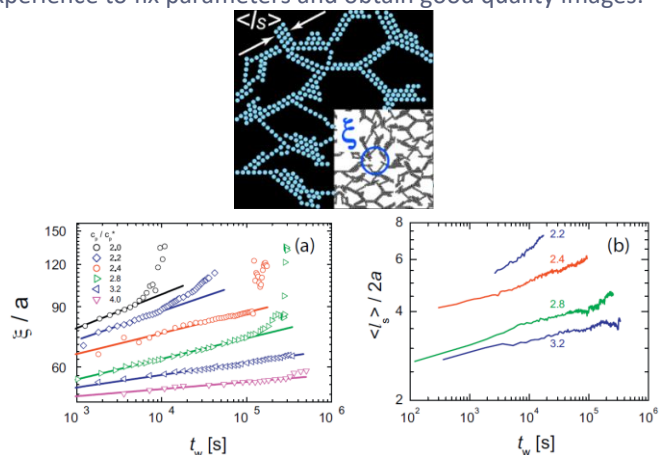


Figure 1: top = Schematic of an emulsion gel with droplets forming a network of strands l_s with cages with mesh size ξ - bottom = ξ and l_s evolution for different xanthan concentrations (ref : Teece & al., Colloids and Surfaces A: Physicochem. Eng. Aspects 458, 2014, 126-133)

In this note we propose to use Turbiscan technology with Static Multiple Light Scattering method to predict stability time of O/W emulsion + different polymer by in correlating the initial size variation with the destabilisation time (both are measured at early stage with the Turbiscan) which is directly related to the shelf life. The results will be compared with data extracted from the Teece publication.

SAMPLES DESCRIPTION

O/W systems analyzed in this note are similar to the ones studied in the publication but closer to the industrial systems in terms of components and droplet size as given in the table below.

	In this note	Teece & al.
Oil	Sunflower	PDMS
Continuous phase	Water + tween20 + NaCl	Water + 1,2-ethane diol
Volume fraction	0.05	0.21
Droplet size (μm)	2.0	0.3
rg/a	0.04	0.62
Polymer nature ¹	Xanthan (HEC, Carrageenan)	Xanthan
Polymer c/c* range	3.5 to 10	2.4 to 4.8

¹Note that NaCl is added to polymer during preparation.

PHENOMENON & RESULTS

SMLS analysis with Turbiscan Technology

Analyses on the emulsions have been performed at ambient temperature with the Turbiscan®. The typical evolution for such emulsions in the reference mode is presented on the figure below.

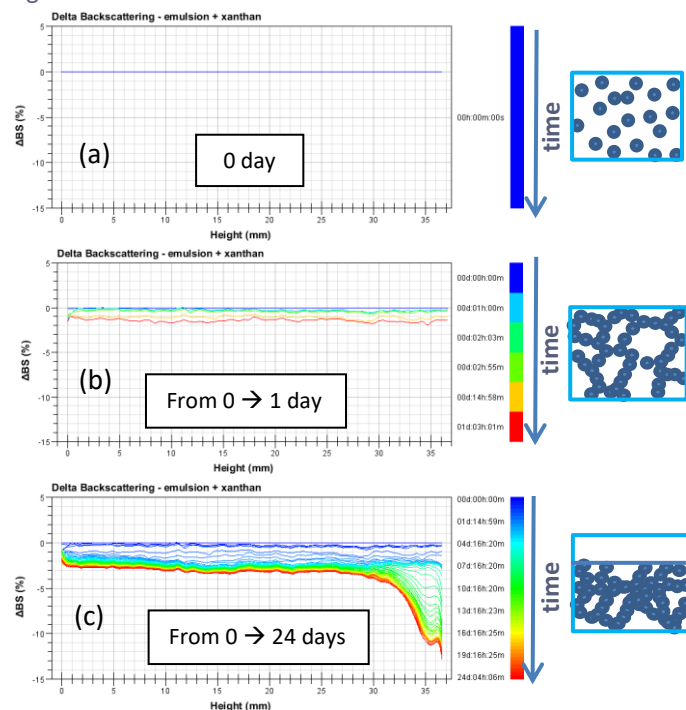


Figure 2: Delta-backscattering for formulation with xanthan at 25°C and schematic representation of the emulsions droplets.

The samples evolve as described in figure 2 :

- (a) The sample is rather homogeneous at *time 0*, the droplets are well dispersed
- (b) *During the first day*, the signal evolves all over the height of the sample meaning size variation → the droplets form a percolation network with strands of droplets
- (c) The decrease of the backscattering level at the top of the sample enables to detect *early* clarification at the top of the sample → the system collapses

Correlation with Teece&al. results

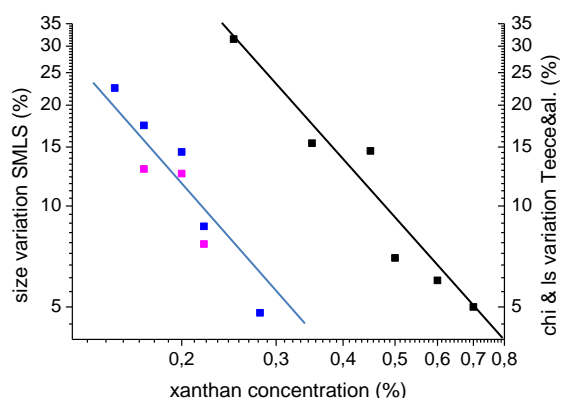


Figure 3 : Size variation measured with SMLS compared with ξ and l_s variation data obtained with confocal microscopy

The figure 4 shows that even the compared systems are not exactly the same in terms of concentrations, interactions, the evolutions are similar. SMLS enables to monitor size evolution. Both techniques show that size variation decreases with polymer increase and even for samples with large xanthan concentration comparable with commercial products.

Comparison with other methods

As explained before, Turbiscan signal measured at rest and without dilution enables to monitor size variation over the first days of analysis.

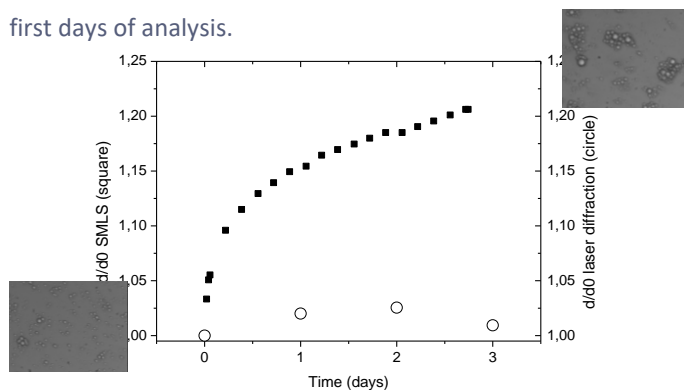


Figure 4: Size variation measured with SMLS (full squares), laser diffraction (open circles) and images with microscopy

We see that only measurement at rest enables to monitor size evolution as emulsion gel network is weak and with a low yield.

CORRELATION TO PREDICT STABILITY

The stability time is measured with Turbiscan, it enables to detect destabilization very earlier than visual observation but for the comparison with Teece & al. results, stability is given at visual observation for all data. The following figure gives the correlation between size variation measured after 1 day and stability time of the samples.

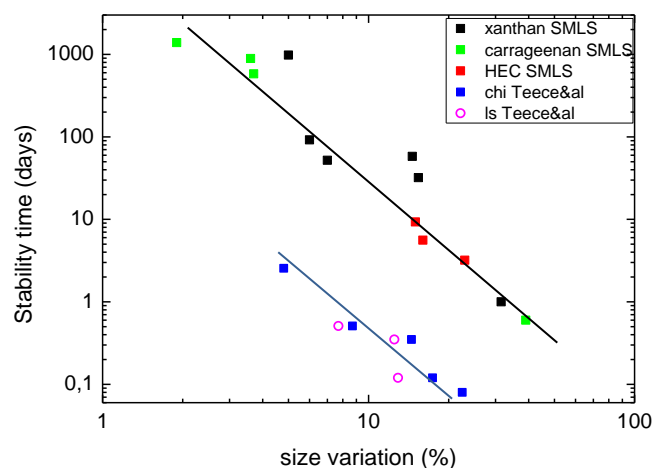


Figure 5: Stability time versus flocculation rate

The data show a good correlation, the lowest the size variation, the longest the stability. When the particle size evolves less than 4%, the emulsion gels will be stable more than 2 years. The results obtained with SMLS are in agreement with confocal microscopy measurements which show the same evolution, not overlaid because the systems have not same concentration, droplet size. The systems tested in this note are 100 times more stable (stable more than 1 year) than the ones tested by Teece as the objective is to analyse samples close to commercial applications and needs in terms of long shelf-life.

SUMMARY

The Turbiscan enables to build a method to predict long term stability of emulsions stabilized with polymers. This method consists in correlating the size variation in the first day with long term stability.

On this case study, measuring the particle size variation over 1 day enables to predict visual stability over more than two years. Note that the Turbiscan stability measurement in backscattering mode is more sensitive than naked eye, up to 50 times faster than eye observation.