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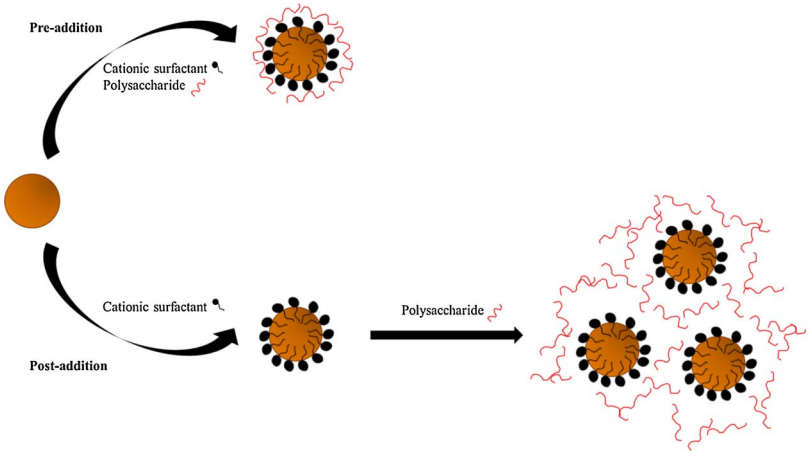
Biopolymer scleroglucan as an emulsion stabilizer

S. El Asjadi[a,b], Q.A. Nederpel[a], I.M. Cotiuga[a], S.J. Picken[b], N.A.M. Besseling[b], E. Mendes[b,*], B.J. Lommerts[a]

[a] Latexfalt B.V., Koudekerk aan den Rijn, The Netherlands
[b] Department of Chemical Engineering, Delft University of Technology, The Netherlands

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we investigated the Stabilization of bitumen emulsions by scleroglucan, a rigid triple-helix forming biopolymer, in combination with a pH-sensitive cationic surfactant. Various aspects of the emulsification process and the final composition influence the Stabilization. We examined two different methods to add scleroglucan to the emulsion: either by adding it to the aqueous surfactant solution before emulsification, denoted 'pre-emulsification addition' (pre-EA), or by addition to the emulsion after emulsification (post-EA). We investigated scleroglucan concentrations in the aqueous phase ranging between 0.017 and 0.07 w/w%. The emulsions were evaluated according to the European EN 13808 standard used for cationic bituminous emulsions, as well as by rheological analysis. We observed an improvement of the storage stability upon pre-EA at a biopolymer concentration as low as 0.017 w/w% in combination with an increased particle size, whereas the breaking index (characterising breaking of the emulsion in presence of 'aggregates' = stones) was not influenced. The rheological data show a minor viscosity increase by scleroglucan in the pre-EA formulation at low scleroglucan concentrations (0.017–0.05 wt.%) where Stabilization already improved dramatically. This indicates that the stabilization mechanism is not only governed by a viscosity increase but also by interfacial stabilisation effects were polymer is adsorbed onto the adsorbed surfactant. In a separate experiment we changed the conformation of scleroglucan by subjecting it to extreme pH values and by dissolution in DMSO, in order to study the role of the triple helix conformation in the stabilization mechanism. Scleroglucan becomes less effective in a denatured and

* Corresponding author.
E-mail address: e.mendes@tudelft.nl (E. Mendes).

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hydrolysed state confirming the crucial role of the triple helix conformation in the Stabilization of bitumen emulsions.

1. Introduction

Bitumen is a residue obtained from crude oil through a distillation process and consists of four groups of components, i.e. asphaltene, saturates, aromatics and resins. Thus, forming a complex mixture of hydrocarbons with some traces of sulphur, nitrogen, and oxygen, as well as metals like vanadium and nickel [1]. The composition depends on the crude oil source and distillation process. Therefore, the properties of bitumen can strongly vary such as viscosity at 60 °C which can vary between 50 and 930 Pa s [1]. At this temperature bitumen behave as viscous liquid and viscosity is almost constant with shear rate. According to Rodriguez-Valverde et al. [2] the charge of bitumen depends on the pH of the medium. In an acidic environment, the polar asphaltene fraction becomes positively charged. In a more basic environment it may be charged negatively. Bitumen can be emulsified into O/W (Oil-in-Water) type emulsions and used for pavement constructions. Bitumen emulsions have many environmental benefits such as the elimination of emissions associated with heating and solvents [3]. These emulsions can be cationic, anionic or non-ionic depending on the chosen emulsifier. They are usually designed as cationic emulsions in the pavement industry where the surface of the bitumen droplets is coated with a positively charged emulsifier giving the droplet a positive surface charge. This positively charged surface will provide good adhesion with the negatively charged gravel/aggregates used during pavement [1,3,4]{Cotiuga, 2010 #153}. The storage stability of such emulsions is crucial, since we aim to obtain a long shelf life and good processability. However, it is also required that the emulsion sets instantly on the aggregates during paving. These conflicting requirements represent a challenge for bitumen emulsion formulations. Furthermore, the storage stability of these emulsions depends strongly on the viscosity of the used bitumen. The higher the bitumen viscosity, thus a lower penetration grade and a higher density, the more difficult it becomes to achieve complete emulsification resulting in a less stable emulsion. This makes it difficult to emulsify high viscous types of bitumen into stable emulsions even with a higher emulsifier content [1,3].

When considering the storage stability of emulsions, it is important to distinguish between thermodynamic stability and kinetic stability [5,6]. All cationic bitumen emulsions are thermodynamically unstable and it is the rate by which several destabilization processes occur (sedimentation, coalescence, flocculation, aggregation, etc.) that determine the lifetime of an emulsion [6].

Lack of stability of bitumen emulsions can lead to the formation of solid sediment causing severe problems in storage tanks, spray trucks, pipes, pumps, etc. In particular this is the case with emulsions produced from high-density bitumen. Improved lifetime of cationic bitumen emulsions can be obtained by increasing the emulsifier content, which will induce smaller droplets [7]. Although this improves the storage stability, it is likely to have an adverse effect on the setting[1] properties of such emulsions, because the concentration of free surfactant after emulsification is likely to be higher, unless more intense emulsification is applied. An increase of stability is also achieved by adding solvent to the bitumen phase. The density difference between the bitumen and water phase decreases by adding solvent. However, this is not attractive from an environmental point of view, as the solvent needs to evaporate. According to Firoozifar et al. [8] lowering the pH to 1.5 also gives rise to a more stable emulsion. This way of increasing the stability is not preferred from a practical point of view as it is considered too acidic. Another possibility is to use high-molecular-weight water-soluble polymers as rheology modifier [9,10]. However, the increase of viscosity will negatively affect the processability of the emulsions, e.g. spraying, pumping, etc. Thus, to improve emulsion properties without affecting its setting behaviour and processability, we looked into biopolymers that tend to adsorb onto the cationic surface of the droplet and thus will not affect the viscosity of the emulsion. Lommerts et al. [11] found that the polysaccharide scleroglucan improves the storage stability of cationic bitumen emulsions without affecting its proccesability.

Polysaccharides are frequently used to stabilize O/W emulsion through various mechanisms: 1) Increasing the viscosity and slowing down the movement of the droplets, including sedimentation [9,10] 2) adsorption onto the oil droplets creating steric hindrance, thus preventing aggregation and coalescence [10,12], and 3) The formation of a three-dimensional network (a gel) creating a sufficient yield stress which prevents sedimentation. When the polymer solution comes in contact with a surface, like that of bitumen particles, polymers may or may not adsorb. For a polymer chain to adsorb, it needs a gain in adsorption energy that compensates for the loss in conformational and translational entropy. Rigid polymers possess less conformational entropy, and thus adsorb much more easily than flexible polymers [13].

Previous studies have shown that a certain polysaccharide of the class 1,3-β-glucans work as a bitumen emulsion stabilizer as it is chemically and physically stable at temperatures up to 50 °C and pH values as low as ~2 (the typical conditions used to produce cationic bitumen emulsions). As observed by Lommerts et al. [11], a significant improvement of the storage stability of a cationic bitumen emulsion occurs when this polysaccharide is added at very low concentrations to the soap phase before emulsification. This biopolymer, known as scleroglucan, is a neutral polysaccharide produced by the fungus *Sclerotium rolfsii* by an aerobic fermentation process [14,15]. Scleroglucan is a branched neutral homopolysaccharide consisting of a (1 → 3)-linked β-D-glucan linear main chain with (1 → 6)-linked β-D-glucopyranosyl groups attached to every third residue along the main chain [14,16,17]. Scleroglucan is produced by the fungus, in the form of linear rod-like triple helices held together by intermolecular hydrogen bonds [18,19]. Hydrogen bonding induced by water molecules are formed between main chain/side chain and side chain/side chain as presented by Okobira et al. [19] The driving forces for the high stability of the triple helix are: 1), a dense hydrogen-bonding network at its center. 2), inter-chain hydrogen bonds between main-chain and lateral glucose residues, 3) when dispersed in water, H-bonds between the main chains and the water molecules as well as side/main chains H-bonds or side chain / side chain H-bonding via water molecules [18–20]. The chemical composition of the scleroglucan backbone, the main chain/side chain and the side chain/side chain hydrogen bonding are presented in Fig. 1a) and b). Fig. 1c) is a simplified artistic impression of scleroglucan without side chains.

The triple-helix is very stiff, with a persistence length of approximately 150 nm at room temperature [17,20,21], making it a good candidate to adsorb onto surfaces. Due to the fact that the adsorption on a surface of a stiff polymer chain hardly influences the chain entropy.

In the present study, we investigate the stabilization ability of Scleroglucan in a 40/60 pen-grade bitumen emulsion and the factors that may influence such systems, and we formulate a hypothesis for the underlying stabilization mechanism.

[1] Setting is the breaking process of sprayed cationic bitumen emulsion on the aggregates used during pavement.

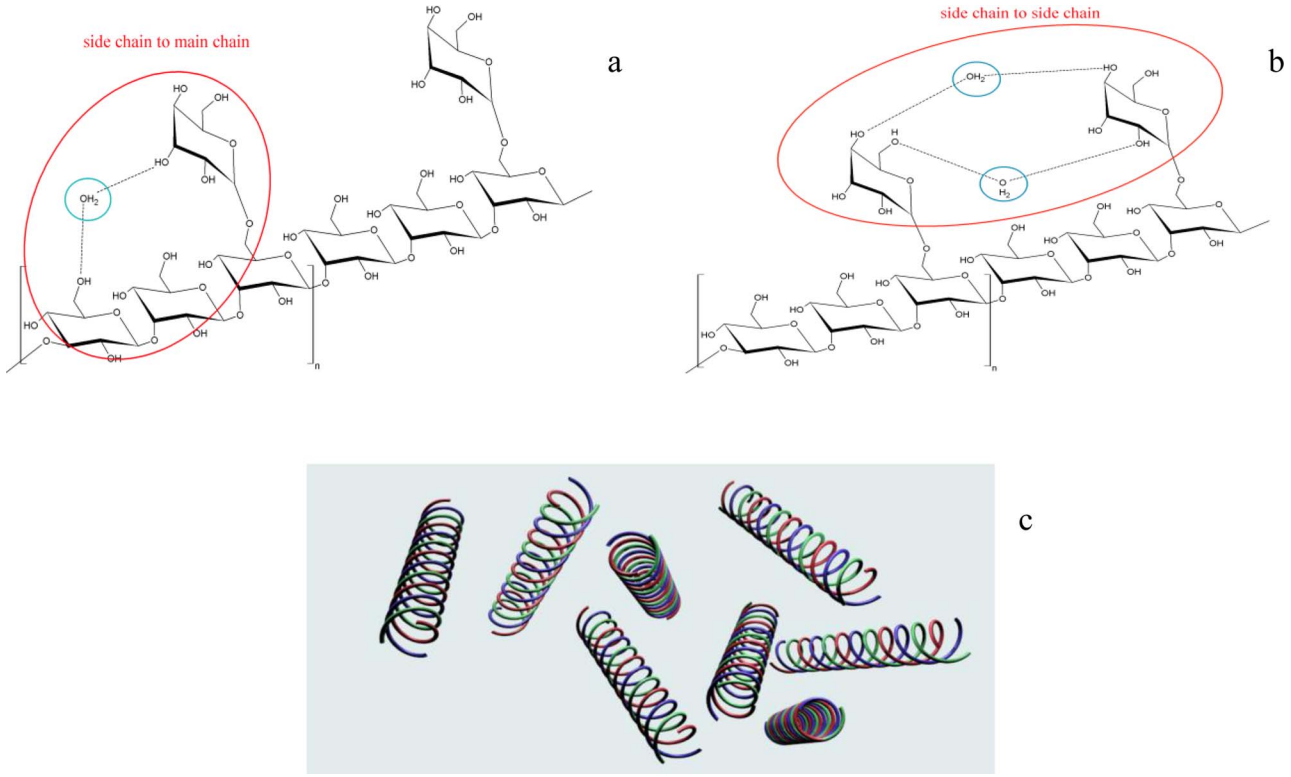

Fig. 1. Repeating unit of scleroglucan, induced hydrogen bonding by water molecules a) between main chain/side chain - b) side chain/side chain - c) Artistic impression of scleroglucan triple helix held together by intermolecular hydrogen bonds (the side chains are not presented).

2. Experimental

2.1. Materials

Biopolymer Scleroglucan (Actigum® CS 11, supplied by Cargill France SAS, Baupte, France) is a branched neutral homopolysaccharide consisting of a (1 → 3)-linked β-D-glucan linear main chain with (1 → 6)-linked β-D-glucopyranosyl groups attached to every third residue along the main chain. 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 $\eta_{@\,60°C} \geq 175\,Pa.\,s$ (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). A food grade vegetable oil was purchased from Mosselman N.V. (Belgium) and used as a powder dispersing agent. All other chemicals used were of analytical grade. An Atomix emulsification unit (Emulbitume, France) is used to prepare the emulsions.

2.2. Emulsion preparation and characterization

The soap phase was prepared by heating water and adding hydrochloric acid and a C_{18} di-amine emulsifier in the range of 0.2 and 0.3 w/w% whilst 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 5 fractions to which mixtures of Actigum® CS11 suspended in food grade vegetable (oil acts as dispersion agent for Actigum® CS11), in a 1:2 wt ratio, were added in order to obtain the following scleroglucan concentrations: 0 w/w%, 0.05 w/w%, 0.1 w/w%, 0.15 w/w% and 0.20 w/w% in the soap phase. The oil facilitates the swelling followed by dissolution to avoid the formation of lumps. In this way, homogenous solutions were readily obtained. 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 resulting emulsions will be referred to as 'pre-EA' emulsions ('pre-emulsification addition'). A part of the emulsion with 0 w/w% scleroglucan was stored at a temperature of 50 °C for 5 h, to be used for the manufacturing of a second series of emulsions, denoted 'post-EA' (post emulsification addition) emulsions. After dividing the 0 w/w% scleroglucan emulsion into five fractions, Actigum® CS 11 in food grade vegetable oil (in a 1:2 wt ratio) was added to obtain the same concentrations as in the pre-EA emulsions.

The emulsions were characterized using methods described in the European EN 13808 standard used for bituminous emulsions [22]. For instance, the breaking index of the emulsions is measured according to NEN-EN 13075. This is a titration method where aggregates (Forshammer SE filler from Per Nycander with a mean Particle size of 0.223 mm) are added at a rate of 1 g/s to 100 ml emulsion of 25 °C under constant stirring. The breaking-index increases upon increasing free-surfactant concentration, because surfactant adsorbing at the aggregates slows down the aggregation between filler particles and emulsion droplets. The emulsion is considered broken once one is no longer able to stir. The solid content of the emulsion is determined by means of evaporation of all volatile components (predominantly water) and determination of the final weight. A laser diffraction particle size analysis instrument Microtrac S3500 from Anaspec Solutions is used to analyse the particle size by feeding the Microtrac a 10 w/w% emulsion, which was made by diluting the original emulsion with the soap-phase. The storage stability was measured according to NEN 12847, where the emulsion is poured into a cylindrical glass vessel. After 7 days the water content (wt.%H_2O) of the top and bottom layer is determined by means of evaporation. The NEN 12847 storage stability is defined by the following equation.

$$Storage\ Stability\ (\%) = wt.\ \%H_2O_{top} - wt.\ \%H_2O_{bottom}$$

The NEN 12847 also describes the methodology used to determine the water content of the layers. The smaller the absolute value, the better the storage stability is. A positive value indicates sedimentation whereas a negative value indicates creaming.

The pH value of the emulsion was measured using a calibrated Perkin Elmer pH meter.

2.3. Preparation of scleroglucan solutions in H_2O and DMSO

Aqueous solutions of scleroglucan having pH 1, 2, 3, 5, 9, 11, 13 (HCl used as acid and NaOH as base) were prepared by dissolving scleroglucan at 50 °C for 2 h. Subsequently, the biopolymer is precipitated using isopropanol, dried and grinded. The same protocol is followed for a DMSO solution of scleroglucan. The recovered biopolymer is then used to prepare a range of emulsions in the same manner as described under section 2.2. using the pre-EA method. This will allow us to determine in which conditions scleroglucan is still useful as an emulsion stabilizer. Furthermore, the role of the triple helix can be evaluated.

2.4. Rheological analysis

The viscoelastic properties of the emulsions were investigated using a concentric cylinder geometry with a bob diameter of 28.06 mm, a bob length of 42.00 mm, and a gap of 1.88 mm 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 without a needle and fed to the cup as slow as 1–2 cc/min and remained unperturbed for 15 min before starting the experiment. After this conditioning step, a time sweep was performed, using a strain of 0.2% at a frequency of 10rad/sec, in order to verify the conditioning time needed for the sample. This approach showed that 15 min are enough to stabilize the sample. (see Supporting information Fig. S1).

A dynamic strain sweep study was then performed for all samples, that is, strain amplitude was varied while angular frequency of $\omega = 10$ rad/s was kept constant. The strain amplitude varied from ($\gamma = 0.01\%–1000\%$) collecting 10 point per decade with a sampling time of 3 s. All experiments were performed at a temperature of 25 °C.

2.5. Fourier transform infrared spectroscopy

Aqueous solutions of 0.2 w/w% scleroglucan, having a pH of 1 and 2, were prepared by dissolving scleroglucan at 50 °C for 2 h. Furthermore, a neutral aqueous solution of 0.2 w/w% glucose was prepared and used as a reference in order to detect the presence of glucose molecules formed by hydrolyses of scleroglucan. A BioRad UMA 500 microscope coupled to a BioRad FTS 6000 spectrometer was used to record the FTIR spectra. The spectral resolution used was 4 cm^{-1}, while co-adding 60 scans.

3. Results

3.1. Scleroglucan in bitumen emulsions: stability and rheological properties

To determine whether scleroglucan has any stabilization properties two emulsions where prepared. These two emulsions are produced in the same manner and only differ in terms of biopolymer addition. As a preliminary step, for a qualitative evaluation of potential polysaccharide effects, two emulsions were prepared. In Fig. 2 we present two 40/60 penetration bitumen emulsions stored at a 20 °C for 7 days in order to determine the storage stability. We can clearly distinguish between a stable and a non-stable emulsion. The emulsion on the left is stabilized by adding scleroglucan. On the other hand, the emulsions on the right is only stabilized by surfactant. This clearly indicates the stabilizing properties of scleroglucan.

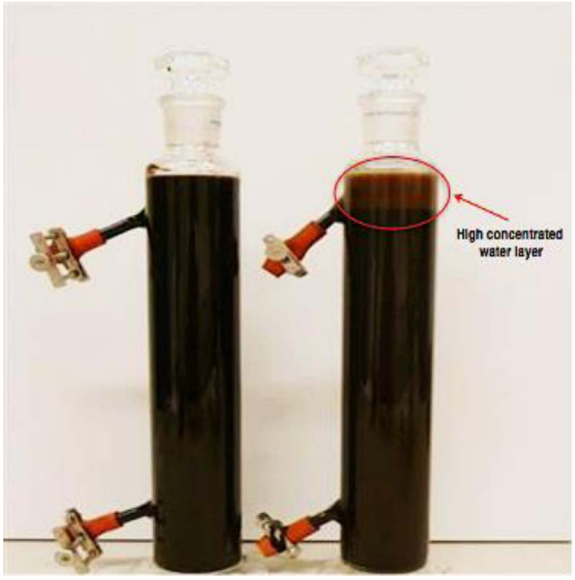

Fig. 2. Emulsion stored at 20 °C for 7 days according to NEN 12847. Left: A 40/60-penetration bitumen emulsion stabilized with scleroglucan, right: A 40/60 penetration bitumen emulsion without scleroglucan. The top-layer, where a concentration difference is distinguishable, is shown in the right storage cylinder.

The effect of biopolymer concentration and addition method (i.e. pre-EA vs. post-EA) was investigated using oscillatory rheometry tests, in which the strain amplitude (γ) was varied at a fixed frequency ($\omega = 10$ rad/s). Results are shown in Fig. 3. The viscoelastic properties are independent of the strain amplitude (γ) until a critical value (γ_c) is reached. At $\gamma > \gamma_c$, the viscoelastic properties become dependent of the strain amplitude.

The emulsion containing no biopolymer exhibits linear behaviour until a γ_c of about 4% is reached. At $\gamma > \gamma_c$, an increase of the loss modulus is observed suggesting structural rearrangements of the droplets. The storage modulus for this emulsion cannot be measured with our equipment, as it is very low. Addition of small amounts of biopolymer, 0.017 w/w% in the post-EA method increases the moduli by almost 1 decade. Further addition of biopolymer results in a further increase of the moduli, where the difference between *G'* and *G"* becomes very small, until *G'* becomes higher than *G"* at biopolymer concentration, 0.07 w/w%, indicating that elastic behaviour dominates at an angular frequency of 10 rad/s. For the pre-EA, the difference between moduli is more pronounced than for the post-EA. Again elastic behaviour dominates in the pre-EA at 0.07w/w% as *G' > G"*. However, the magnitudes of the moduli of pre-EA emulsion are smaller compared to the post-EA emulsion suggesting a weaker elastic network. The different emulsions with different internal structure have different viscoelastic behaviour. For all the measured samples, three regimes can be distinguished: 1) a linear regime at very low strains amplitudes, < 0.2% for post-EA and < 1% for pre-EA, where *G'* and *G"* do not depend on the strain amplitude 2) a non-linear regime for strain amplitudes in the range 0.2% < γ < 50%, probably induced by the breaking of the biopolymer network that binds the pre-existing emulsion, as a strong decrease of *G'* is observed and 3) an increase of *G"* for strains amplitudes > 50%. For these values of strain as seen in regime 3, increase in G" is probably related to jamming and droplet rearrangements of the emulsion [23]. This increase seen in regime 3 is less pronounced in the pre-EA at polymer concentrations of 0.03 w/w% and up. A possible interpretation of this phenomenon is that polymer coating on bitumen droplets is able to supress such droplets jamming, leading to a decrease of the G" response at high strain amplitudes that depends on added polymer concentration and method of addition.

In Fig. 4 we have plotted a set of rheological and stability measures as a function of scleroglucan concentration. The storage stability,

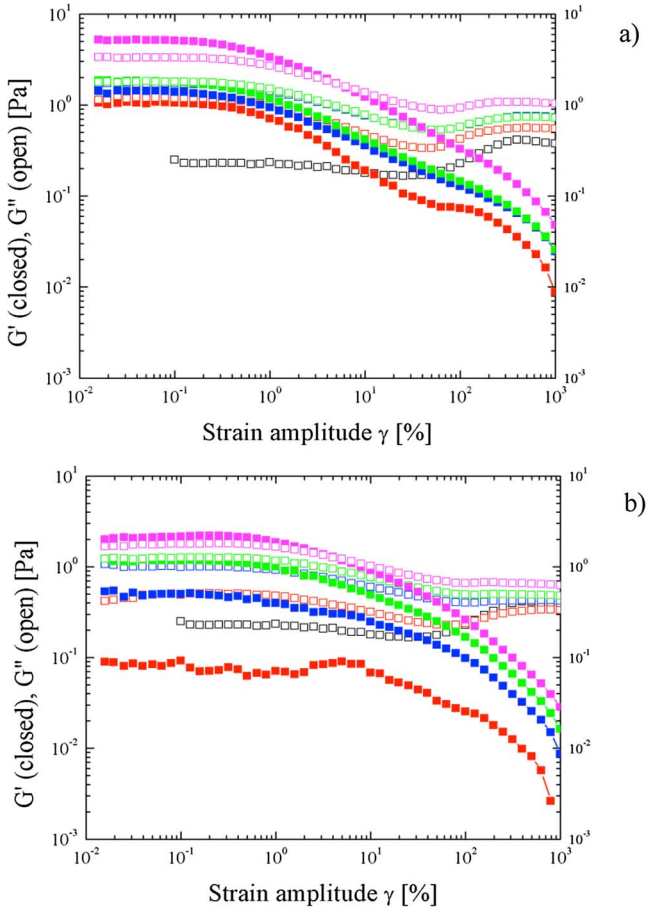

Fig. 3. Dynamic moduli (G' storage modulus, G" loss modulus) at ω = 10 rad/s of the a) post-emulsification addition:□ G" 0 w/w%, ■ G' 0.017 w/w% □ G" 0.017 w/w%, ■ G' 0.03 w/w% □ G" 0.03 w/w%, ■ G' 0.05 w/w% □ G" 0.05 w/w%, ■ G' 0.07 w/w% □ G" 0.07 w/w% and b) pre-emulsification addition emulsions, same markers as with a.

according to NEN 12847 as described in the paragraph 2 above, is displayed in Fig. 4a. The storage stability shows a significant improvement at concentrations as low as 0.017 w/w% scleroglucan for the pre-EA emulsions, which confirms the findings of Lommerts et al. [11]. For the post-EA emulsions we observe the same level of improvement of the storage stability at biopolymer concentrations of 0.05w/w% or higher.

The magnitude of the complex viscosity at γ=0.1% and $\omega = 10\,rad/s$, as a function of scleroglucan concentration is plotted in Fig. 4b for both emulsion preparation methods. The strain value selected for the complex viscosity is well within the linear viscoelastic region. A larger increase of the magnitude of the complex viscosity is observed when the biopolymer is added post-EA. The mean particle size is shown in Fig. 4c. As compared to emulsions made in the same way, but without scleroglucan, a larger mean droplet size is observed upon addition of biopolymer prior to emulsification, whereas no significant effect on the particle size is observed when addition of biopolymer takes place post emulsification. The breaking index (Fig. 4d) remains unchanged for pre-EA as well as for post-EA (between 100 and 105), indicating that the free emulsifier concentration remains the same. The emulsions without biopolymer and with 0.017 w/w% biopolymer post-EA formed a solid layer at the bottom of the cylinder after 7 days, which was not redispersible. The post-EA emulsions with higher biopolymer concentration show this behaviour after a longer time (~3 weeks). However, pre-EA emulsions do not show this behaviour. Even after 6 months, when sedimentation has occurred, the emulsion stays redispersible. Pre-EA of scleroglucan not only slows down sedimentation but also prevents coalescence, as the emulsion stays redispersible over a long period of time.

3.2. Scleroglucan stabilized emulsions and the role of triple helix

Scleroglucan has been extensively investigated by Rau et al. [16], Stokke et al.[24] and Sletmoen et al. [20]. They all mention the existence of linear rod-like triple helices held together by intermolecular hydrogen bond. The triple-helix conformation may play an important role in the Stabilization of emulsions. It has been established that the triple helix unwinds into random coils at temperatures > 135 °C. This helix-coil transition can also be established by pH values > 12.5 in aqueous solutions at room temperature, and by dissolution in DMSO [25]. At pH 1, the scleroglucan side chains are hydrolysed and a solution of glucose and a precipitate of curdlan are obtained. Curdlan is a linear polysaccharide which has the same chemical structure as the backbone of scleroglucan [20,24]. Due to the absence of side chains it is less soluble in water and will eventually precipitate. In a separate experiment, we investigated the effects of pH by subjecting scleroglucan to aqueous solutions at pH values between 1 and 13 and to DMSO, in order to study the role of the triple helix conformation in the stabilization mechanism. Scleroglucan was recovered after these treatments and used to stabilize bitumen emulsions by adding 0.04w/w% pre-treaded scleroglucan to the soap-phase, pre-EA. The storage stability of these emulsions is presented in Fig. 5.

The values of the storage stability when scleroglucan was subjected to pH 2–11 are similar to those observed when untreated scleroglucan was used (storage stability of 0.1% with 0.05w/w% scleroglucan). When scleroglucan was pre-treated with pH 1, it results in a non-stable emulsion as seen in Fig. 5. It is not able to stabilize the emulsion due to a decreased solubility of scleroglucan. In order to verify the hydrolysis of the side chains, infrared spectra were measured of a pH 1 solution containing 0.2 w/w% scleroglucan, of a pH 2 solution containing 0.2 w/w% scleroglucan and of a solution of 0.2 w/w% glucose as reference. This is presented in Fig. 6.

The scleroglucan solution of pH 1 exhibits an extra peak at 1020 cm^{-1} similarly to the glucose solution. This peak does not appear in the scleroglucan solution of pH 2. This indicates that hydrolysis took place at pH 1, leading to a non-stabilizing molecule. However, the storage stability of this emulsion is better compared to the emulsion without scleroglucan (NEN 12847 storage stabilities 7% and 25% respectively). This remaining stabilization ability is probably due to incomplete hydrolysis of scleroglucan.

At pH 13 the triple helix structure denaturises into single-molecule random coils. The same happens in DMSO were scleroglucan is known to denature into single-molecule random coils as well [18]. The storage stability using scleroglucan denatured in DMSO is 13.9%, which is similar to the storage stability with scleroglucan pre-treated at pH 13: 12.9%, much worse than for native scleroglucan. These observations tell us that the triple helix structure of the untreated scleroglucan is important for stabilizing the emulsions. Polymer-surfactant complexes can probably only be formed when the triple helix is intact.

4. Discussion

Data Presented in Paragraph 3 are apparently puzzling. Stokes' law tells us that a high viscosity and small particle sizes reduces the rate of sedimentation [26,27]. Even though the modulus of the dynamic viscosity at a finite frequency is not the same as the zero-shear viscosity appearing in Stokes' law, we expected a correlation between the magnitude of the dynamic viscosity and the stability of the emulsion against sedimentation. With this in mind, we expected that the overall increase of the dynamic viscosity and the limited effect upon the particle size upon post-EA of scleroglucan would give rise to an improvement of the storage stability. The small effect upon viscosity, and the increased droplet size occurring with pre-EA raises the expectation that pre-EA would lead to less effective stabilization. However, pre-EA results in

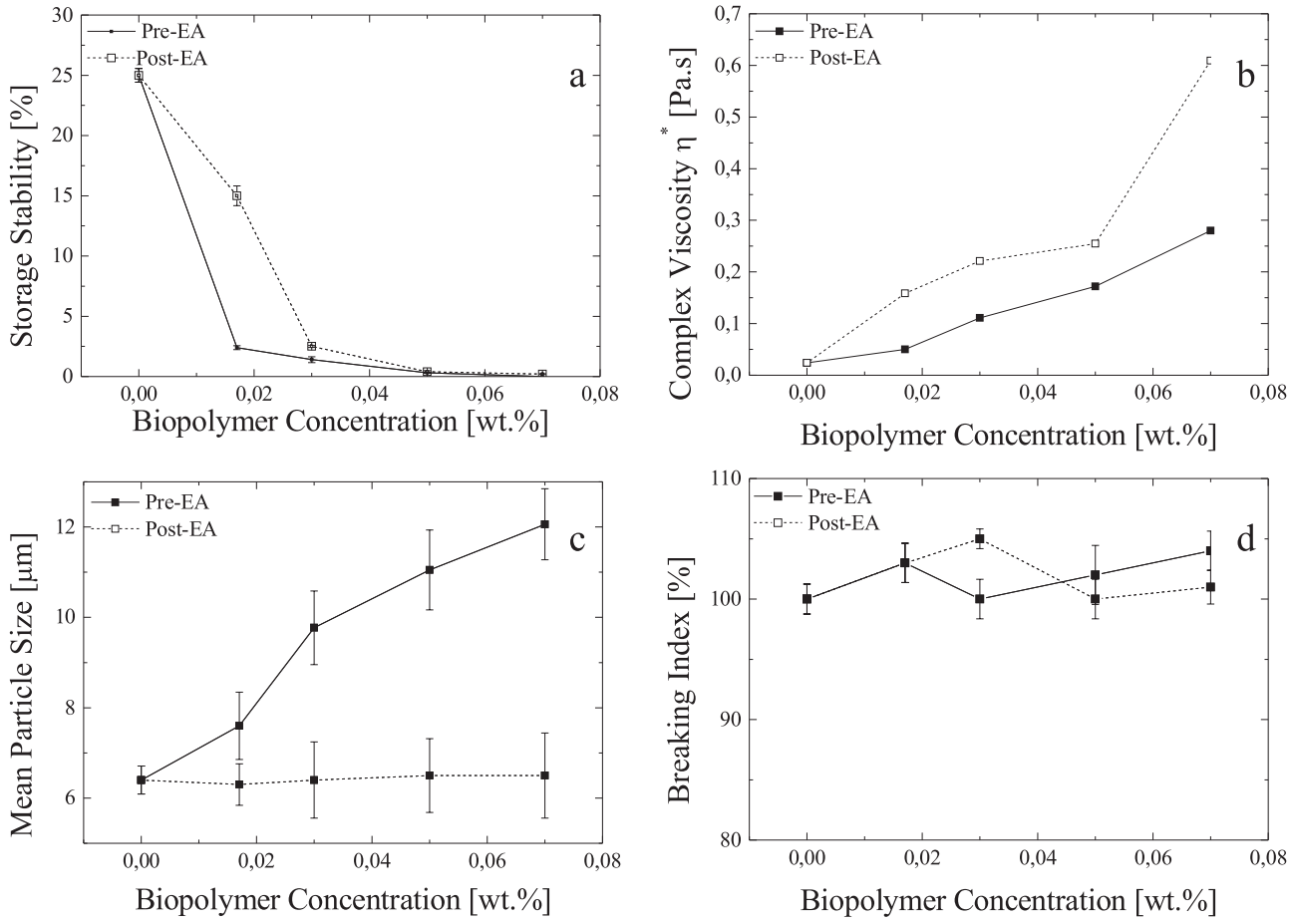

Fig. 4. Dependency of several properties of bond coat emulsions upon scleroglucan concentration (pre-EA and post-EA): a) Storage stability according to NEN 12847 (%) - b) Magnitude of the modulus of the complex viscosity η^* at $\gamma = 0.1\%$ and $\omega = 10$ rad/s (Pa.s) extracted from the strain sweeps presented in Fig. 4c) Mean particle size (µm) and d) Breaking Index value according to NEN-EN 13075.

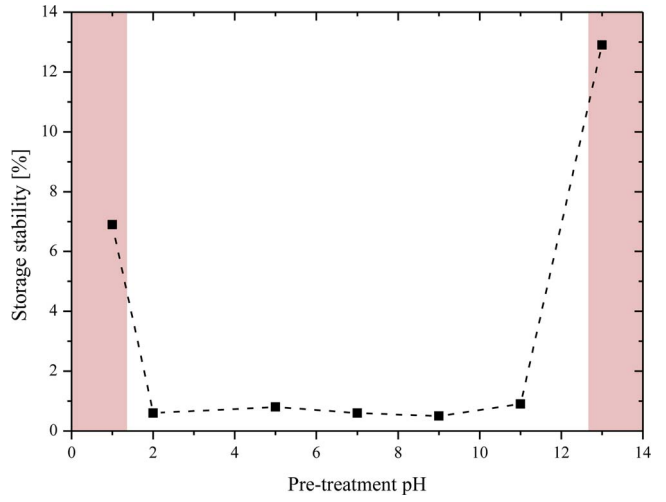

Fig. 5. Influence of pH pre-treatment of scleroglucan on its stabilizing effect in pre-EA emulsion formulations.

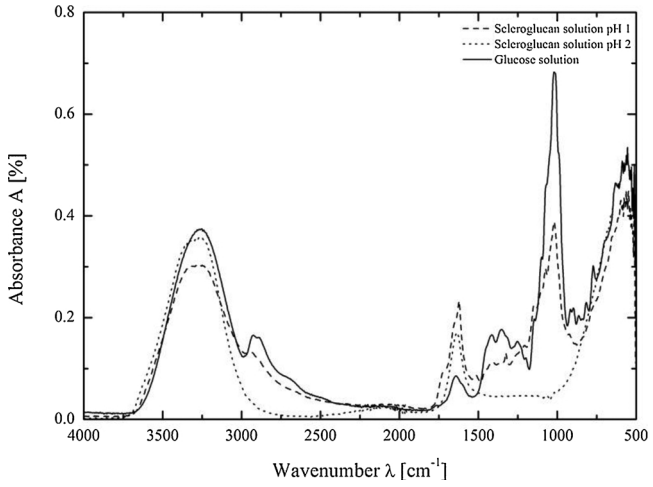

Fig. 6. Infrared spectrum of Scleroglucan solutions at pH 1 and 2, glucose solution. The peak at 1020 cm^{-1} emerges for the glucose solution as well as the scleroglucan solution of pH 1.

much better stabilization. A significant improvement of the storage stability, comparable with that in the pre-EA, is only observed in the post-EA systems at biopolymer concentrations of 0.03 w/w% or higher, whereas for the pre-EA emulsions we see significant improvement of the storage stability already at concentrations as low as 0.017 w/w%. Both addition methods result in an improvement of the storage stability. However, a larger amount of biopolymer is needed to achieve the same stability in the post-EA method. Looking at these results we can distinguish different Stabilization mechanisms. The internal structure of the emulsion without biopolymer is given by emulsion droplets coated with surfactant, which induces electrostatic stabilization against droplet aggregation. However, as shown in Fig. 5a, this is not enough to stabilize the bitumen emulsion under study. The increase in G" at high strains may be attributed to droplets jamming and rearrangements as

observed by Knowlton et al. [23]. One is tempted to conclude that larger aggregates are formed indicating that destabilization of the colloidal system has taken place. For the emulsions with biopolymer one must distinguish between the pre-EA en post-EA emulsions. The primary internal structure constitutes bitumen droplets, which are electrostatically stabilized by a cationic emulsifier, as in the emulsion with no biopolymer. However, addition of biopolymer changes the internal structure, which will have an effect on the viscoelastic behaviour of the emulsion and ultimately on the emulsion stability. The post-EA emulsions show a more pronounced elastic behaviour, shown in the strain sweep at $\omega = 10$ rad/s, as compared to the pre-EA. This observation raises the expectation that post-EA would result in a more stable emulsion compared to the pre-EA. However, we have already shown that the pre-EA is more effective in stabilizing the emulsion against sedimentation and preventing coagulation. The elastic behaviour in the post-EA is destroyed already at 0.4% strain amplitude as can be seen in Fig. 3a. The structure responsible for the increase in viscosity is no longer able to reform and keep the system from undergoing structure rearrangement. However, the rate of rearrangement is suppressed compared to the emulsion without biopolymer, especially at high biopolymer concentrations (> 0.03 wt.%). Nevertheless, aggregation is only suppressed and not prevented in these emulsions, as indicated by the observed increase in G" at higher strain amplitudes. Aggregation decreases the lifetime of an emulsion as it enhances sedimentation. The rheology experiments clearly show a suppression of aggregation but it is not entirely prevented. In the pre-EA, the biopolymer is added to the soap-phase prior to the emulsification process. As we see an increase of stability in these emulsions, we can hypothesise that emulsifier and Biopolymer interact in the soap-phase creating a complex stabilizer. This increased stability is given by emulsion droplets that are stabilized by a cationic emulsifier and polysaccharide adsorbed at the droplet interface. Polysaccharide-surfactant mixtures are known to change the interfacial properties at the oil/water interface. These mixtures tend to lower the interfacial tension and increase interfacial activities supporting the emulsification [28,29]. This is followed by a quick adsorption of surfactant and polymer incorporation in the adsorbed surfactant layer acting as a steric barrier. This phenomenon is observed in the Hydrolyzed Polyacrylamide (HPAM) / Dodecyltrimethylammonium (DTAB) mixtures as well as hydroxypropyl cellulose/lecithin mixture as shown by Dong et al. [28] and Mezdour et al. [29], respectively. Li et al. [30] used dissipative particle dynamics simulation to study the properties of the oil/water/surfactant system in the absence and presence of polymer. They observed that the surfactant molecules become straighter and more ordered at the interface. The interface thickens with the number of polymer chains due to the increasing of polymer chains adsorbed at the interface. However, we cannot exclude that a weak gel is also formed and plays a role in the system by helping to further stabilize (coated) bitumen droplets against sedimentation. The fact that we do observe an improvement of the storage stability in the post-EA emulsions compared to the emulsion with no addition of polymer may also indicate this trend. Furthermore, polysacharides such as modified cellulose (i.e. methylcellulose) does exhibit complex formation with common ionic surfactants such as SDS and CTAB. Surfactant effects on the gelation of methylcellulose using micro-differential scanning calorimetry (DSC) have shown that surfactants are responsible for a salt-in effect on methylcellulose, which shifts the sol-gel transition of methylcellulose to higher temperature, indicating formation of complexes taking part in the gel structure [31,32]. Therefore, it is to be expected that this effect is also present in our samples, forming a gel by exhibiting complex formation between Scleroglucan and surfactant. This was sugested by Bias et al. [33] where scleroglucan-surfactant interaction leading to complex formation was the explanation of rheology studies on those systems.

The system formed by the pre-EA is able to support strains up to 1% and, as seen in Fig. 3b, shows elastic behaviour only at the highest biopolymer concentration at the given frequency. At high strains, > 50%, we observe an increase in G" at the lowest biopolymer concentration only. With higher polymer concentration, the destabilization of the emulsions is suppressed. These emulsions are more stable, where gel-formation is not the driving force as these emulsions exhibit lower storage and loss moduli and a larger amount of biopolymer is needed to form the same gel strength as in the post-EA. Scleroglucan, in the pre-EA emulsions, not only improves the stability against sedimentation but also coagulation is prevented. We presume that an adsorbed layer of hydrated scleroglucan facilitates redispersiblity of the emulsion. These observations suggest that biopolymer-surfactant interactions play a role in a more complex Stabilization mechanism where coagulation of the droplets is prevented by scleroglucan adsorbed at the droplet surfaces forming a second layer as described by Bouyer et al. and Klinkesorn [34,35]. The hypothesis formulated above provides directions for further investigations in order to elucidate the stabilization mechanism and detailed structural information on these systems. A full characterization study concerning the interaction between scleroglucan the surfactant and the droplet surface is necessary.

5. Conclusion

It was found that scleroglucan addition before emulsification (pre-EA) results in a far better stabilization than addition after emulsification (post-EA), even though we observed a higher viscosity and smaller droplets upon post-EA. This is somewhat paradoxical, as Stokes' law states that an increased viscosity and a smaller droplet size slow down the sedimentation/creaming of an emulsion, which would improve the storage stability. In order to achieve sufficient stability upon post-EA, much more scleroglucan is required, leading to a higher viscosity. Furthermore, coagulation of droplets upon sedimentation is not prevented using post-EA. These observations indicate that the mechanisms of Stabilization for the pre-EA and post-EA emulsions differ. When scleroglucan is added to the aqueous surfactant solution prior to emulsification, more surfactant is available for binding with scleroglucan. After emulsification, most surfactant is bound already to the emulsion droplets, so that it is not available to bind with scleroglucan when added post-EA. The fact that the droplet size remains larger upon pre-EA is further indication that scleroglucan binds surfactant, because a larger droplet size is explained by a smaller amount of surfactant available for emulsification. This indicates that biopolymer-surfactant interaction is crucial for the storage stability of the emulsions. The conformation of scleroglucan is crucial in obtaining sufficient emulsion stability. The enhanced stability against coagulation of pre-EA emulsions, reflected in the redispersability of sedimented emulsions, is most likely due to scleroglucan adsorbed at the surfaces of emulsion droplets, yielding steric stabilizations. Structural change of scleroglucan i.e. denaturation of the triple helices and hydrolysis of the side chains, influence the biopolymer-surfactant interaction and diminish its effectivity as an emulsion stabilizer. It is known that rigid polymers, like the scleroglucan triple helix, adsorb easier than random coils, such as denatured scleroglucan. Our findings suggest that interfacial stabilisation effects such as the lowering of the interfacial tension, increasing interfacial activities and the incorporation of polysaccharides into the interfacial surfactant layer play a major role in the emulsion stabilization. We cannot exclude, however, that the formation of a (weak) gel is simultaneously taking place in bulk and also playing a role in the stabilization process.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.colsurfa.2018.02.035.

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