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ARTICLE

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Delayed yielding of oil/water emulsions in presence of stabilizing biopolymer

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Abstract

This study investigates the stabilization of oil/water emulsions as a function of addition of a biopolymer (scleroglucan) which acts as an emulsion stabilizer. Rheological characterization in the form of controlled stress creep measurements has been carried out and it reveals the colloidal gel exhibiting a delayed yielding in a certain applied stress window. The delay time and stresses that an emulsion can withstand depend strongly on the concentration of added scleroglucan. Increasing polymer concentration, however, is limited to a maximum value, above which a limited effect on the delay time is observed. Investigating of the emulsion under study was visualized by means of cryo transmission electron microscopy which shows adsorption of scleroglucan onto the surface of the oil particles and a gel-like structure that connects the oil phases. The results mentioned in this study support that scleroglucan-surfactant interactions play a key role in the stabilization of the oil/water emulsion.

KEYWORDS

coatings, polysaccharides, rheology

1 | INTRODUCTION

Understanding and controlling yielding of colloidal gels is of primary industrial interest with problems ranging from application of products (such as deposition, spraying, etc.) to transport and storage. It is well known that gravitational forces limits the shelf-life of colloidal solutions, suspensions and colloidal gels, and the relation between shelf-life, stress, and delayed failure may provide valuable information on how to engineer the increase of τ_d that will result in a longer shelf-life. While this approach can be used to access industrial applications in areas such as in coatings, drug delivery, paints and cosmetics, and so on, it is to be noted that industrial formulations usually contain a variety of added components that play a structural and kinetic role that is not always clear to pinpoint. In many cases, industrial colloidal gels cannot even be produced without such additives, making their study and understanding their performance even more difficult.

Colloidal gels are described as a system where particles attract each other forming aggregated colloidal particles.[1] These aggregates grow as fractal clusters creating a solid-like gel which is also known as a percolated network structure.[2,3] These colloidal systems have a characteristic mechanical response when subjected to stress. The response to an imposed stress depends on the structure of the gel, the energy barriers to flow, and the

recombination rates of the physical bonds that hold the gel together. Typically, for sufficiently small applied stresses and relatively short times, the material responds as a mechanically stable elastic solid[3–5] and the observed strain is independent of time. However, for higher applied stresses that are maintained for longer times, catastrophic yield of the gel is observed. This is known as delayed yielding, delayed failure, or delayed collapse, and it is associated to a delay time, τ_d.[1,3,6] This delayed failure is also observed in polymeric gels and is often described as an exponential dependence of τ_d on the applied stress. The delay time, τ_d, decreases with increasing stress. In gels, such behavior results from stress-enhancement of the thermal relaxation of individual bonds within the network as presented by Skrzeszewska et al. and Bonn et al.[7,8] Although similar relation between stress and delay time is also applicable for colloidal gels[4,5], Sprakel et al.[1] found that the delay time exhibits two regimes reflecting the heterogeneous and multiscale structure of colloidal systems. The two regimes are universal for colloidal gels and can be explained by generalizing the bond-rupture model and the intrinsic heterogeneity of colloidal gels. Their model distinguishes two regimes, one at high σ, where the rupture rate is higher than the rate of recombination, resulting in an instant failure and in line with the single-bond-rupture model for polymer gels and another regime, for low enough applied stress, where the rate of bond-rupture is smaller than the reforming rate making it unlikely that failure readily occurs. Both regimes exhibit exponential dependency of τ_d on σ, but with different characteristic stresses. These features describe the two different observed delay regimes.[1,3]

Within this context, we present here a study on creep of a bitumen emulsion as a colloidal system which is stabilized by scleroglucan[9,10] and try to elucidate the contribution of polymer to the behavior of these gels. This biopolymer is a neutral polysaccharide produced by the fungus *Sclerotium rolfsii* by an aerobic fermentation process[11,12] in the form of linear rod-like triple helices held together by intermolecular hydrogen bonds.[13,14] As the rod-like polymer is used as an emulsion stabilizer, it is expected to coat the bitumen particles. However, scleroglucan itself can also form a gel and may also connect neighboring emulsion droplets.[9,10]

Creep tests were performed to access the stabilization properties in terms of delayed failure of bitumen emulsions with increasing scleroglucan concentration. We will explore the jamming/percolation/gelation behavior of a colloidal system with increasing amount of biopolymer in order to assess the stabilizing properties of scleroglucan.

It is worth noting that this somewhat industrial scleroglucan stabilized bitumen water system has some very useful features that allow the investigation of the more fundamental colloidal gel stability phenomenon. As show previously (S. El Asjadi, 2017 #486), the stabilization of the emulsion occurs at a remarkably low scleroglucan content, the gravitational stress itself on the bitumen particles is remarkably small, due to a small density difference, and the particles are extremely well dispersed as they result from extensive experience of an industrial scale bitumen emulsification process. Finally rather large sample volumes are available allowing easy visual inspection of the overall emulsion stability, and facilitating high precision rheological characterization.

2 | EXPERIMENTAL SECTION

2.1 | Materials

Scleroglucan, BioStab MY (supplied by Latexfalt BV, Koudekerk aan de Rijn, The Netherlands) is used as a biopolymer stabilizer. Redicote E9 (AkzoNobel Surface Chemistry AB, Stenungsund, Sweden) is a fatty amine emulsifier origination from a fatty acid where the acid group is replaced by a diamine [(N-hexadecanoic-1,3-propanediame)-1,3-propane diamine]. The bitumen used, with dynamic $\eta_{@60\,^\circ C} \geq 175$ Pa s (penetration grade 40–60 mm/10), was supplied by Total (Total refinery, Belgium) and was tested according to the EN 12596 test method by the supplier. This is the same bitumen as used in commercially available bond coats (Modimuls TT, produced and commercialized by Latexfalt BV, The Netherlands). All other chemicals used were of analytical grade. An Atomix emulsification unit (Emulbitume, France) is used to prepare the emulsions.

2.2 | Sample preparation and characterization

The soap phase was prepared by heating water and adding hydrochloric acid and a C18 di-amine emulsifier in the range of 0.2 and 0.3 wt%/wt% while stirring. Hydrochloric acid was added until a pH value around 2 is reached, in order to activate the surfactant, protonating and hence charging the amine moieties. The soap phase was divided into five fractions to which mixtures of scleroglucan predispersed in food grade vegetable oil, in a 1:2 weight ratio, were added in order to obtain the following scleroglucan concentrations: 0, 0.05, 0.1, 0.15, and 0.20 wt%/wt%. The oil prevents the formation of lumps by facilitating dispersing, followed by rapid dissolution. In this way, homogenous solutions were obtained. The emulsions were produced from the above-mentioned

bitumen. Both the soap phase and the bitumen were fed at elevated temperatures, 50°C and 148°C, respectively, to an Atomix emulsification unit.

The solid content of the emulsion is determined by means of evaporation of all volatile components (predominantly water) and determination of the final weight. The value of the solid content is in a range between 42.7 and 43.2 wt%. The amount of scleroglucan within the final emulsion corresponding to the soap-phase content can be found in the Table 1.

A laser diffraction particle size analysis instrument Microtrac S3500 from Anaspec Solutions is used to analyze the particle size by feeding the Microtrac a 10 wt% emulsion, which was made by diluting the original emulsion with the soap-phase. The average particle size range between 7.5 and 15 μm. The pH value of the emulsion was measured using a calibrated Perkin Elmer pH meter giving us a pH value between 2.2 and 2.3.

2.3 | Rheology

The emulsions were investigated using a concentric cylinder geometry with a bob diameter of 30.28 mm, a bob length of 42.00 mm, a gap of 5,920 μm on an ARG2 rheometer with a Peltier temperature control system from TA Instruments, using a solvent trap to prevent evaporation. The emulsions were loaded by means of a syringe and remained unperturbed for 15 min before starting the experiment. Creep experiments where performed with stresses ranging from 25 to 0.0005 Pa depending on the polymer concentrations at a temperature of 25°C. These sets of experiments are used to determine the delay time of the oil/water emulsions as a function of the biopolymer concentration.

2.4 | Cryo transmission electron microscopy

About 3 μl of the sample was casted on to a Cu 200 mesh Quantifoil grid and blotted against filter paper for 3 s following which it was plunged into liquid ethane using Leica Vitribot. The vitrified samples were then transferred to a Gatan cryo specimen holder which was further loaded into a JEOL JEM-1400 Transmission Electron Microscope. The specimens were then imaged at an acceleration voltage of 120 kV under low dosage conditions.

3 | RESULTS

3.1 | Creep tests of biopolymer stabilized oil/water emulsions

The prepared emulsions are subjected to various stresses ranging from 0.005 to 10 Pa depending on the scleroglucan concentration. The resulting strain is measured as a function of the time and is shown in Figure 3. We can distinguish three different creep profiles, depending on the applied stress and the scleroglucan concentration in the oil/water system. A schematic overview is represented in Figure 1 (graph 1) explaining the different types of curves.

We observe an initial creep response which is elastic for the three different creep profiles. However, at very high stress instant failure occurs and no time-independent creep is observed. Thus, at very high stresses, we do not observe a delay time (τ_d). This instant failure is present in every emulsion shown in Figure 1. The magnitude of the applied stress for instant failure depends strongly on the scleroglucan concentration. In the emulsion with no scleroglucan, instant failure already occurs at a stress as low as 0.005 Pa (Figure 1, graph 2). In these emulsions, no delay time is observed. The stress where *instant failure* occurs increases with increasing scleroglucan concentration. For the emulsion with 0.20 wt% scleroglucan, this stress reaches a value of 6 Pa (Figure 1, graph 6.). At a certain stress, depending on the emulsion, we observe a delayed failure or a delay time (τ_d). The delay time (τ_d) and the duration of this phenomenon depends strongly on the applied stress and scleroglucan concentration. As mentioned before, in the emulsion without scleroglucan, a delayed failure is not observed. This system apparently is not

TABLE 1 Concentration of scleroglucan at different stages of emulsion preparation

Scleroglucan/oil in soap-phase (wt%/wt%)	Scleroglucan in soap-phase (wt%/wt%)	Solid-content (wt%/wt%)	Water-content (wt%/wt%)	Scleroglucan final emulsion (wt%/wt%)
0	0	42.7	57.3	0
0.05	0.17	43	57	0.01
0.1	0.033	43.1	56.9	0.019
0.15	0.05	43.2	56.8	0.028
0.20	0.067	42.9	57.1	0.038

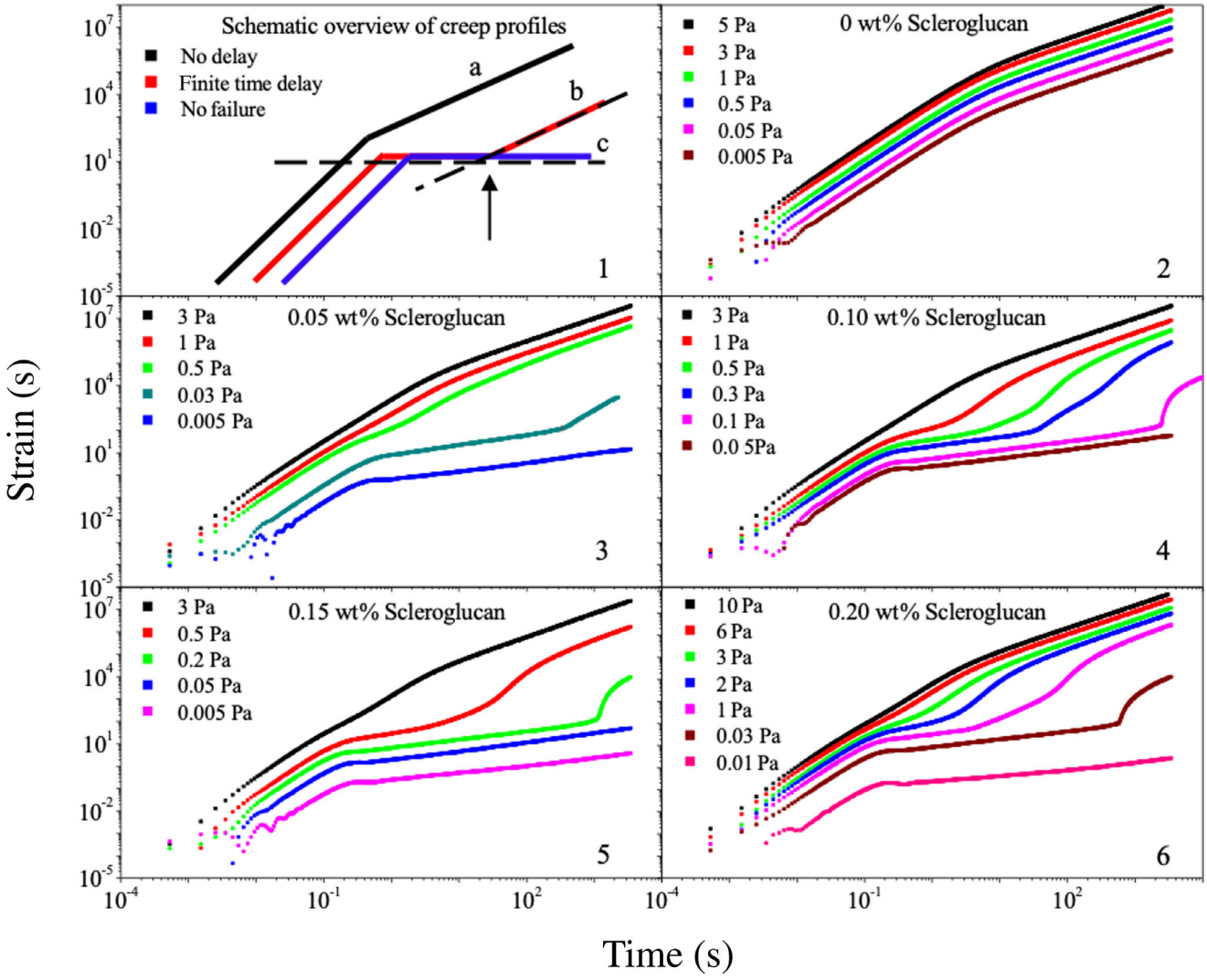

FIGURE 1 (1) Schematic overview of the different creep profiles observed in the creep experiments. The arrow indicates the delayed yielding time. This intercept of two lines results in the delay time at a certain stress. These delay times are calculated and plotted in Figure 2. At very high stresses, the initial response is elastic and at a certain time instant failure occurs (Line a). There is no delay time observed. At high stresses, the initial response remains the same, a time-independent region occurs (Line b). However, this is only for a finite time. At this point, the sample fails and the strain increases sharply. At low stresses, the initial response is the same (Line c). At a certain point, the strain becomes nearly independent of time. No failure is observed over the entire duration of the experiments. (2–6) Creep response of oil in water emulsion at 41 wt%: (2) 0 wt% biopolymer, stress = 5.0–0.005 Pa, (3) 0.05 wt% biopolymer, stress = 3–0.005 Pa, (4) 0.10 wt% biopolymer, stress = 3–0.05 Pa, (5) 0.15 wt% biopolymer, stress = 3–0.005 Pa, and (6) 0.20 wt% biopolymer, stress = 10–0.01 Pa [Color figure can be viewed at wileyonlinelibrary.com]

capable to withstand even low stresses of 0.005 Pa. The emulsions with scleroglucan show a delay time that becomes more prominent at lower stress levels. We also observe that the *resistance to stress* is stronger for emulsions with a high scleroglucan content. A content of 0.05 wt% can withstand a stress of 0.5 Pa (Figure 3b), for the 0.20 wt % scleroglucan emulsion a stress of 3 Pa. Note that the duration of τ_d is relatively short for these stresses. As the delay time depends on the applied stress, a plot with the stress as a function of the delay time τ_d is generated (Figure 2) for each emulsion.

The emulsion without scleroglucan showed no delay time and therefore is not included in Figure 2. A power law regression is plotted and shows an exponential relation between the applied stress and the delay time. The stress observed in this emulsion due to gravitational forces can be estimated using the following equation where the density difference is 36 kg/m^3 and radius 5 μm.

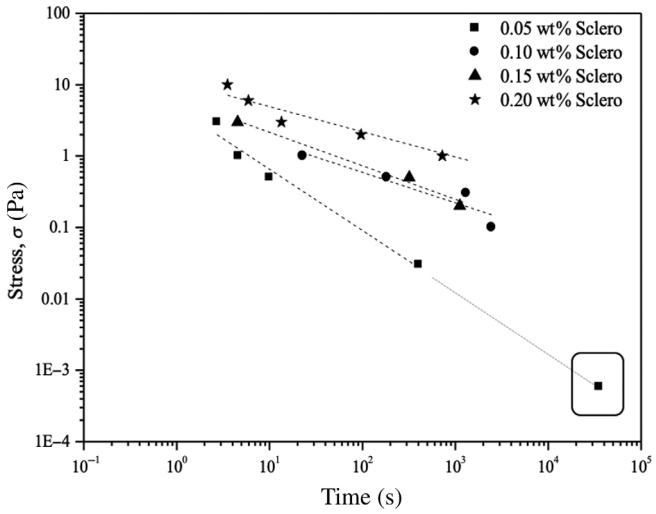

FIGURE 2 Stress as a function of the delay time. ■ 0.05 wt% scleroglucan, • 0.10 wt% scleroglucan, ▲ 0.15 wt% scleroglucan, and 0.20 wt% scleroglucan. A power law regression is used to extrapolate to the stress excerted by gravitational forces. The data point inside the square for 0.05 wt% is the estimated delay time calculated using Equation (1) and is also plotted in Figure 3

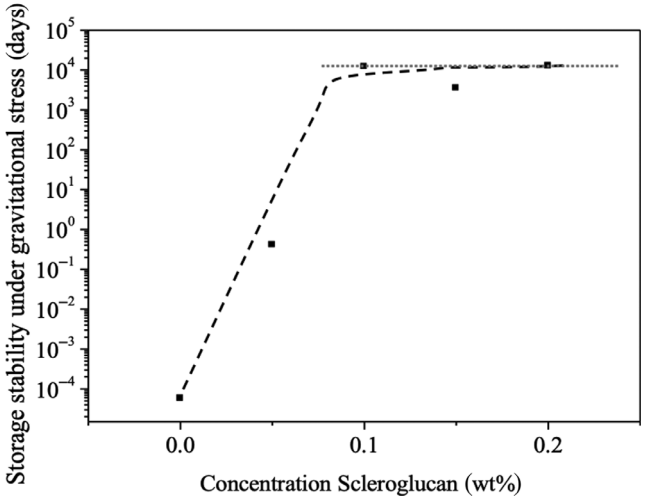

FIGURE 3 Delay time under gravitational stress in function of the scleroglucan concentration. Note the time scale is in days, not seconds

$$
\begin{aligned}
&F_T = F_b - F_a \\
&F_T = g \cdot \Delta\rho g V_b = g \cdot \Delta\rho \frac{4}{3}\pi R^3 \quad A = 4\pi R^2 \\
&\sigma_{\text{buoyancy}} \approx F_T / A \\
&\sigma_{\text{buoyancy}} = 5.9E^{-4}\ \text{Pa}
\end{aligned}
\tag{1}
$$

Using the power law regression and the estimated stress, the delay time at gravitational forces can be calculated. An example of such calculation is depicted in the notes section and plotted in Figure 2 as illustration. The calculated delay time is plotted in function of the scleroglucan concentration and can be found in Figure 3.

The delay time in Figure 3 shows a strong scleroglucan dependency. We observe a significant increase of the delay time when we increase the scleroglucan concentration from 0 to 0.05 wt%.[1] This increase stagnates at a scleroglucan concentration of about 0.1 wt%. Beyond this point, an increase of polymer does not seem to result in an increase of the observed delay time. As an increase of the delay time can be correlated to the stability of the emulsion under investigation, we can state that the introduction of scleroglucan gives rise to a substantially more stable emulsion. The stabilization properties of scleroglucan are already present at very low concentrations, at or below 0.05 wt%.

3.2 | Visualization of O/W system stabilized with scleroglucan

Cryo transmission electron microscopy (Cryo-TEM) images were taken to gain more understanding on the structural composition of the oil/water system and the behavior of scleroglucan as a stabilizer. We studied the emulsion with a biopolymer concentration of 0.04% scleroglucan which is the standard used in industrial application of the described system. In order to prevent the emulsion from collapsing, thus losing the internal structure, the samples where studied at cryogenic temperatures (liquid-nitrogen temperatures). These images are presented in Figure 4.

Inspecting Figure 4, we can distinguish two different phenomena. We observe adsorption of scleroglucan chains onto the surface of the droplets creating a barrier that induces a more stable emulsion in terms of aggregation and coagulation,as these adsorbed molecules create a highly hydrated mantle on the droplet surface . This can contribute significantly to a reduced coalescence of the droplets. Furthermore, the biopolymer creates a network in the water-phase resulting in a more stable emulsion in terms of sedimentation or creaming. These two stabilization mechanisms generate a colloidal system with an increased stability that can withstand sedimentation and aggregation/coagulation forces.

4 | DISCUSSION

The emulsion without polymer does not show the behavior of a colloidal gel, as a delay time (τ_d) is not observed even at low stresses of 0.005 Pa (Figure 1, graph 2). The polymer modified emulsions exhibits the

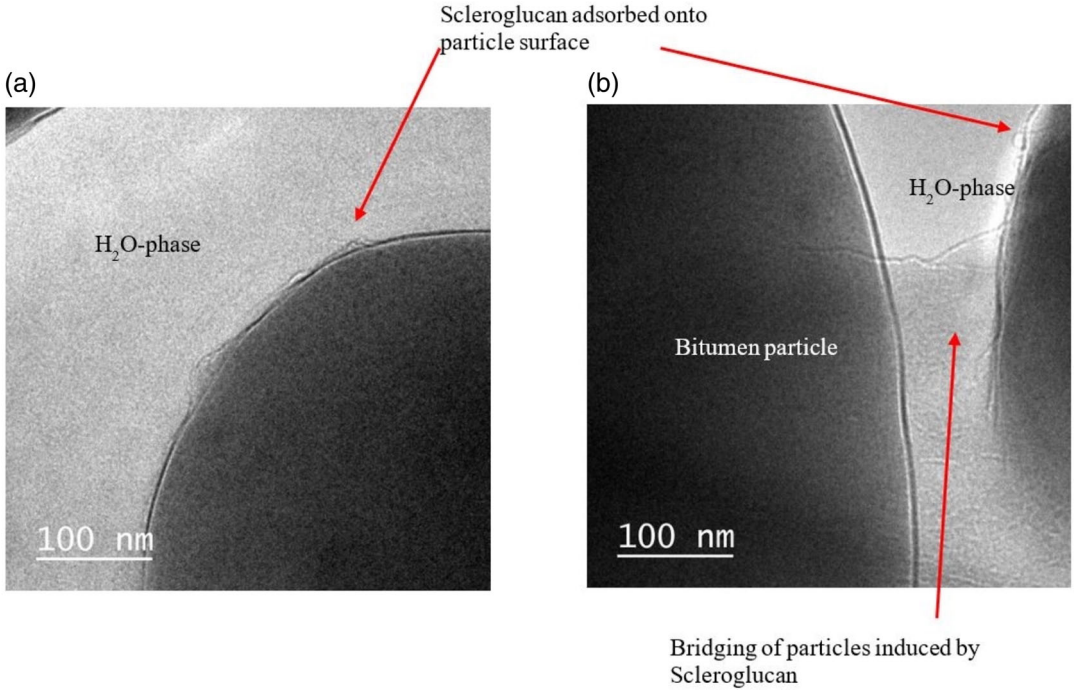

FIGURE 4 Cryo-TEM images of an oil/water emulsion with 0.04 wt% scleroglucan and a solid content of 43 wt%. (a) Scleroglucan is adsorbed onto the droplet's surface. (b) Observation of adsorbed scleroglucan onto the droplet's surface and gel-like structure between particles. Cryo-TEM, cryo transmission electron microscopy [Color figure can be viewed at wileyonlinelibrary.com]

behavior of a colloidal gel (Figure 1 graph 3–6). We observe the typical three regimes mentioned by Sprakel et al. and Lindström et al.: (a) elastic response, (b) time-independent creep, and (c) sudden failure.[1,3] The observed delay time strongly depends on the applied stress and decreases with increasing stress as is also observed by Gibaud et al. and Gopalakrishnan et al..[4,5] Beside the effect of the applied stress on the delay time, a second parameter is investigated, namely the polymer concentration. Our results clearly show a delay time (τ_d) dependency on the scleroglucan concentration. An increase in polymer concentration results in an increase of the delay time and the sudden failure is postponed. During this delay time, our results suggest that the particles in the gel network undergo fully elastic reversible displacements and this is attributed to the complex viscoelastic response of the gel. At the moment gel failure occurs, the gel network integrity is permanently lost due to irreversible plastic rearrangement. This becomes interesting when designing emulsions for industrial application. We observe that at a certain polymer concentration a maximum in the delay time is reached and increasing the polymer content will not result in a further increase of delay time (Figure 3). We can correlate the delay time of the sudden colloidal failure to the stability of emulsions. Hence, addition of scleroglucan results in a more stable emulsion. This last parameter is important during formulation, storage, and application of industrial emulsions. The uniqueness of scleroglucan in our system is due to its capacity to stabilize emulsions at ultra-low concentrations such as 0.05 wt%.[10] Other stabilizers are reported to stabilize at only at much higher concentrations. For example, Traynor reported that emulsions with a xanthan concentration of 0.3 wt% exhibited no sign of phase separation. The storage stability in those system increases when the xanthan concentration is higher than 0.3 wt%. Comparing those concentration to the concentration of scleroglucan used here, one immediately notices the ability of scleroglucan to stabilize our system with increasing of storage stability already starting at 0.05 wt%. The Cryo-TEM images clearly show the adsorption of scleroglucan onto the surface of the emulsion particles. This was already assumed by Lommerts et al. and El Asjadi et al..[9,10] The adsorbed layer of polymer creates steric hindrance, through a hydrated mantle, enhancing the stability of the emulsion during storage. This barrier will prevent the emulsion particle from aggregating and coagulating. A second stabilization mechanism is visually observed. A gel-like structure in between particles creating a weak gel, probably with a yield stress keeping the particles suspended. We believe that these two stabilization mechanisms are responsible for the increased delay time (τ_d) observed in the creep experiments.

5 | CONCLUSION

The oil/water emulsion with scleroglucan exhibits the behavior of a colloidal gel resulting a delayed yielding of the emulsion when stress is applied. We observed a stress dependency of the delay time, increase in stress results in a decrease of the delay time, in these emulsions. However, we also observe a polymer concentration dependence of the delay time. Increasing the polymer concentration results in a delay in the catastrophic colloidal failure. The delay time reaches a plateau and beyond this point an increase of polymer concentration does not result in a further increase in delay time. This increase in stability is attributed to the presence of two stabilization mechanisms that are formed upon addition of Scleroglucan, that is, (a) adsorption of Scleroglucan forming a polymer brush onto the surface of the particles preventing coalescence and (b) a polymer gel in between particles preventing/slowing down sedimentation/creaming depending on the density of dispersed system. This explains the increase in stability observed in the creep experiments. Finally, the use of emulsion storage stability under gravitational stress as a method to probe ultra-low yield stress levels seems to be a viable method to extend rheological data outside the regime that is normally available in rheometry.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

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ENDNOTE

[1] Calculation example: Delay time for 0.05wt% scleroglucan, $y = 4.7088x^{0.858}$ with $y = \sigma_{\text{buoyancy}} = 5.9E^{-4}$ Pa and x = time (s). Solving the equation for x gives a delay time of 35306.4 s or 0.408 day.

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