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Polyhedral oligomeric silsesquioxane as co-surfactant in stabilizing highly concentrated emulsion with an overcooled dispersed phase

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ABSTRACT

This study investigated water-in-oil (w/o) super-concentrated emulsions used as pumpable explosives. The aqueous phase of the emulsions is a supersaturated nitrate salt solution (at room temperature), with a mass fraction of approximately 0.9. Instability of such emulsions arises either from crystallization of the dispersed phase in the system during ageing or under high shear conditions. Here, we report an alternative approach to stabilize emulsion explosives by using Polyhedral Oligomeric Silsesquioxane (POSS) as a co-surfactant to PIBSA (i.e. polyisobutylene succinic anhydride), in replacement of conventional co-surfactants, Span 80 or Tween 80. The interfacial tension, interfacial elasticity, refinement time, stability under high shearing as well as stability during storage have been investigated. It has been found that first, conversely to the standard co-surfactant Span 80, POSS can generate a more complex and very resistant interfacial film that has no tendency to induce crystallization in the system. Second, unlike conventional mixtures, PIBSA-MEA/POSS mixture confers outstanding stability to the emulsion not only under high shearing but most importantly during storage. In presence of POSS the emulsion explosives stabilization occurs through a reinforced interfacial skin rather than the usual mechanical barrier of reverse micelles in the inter-droplet layer. This new mechanism is much more effective than the conventional one and allows for a significant reduction in the total surfactant concentration required to stabilize the sheared as well as un-sheared emulsions. We propose that through the synergetic interaction POSS occupy the free spaces between the bulky polymeric PIBSA molecules and create a reinforced condensed layer at the interface.

1. Introduction

Highly concentrated water-in-oil emulsions with an oversaturated solution of inorganic salts as the dispersed phase are unique complex systems, playing an important role in manufacturing of liquid explosives, nutritious foods and drug delivery systems. However, like other emulsions, these kinds of compound are thermodynamically unstable, and their instability arises from coalescence of droplets [1,40] and/or crystallization of the dispersed phase in the system during aging or under high shear conditions [4,37,33,34,42,32]. Crystallization decreases the efficiency of the application while coalescence (evolution of a droplet size) is accompanied by changes in the rheological properties and thus could affect transport and technological applications of the emulsions. The compositions that can yield stable emulsions remain a challenging issue because of the contradictory requirements for a surfactant to stabilize such emulsions under intense shearing (e.g. during pumping) and those related to their stabilization on storage. In most cases these conflicting requirements can be satisfied by using combinations of different surfactants, in particular mixtures of polymeric and low-molecular-weight compounds. It is supposed that, because of their high mobility, low-molecular-weight surfactants improve stability under the shearing conditions present during emulsification and transportation in application, whereas polymeric surfactants are expected to stabilize emulsions during storage through steric effects between droplets [11,18,42]. This study focuses on liquid explosives compositions where crystallization rather than coalescence is the dominating mechanism of instability [34]. Additionally, in this case, crystals are not necessarily confined to their original droplet size and shape but can break through the films separating droplets [34,37,33,42]. The standard binary mixture used to stabilize these emulsions is the combination of polyisobutylene succinic anhydride (PIBSA) derivatives with a low molecular weight surfactant, sorbitan monooleate (SMO, Trade name Span 80). Using SANS, Reynolds et al. [24–25] demonstrated that PIBSA-derivative surfactants form a monolayer

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at the w/o interface and reverse micelles in the oil. The surfactant monolayer has no ability to resist the penetration of crystallinity throughout the substance; the emulsion is stabilised by a significant number of surfactant rich reverse micelles a few nanometres in diameter in the thin film between droplets [27]. The highly unstable emulsions are those in which the reverse micelle concentration is very small [27,26]. In this sense a large amount of this surfactant is required to effectively stabilize the emulsion during storage. Even though this constitutes a serious problem as it significantly increases the production cost of the emulsion, PIBSA-based surfactants are still the preferred polymeric surfactants for emulsion explosive stabilization due to their high tolerance in impurities. On the other hand, many studies demonstrated that Span 80 as co-surfactant greatly improves PIBSA-based emulsions stability during pumping [11] and emulsification [18] but has a negative impact on the emulsion stability during storage [27,18,11,42,41]. The incompatibility between the hydrophobic tail of PIBSA (38 carbon atoms) and Span 80 (17 carbon atoms) reduces their molecular interaction at the interface as well as in the reverse micelles; thereby disrupting the interfacial film packing [43]. Additionally, during ageing, Span 80 further accelerates crystallization of the dispersed phase by displacing PIBSA molecules from the interface and then building up multilayers which induce heterogeneous nucleation from the interface [28]. It is interesting therefore to study other co-surfactants which could improve the stability of PIBSA-based emulsion under high shear without causing a drastic decrease of the stability during storage.

Different types of co-surfactants to PIBSA-derivatives in stabilization of highly concentrated emulsion explosives have been developed but the results are rather rarely published (most of the data are proprietary), though some interesting exceptions are known: admixture of 1–4 % sorbitan and oleic acid [45]; low molecular weight PIBSA-MEA (Mw = 750 g/mol) [4]; combination of animal oil and fatty acids [11] or alkylamine ethoxylated [29]. In a systematic study of binary surfactant mixtures, prepared by mixing a PIBSA-derived with a series of non-ionic oil soluble (Spans) and water soluble (Tweens) compounds, Sanatkaran et al. [30] demonstrated that the Tween family provides better co-surfactants to PIBSA than does the Span family. e.g., PIBSA-MEA/Tween 80 mixture enables surfactant compositions that provide better stability on shelf as well as under high shearing than PIBSA-MEA/Span 80 system.

Due to increasingly demanding legal and consumer requirements (emulsions be non-toxic, biocompatible, mild on the skin, are ecologically acceptable, etc.), the reduction in the use of surfactants to stabilize emulsions becomes necessary. Moreover, despite the observed synergy in some binary mixtures, no co-surfactant in this category is claimed to either improve or maintain the level of stability impacted by PIBSA to the emulsion during storage; they all compromise at some extend the shelf life of unsheared PIBSA - based emulsions. This presents a significant problem caused by the lack of ability of co-surfactants of this family to improve the strength of PIBSA monolayer at the droplet surface and/or the strength of the mechanical barrier of reverse micelles between drops. On the other hand, though the synergetic interaction between classical surfactants and conventional nanoparticles is known to generate rigid films with outstanding properties around droplets [7–9,12–15,41], the latter are not viable alternatives co-surfactant to PIBSA derivatives. First, due to their large size and their inherent inability to reduce the interfacial tension, are less much effective in terms of rapidly covering the naked interfaces and favouring break-up during emulsification [2,3,5,6,19]. Second, it is well known that emulsion films and high-concentrated polyhedral emulsion droplets stabilised by solid particles are very sensitive to mechanical disturbances [20,3,21] and thus makes highly concentrated emulsion (HCE) unstable under shear. With this in mind, the examination of the possibility of using Polyhedral Oligomeric SilseSquioxane (POSS) as co-surfactant in stabilizing emulsion explosives becomes necessary.

POSS are a unique class of colloids. They possess a hybrid inorganic–organic architecture with inner inorganic framework of silicone and oxygen with general formula $[RSiO_{1.5}]_n$ (R = H, alkyl, aryl or alkoxyl) and embody a range of polar structures and functional groups [10]. POSS nanostructured chemicals, with sizes of 1 to 3 nm in diameter, can be considered as the smallest possible particles of silica or molecular silica. The presence of organic substituents on its outer surface distinguishes these compounds from silica, silicones, or fillers. POSS compounds offer the following advantages as compared to conventional co-stabilizers. First, unlike many traditional organic compounds (surfactants), they release no volatile organic components, making them odorless and environmentally friendly [10]. Second, unlike, POSS reduce the w/o interfacial tension to the same extent as do conventional surfactants. Moreover, Masalova et al. [35] reported that POSS aminoethylaminopropylisobutyl (Trade name, POSS AM0275) can generate an interfacial layer with completely new properties that are not readily available with conventional surfactants; the resulting emulsions demonstrated outstanding stability against coalescence. In this sense we can anticipate that POSS AM0275 has the potential to reinforce (if there is any synergism with PIBSA-MEA) the rigidity of the PIBSA-MEA monolayer or replace PIBSA-MEA monolayer (if there is antagonism and its binding energy at the interface is higher than the one associated with PIBSA-MEA) by a stronger interfacial layer, which could act as an inhibitor preventing the crystallization in one of the micron-scale aqueous droplets to propagate through the rest of the emulsion, crystallizing all droplets. This could completely change the mechanism of PIBSA-based emulsion stabilization as compared to standard mixtures.

The identified knowledge gap in the field of emulsions stabilized with a mixture of surfactant and POSS nanoparticles is the absence of systematic experimental data in connection with manufacturing and stability (with ageing or under high shear in pump) of HCE with a super-cooled dispersed phase against crystallization of an internal phase. This study continues the above theme in the search for answers to the following main question:" How the use of POSS contributes to the shelf life and stability under shear (which are important for technological applications) of HCE with an overcooled dispersed phase, stabilized by PIBSA-MEA?" Thus, the main goal of this study was to investigate the synergetic (or antagonistic) effect of the mixture between PIBSA-MEA and POSS AM0275 in stabilizing highly concentrated w/o emulsions with a supercooled dispersed phase, in comparison with one of the best surfactant mixtures PIBSA-MEA/Tween80 as well as the standard mixture PIBSA-MEA/Span80.

2. Experimental

2.1. Materials

Monoethanolamine derivative of polyisobutylene succinic anhydride surfactant (PIBSA-MEA) with a total molecular weight of 1109 g/mol, was supplied by Experse Surfactant Technologies (AECI Group, Republic of South Africa). The hydrophobic moiety of this polymeric surfactant is the polyisobutylene chain with a repeat unit of – $C(CH_3)_2$–CH_2 i.e., a chain of carbon atoms with two methyl side groups attached to every second one. The HLB number is not known precisely but will be low (<4).

Sorbitan monooleate (SMO, trade name Span 80; purity $\geq$ 9 9 %) used as a co-surfactant was purchased from Merck. This is an ester formed between sorbitan and oleic acid (oleic acid is a C18 fatty acid with a single cis double bond, written as C18:1). The

hydrophobic moiety of Span 80 is an oleic group with an approximate relative molecular mass of 280. The hydrophilic moiety is the sorbitan group with a relative molecular mass of 168.

Polyoxyethylene sorbitan monooleate (trade name Tween 80; purity ≥ 99 %) used a as co-surfactant was purchased from Sigma Aldrich. This is a non-ionic surfactant derived from polyethoxylated (20 segments) sorbitan and monolaurate and oleate fatty acids with HLB equal to 16.7 and 15 respectively.

POSS aminoethylaminopropyl isobutyl (POSS AM025; purity ≥ 97 %) used as stabilizer in the current study was produced and supplied by Hybrid Plastics, USA. These nanoparticles adopt the structure of an inorganic cage consisting of silica and oxygen and the functional group contains both a more reactive bridging secondary amine as well as the terminal primary amine. The R-group within the molecule is a short hydrocarbon chain i-butyl.

It is worth mentioning that the structures of all stabilizers used in this investigation are summarized in Table 1.

The industrial grade oil Ash-H (density 794 kg/m^3), produced and supplied by Experse Surfactant Technologies (AECI Group, Republic of South Africa), was used as continuous phase media. It contains isoparaffins (80–90 wt%), *n*-paraffins, cycloparaffins (10–15 wt%) and monocyclic aromatics (1 wt%).

The materials were used with no further purification or modification of their properties and all of the molecules considered were soluble within the hydrocarbon oil Ash-H. When used during interfacial measurements, the concentration was 1 wt% for each stabilizer. This translates into the values of molarities reported in Table 1. When used as a sole emulsifier, the concentration of Span 80 or POSS AM0275 taken was 6 wt% in oil.

2.2. Instrumentation

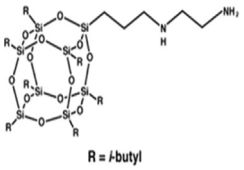
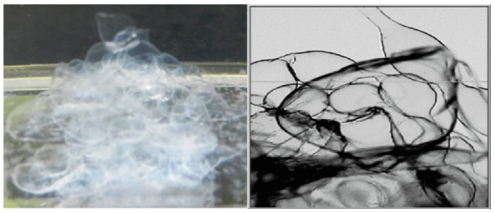
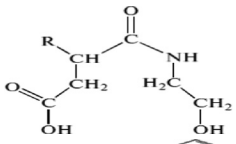
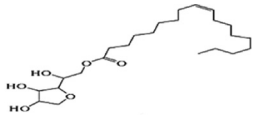
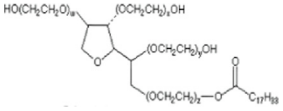
2.2.1. Interfacial properties investigation

Interfacial tension measurements were performed using the Kruss K100 tensiometer with principles of measurements based on the Wilhelmy plate method. Approximately 15 cm^3 of a 60 % inorganic salt solution was placed in a clean 70 mm diameter glass dish. A hydrophilic platinum plate was then suspended vertically from a sensitive force transducer with its lower edge penetrating the surface of the inorganic salt solution. Following was a gradual addition of approximately 50 cm^3 of the oil phase containing 1 wt% of a specific type of stabilizer until the plate was fully submerged. Measurements were then initiated. Each measurement was set up at 10,800 s in order to allow the system to come to equilibrium. The measurement was performed at 25 °C.

The interfacial moduli were determined using a PAT 1 tensiometer supplied by Sinterface Technologies, Berlin, Germany. A full description of the principle of operation has been given elsewhere [39,31]; a summary follows here. The experimental arrangement is normally that the capillary is vertically mounted, and the denser fluid is forced downwards through it to form a droplet in the less dense fluid. This arrangement is known as the suspended droplet case. Occasionally the arrangement is used in that the less dense fluid is forced upwards through a capillary into the denser fluid, the emergent droplet case. The droplet fluid is referred to as the "inner" phase, and the other as the "outer" phase. The basic principle of the operation of this instrument is that the Young-Laplace equation is fitted to the profile of an image of a droplet suspended in the "outer" phase from a capillary. The Young-Laplace equation [23] balances the interfacial tension against gravity, with the interfacial tension tending to reduce the interfacial area and gravity tending to increase it by extending the droplet. This balance leads to certain practical considerations concerning the capillary diameter and the droplet volume. For example, if the droplet volume is too low, the interfacial tension dominates, and the droplet assumes a spherical shape from which the interfacial tension cannot be extracted. If the droplet volume is too high, gravity dominates, and the droplet detaches from the capillary.

The outer phase is contained in an optical glass cuvette, the inner phase is contained in a separate reservoir, the droplet size

Table 1
Interfacial and Interfacial elasticity of stabilizers used in this investigation.

Stabilizer type	Functional/polar group	Interfacial tension (mNm^{-1})	Interfacial elasticity (mNm^{-1})
	Single surfactants		
POSS AM0275	 R = *i*-butyl	3.3	
PIBSA-MEA		8.3	2.9
Span 80		0.6	0.3
Tween 80	 x + y + z + w = 20	0.5	0.5
	Surfactant Mixtures		
PIBSA-Span 80 (10:1)		5.5	–
PIBSA-Tween 80		5	–
PIBSA-POSS AM0275		6.2	–

being controlled by a micropipette driven by a stepper motor: the droplet may be controlled either to a specified volume or a specified area. A light beam is passed through the cuvette, and an image of the droplet is collected by a CCD camera. The Young-Laplace equation is then fitted to the digitized image of the droplet edge. The fitting software requires the absolute dimensions of the droplet, which requires calibration of the CCD chip: this is normally taken off the capillary diameter, which needs to be known accurately. Also needed accurately are the densities of the two fluids, and the value for gravity for the region. These values are entered manually into the instrument software.

The droplet size may be varied sinusoidally, using either volume or area control. This results in an oscillating interfacial tension. The real and imaginary components of the interfacial modulus, E' and E'', are obtained as:

$$E\prime = (A_s/A_0)\cos d,\ E\prime\prime = (A_s/A_0)\sin d \quad (1)$$

Where A_0 is the mean value of the area, A_s the amplitude of oscillation of the area, and d is the phase lag between the interfacial tension and the area, obtained from Fourier transformation.

In current investigation a quartz cuvette was filled with hydrocarbon oil containing 1 wt% of a specific type of stabilizer. The denser phase used as part of measurements was a 60 wt% solution of inorganic salts. A pear shaped droplet of this solution in the oil phase was formed at which point the analysis commenced. Each analytical run was set up at 15,000 s which was done in order to allow for the system to equilibrate. Oscillation experiments were done at amplitude of 0.5 mm and frequency of 1 Hz at 25 ℃.

2.2.2. Emulsion preparation

The emulsification process of emulsions containing 60 wt% of the inorganic salts in the aqueous and stabilized by Span 80 or POSS AM0275 was conducted in 250 g batches using a Silverson L4RT high shear mixer equipped with a fine emulsor screen of 19 mm diameter at 2500 rpm, at room temperature (25℃). The oil dispersion containing 6- wt% of POSS AM0275 in the oil phase was first placed in a glass beaker (150 mL) and stirred at 2500 rpm. Then, the inorganic salts solution was sequentially added to the continuous phase, re-homogenizing for five minutes between additions until the target dispersed phase concentration of 90- wt% was reached.

The emulsification process of emulsions with a supercooled dispersed phase was conducted in 2.5 kg batches by a Hobart N50 mixer (manufactured and supplied by the Hobart Corporation, USA). The oil phase containing the stabilizer system was first placed in the bowl, mixed gently, and heated to about 80° C. Then, the hot inorganic salt solution (83° C) was slowly added, while stirring was maintained, at speed1, to ensure emulsification (average drop size $d_{32} \approx 17$ μm). Rapid mixing at a higher speed (gear 3, the corresponding shear rate $\approx 380\ s^{-1}$ in our experimental conditions) of the mixer was done subsequently for all formulations until a droplet size of 10 μm was reached. The time required during this last phase of emulsion preparation was recorded using a stopwatch and was referred to as the characteristic refinement time. The emulsions were prepared with 90- wt% of the dispersed phase. The dispersed phase of emulsion comprised 80 wt% of inorganic salts in distilled water.

2.2.3. Optical methods:

Optical microscopy and laser diffraction were used to evaluate the samples. The optical microscopy was used for visual observation of structural changes of the materials (droplet size, eventual crystallization). The analyses were carried out with a Leica optical microscope equipped with a digital camera.

The size distribution of dispersed droplets was determined by laser diffraction, using a Mastersizer 2000 device (Malvern Instruments Co.). The measurement procedure is based on sample dispersion, under software control, and the measurement of angle dependence of the intensity of scattering of a collimated He-Ne laser beam. Particle sizes in the range 0.26 to 1500 μ m can be measured. A small amount of each emulsion sample was dispersed in a large volume of oil to form a very dilute concentration of aqueous droplets in oil to avoid the formation of agglomerates. d_{32} was used as a measure of average droplet size in this study.

2.2.4. Rheology methods:

All rheological studies were conducted using a rotational stress rheometer MCR 300 (Anton Paar, Austria) with bob-in-cup measuring units with a sand blasted bob surface in order to minimize the possibility of slip [34]. The experiments were carried out at 30 °C in mainly the following two deformation modes:

- Scanning (sweep) shear rate measurements, with decreasing shear rate from 10^2 to $10^{-5}\ s^{-1}$, which were found to be physically meaningful and which identify the flow curve of the emulsion [36]; Masalova and Malkin, 2007b).
- Amplitude sweep oscillations in the range of strains from 0.1 to 200 % at the constant frequency of 1 Hz.

2.2.5. Emulsion stability under high shearing in pump

Destabilization is a common problem when the emulsion explosive is subjected to high shearing action such as when the emulsion phase is pumped or otherwise transferred into a borehole. During the high shearing conditions as encountered in transport and technological applications of these systems, the dispersed oxidiser salt solution droplets become smaller in size; conversely, the viscosity of the emulsion phase increases. This viscosity increase, though, is undesirable at the pumping stage because it reduces the emulsion explosive ability to flow. Moreover, along with the viscosity increase and smaller solution droplet size, the propensity of the emulsion phase to experience crystallization increases under such high shear conditions; high degree of crystallization may result in the desensitization of the emulsion explosive and can render it non-detonable [11].

Investigation of emulsion stability under high shearing was carried out using a double cylinder pumping system (manufactured and supplied by AECI Group, Republic of South Africa). This system consists of a cylindrical chamber with an outlet orifice of a small diameter (4 mm). A piston shaft is mounted into the chamber, which is moved downward under an applied force. This system is connected to a panel consisting of control valves: a distributor block and regulator are fixed to a wall and serve as the pressure function control of this pumping device. During the operation of this device, the emulsion sample under high pressure (3 bars) is forced out of the chamber through the small orifice. Thus, the prepared and cooled to room temperature emulsion sample is exposed to high shear rates. The shearing process was repeated up to 5 times. Immediately after each shearing step, a sample was analyzed with an optical microscope. To check for an eventual droplet reduction or crystallization of an internal phase.

3. Results and discussion

3.1. Effect of different emulsifiers on the aqueous-oil interfacial properties

This section presents the results as well as interpretation of an investigation of the effect of POSS AM0275, PIBSA-MEA, Span80 and Tween 80 on the interfacial tension at the planar aqueous-oil interface as well as the interfacial elasticity within the system under investigation.

The equilibrium interfacial tension σ of 1 wt% of a specific stabilizer (POSS AM0275, PIBSA-MEA, Span 80 or Tween 80) or their mixtures thereof in the oil phase in contact with 60 wt% ammonium nitrate in the aqueous phase was first measured. Then the interfacial elasticity of a drop of aqueous salt solution immersed in oil containing 1 wt% of a single stabilizer was measured at 0.5 mm amplitude and frequency of 1 Hz. The main results of these experiments, in Ash-H, are presented in Table 1.

It is clear from Table 2 that the interfacial tension of POSS AM0275 is lower than the one associated with PIBSA-MEA and comparable to the ones associated with conventional co-surfactant (Span 80, Tween 80). The cumulative effect of hydroxyl and carbonyl groups could account for the surfactant properties of Span 80 and Tween 80, while the presence of a primary and secondary amines confer to POSS AM0275 its surface activity. In presence of ammonium nitrate the amines increase the hydrogen-bonding strength of the surfactant which, in turn, improves the anchor of the polar head group onto the interface [22]. PIBSA-MEA contains amino, carboxyl and hydroxyl groups which should render it a more effective surfactant because there exists the possibility of an electrostatic type of interaction beside the hydrogen bonding interaction. Their low ability to reduce the interfacial tension as compared with POSS AM0275 could be related to both the existence of some resonance in the head group and the difficulty in packing imposed by steric repulsion between the bulky polymeric PIBSA tails. The electron resonance delocalizes the electron pair of nitrogen atom over the two carbonyl groups in the carboxylic acid structure; this resonance effect together with the high electronegativity of the N atom reduces the charge on the carbonyl oxygen atom. Moreover, the nitrogen atom cannot form hydrogen bonds with the salt also due to electron pair delocalization. On the other hand, conversely to PIBSA-MEA or any of its conventional co-surfactants which cannot generate a strong interfacial film, POSS AM0275 creates a rigid and flexible gel-like barrier at the interface which fully encapsulates the inorganic salts solution (Third column in Table 2). The formed gel-like barrier at the interface was rigid but flexible and altered the shape of the drop, making it impossible to perform any interfacial elasticity measurements and further analysis. This is in line with the findings in Masalova et al. [35].

3.2. Emulsion stabilized solely by Span 80 or POSS AM0275

To further screen different PIBSA-MEA's co-surfactants, we sought to make a highly concentrated w/o emulsion (90 wt%) using a Silverson L4RT high shear mixer equipped with a fine emulsor screen, 19 mm in diameter at 3000 rpm, at room temperature (25C). Then the ageing of the prepared emulsions was investigated using an optical microscope equipped with a digital camera. The visual observations of the main results of these experiments, in presence of Span 80 or POSS AM0275, are shown in Fig. 1.

Unlike Span 80 where multilayer formation triggers crystallization from the surface of bigger drops or inside smaller droplets (nucleation rate scales as the surface does) [41], in the case of POSS AM0275 the nucleation rate scales as the volume does (big droplets crystallize faster than smaller ones) suggesting homogeneous nucleation from within the droplets (Taborek, 1985). This critical finding means that even though POSS AM0275 seems to generate a more complex interfacial film, the latter is more resistant (stability = 144 days) with no tendency to induce crystallization in the system.

3.3. Emulsions stabilized with mixed emulsifier systems

3.3.1. Emulsion behavior under shearing

3.3.1.1. Refining and stability under shearing. Here, the discussion on emulsion stability concerns the stage of emulsification. Refinement is the process of reduction of the emulsion's droplet size by shearing, in this case, down to d_{32} = 10 μm. At this stage, dynamic stability under the mechanical forces used to refine the emulsion is the main consideration. As the quantitative measure of the kinetics of this process, we have chosen the characteristic refinement time. We realized this by placing the oil phase containing 17 wt% (≈1 wt % total emulsion) of PIBSA-MEA in mixtures with a specific co-surfactant (Span80, Tween 80, or POSS AM0275), in a ratio of 10:1, in the bowl. Then, the hot inorganic salt solution (83° C) was slowly added, while stirring was maintained, at speed1, to ensure emulsification (average drop size $d_{32} \approx 17$ μm). Rapid mixing at a higher speed (gear 3, the corresponding shear rate ≈ 380 s^{-1} in our experimental conditions) of the mixer was done subsequently for all formulations until a droplet size of 10 μm was reached. The time required during this last phase of emulsion preparation was recorded using a stopwatch and was referred to as the characteristic refinement time.

It is worth mentioning that for emulsions prepared without PIBSA-MEA, only 6 wt% of the stabilizer was used. The main results of these experiments are presented in Fig. 2. Results related to single surfactants are added for comparison purpose.

It is clear that a synergism exists between POSS AM0275 and PIBSA-MEA which enhances emulsion stability. PIBSA-MEA/POSS AM0275 mixture forms a stable highly concentrated emulsion (HCE) with reduced refinement time (40 min) in contrast to the higher refinement time associated with emulsions prepared with PIBSA-MEA alone (45 min) or to the completely unstable emulsions with POSS AM0275 (emulsion crystallized during the refinement process before reaching 10 μm) (not show here). However, despite the synergism, the latter mixture does not significantly reduce the refinement time as compared to conventional mixtures (PIBSA-MEA/Span 80 or PIBSA-MEA/Tween 80). It is likely that the high temperatures used (83° C) hinder or delay the structuring of POSS AM0275 at the interface into a rigid and flexible interfacial skin (observed at room temperature during interfacial measurements) or the interfacial film still forms at high temperature and opposes droplet break up.

3.3.1.2. Rheological properties. The dispersed phase concentration was fixed at 90 wt% and the average droplet size was 10 μm for all samples. The Foudazi-Masalova model is usually a suitable method to describe the flow behaviour of HCE (Tshilumbu et al., 2013). However, it is not applicable for calculation of pumping characteristics of emulsions, such as pressure drop versus flow rate, due to its complexity. Bearing in mind the fact that the choice of the flow curve fitting equation is unimportant for the estimation of pumping characteristics (Malkin et al. (2004), the emulsion sys-

Table 2
Summary of Herschel-Bulkley parameters and experimental values of G_p, B_n, El.

Stabilizer type	k	n	τ_y [Pa]	G_p [Pa]	B_n*10^3	$El*10^3$
PIBSA-MEA	36	0.44	34.5	884	42	1065
PIBSA-MEA/Span 80	37	0.42	18.2	550	33	1000
PIBSA-MEA/Tween 80	27	0.43	14.3	435	29	870
PIBSA-MEA/POSS AM0275	36	0.43	27.8	805	45	1298

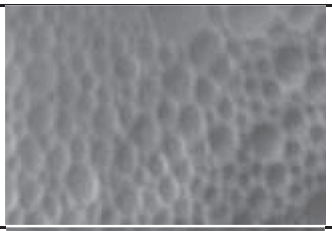
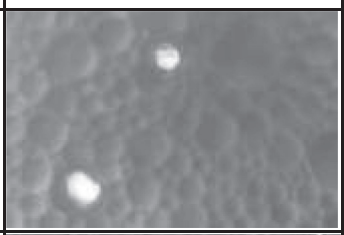
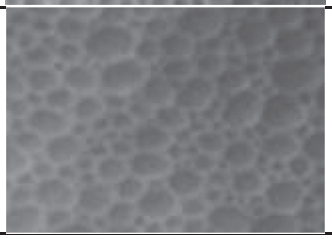
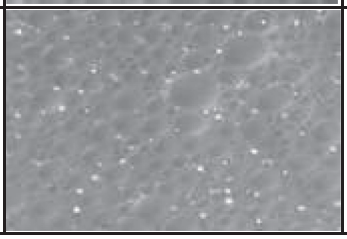
Emulsifier type	Microscopy Fresh Emulsion	Microscopy aged Emulsion	Observation
POSS AM0275			Crystallization inside drops on day 144
Span 80			Crystallization from interface from day 20

Fig. 1. Microscopic images of emulsions prepared using Span 80 or POSS AM0275.

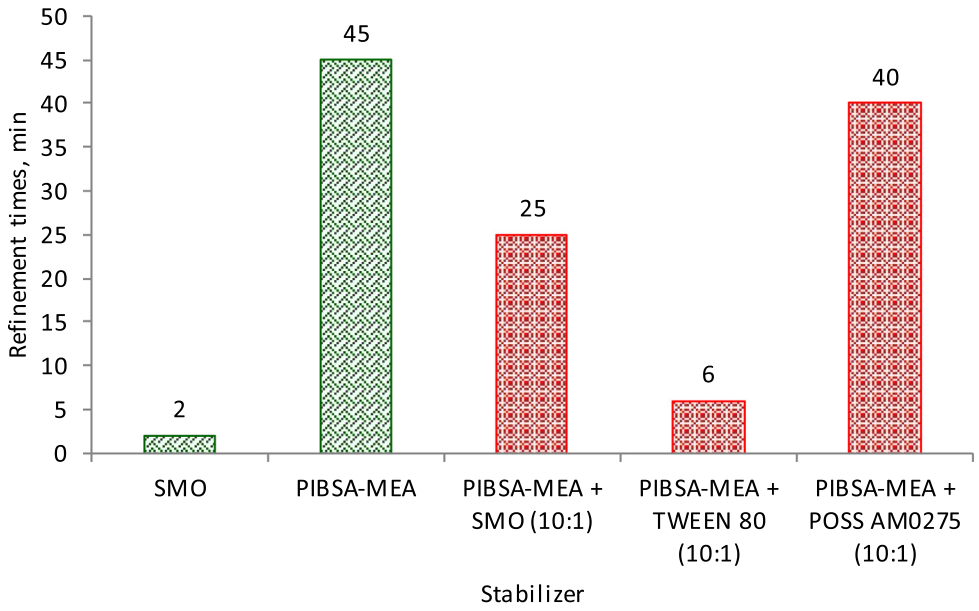


Fig. 2. Effect of a co-surfactant on the refinement time of emulsions stabilized with PIBSA-MEA (total surfactant concentration, 17 wt%).

tems under study were described by the Herschel-Bulkley model (equation (2)).

$$\tau = \tau_y + k\dot{\gamma}^n \quad (2)$$

Where τ_y (yield stress), k (consistency) and n (flow index) are fitting parameters.

As shown in Fig. 3 the Herschel-Bulkley model showed a satisfactory fitting of flow curves over the upper and lower range of shear rates.

The fitting parameters of the Herschel-Bulkley model on experimental data for all samples are summarized in the three first columns in Table 2.

Structure formation in HCE in the presence of mixtures of PIBSA -MEA and different co-surfactants is confirmed by the results of measurements of the elastic modulus. The frequency dependence of the elastic modulus is absent in a wide frequency range that is typical for solid-like behaviour of emulsions at low amplitude of deformation. Therefore we can consider the plateau modulus values as the characteristic of elasticity of emulsion explosive. Then, it is reasonable to consider the amplitude dependence of the elastic modulus, bearing in mind that the values obtained at low amplitudes correspond to the linear viscoelastic behaviour of emulsions. Experimental data obtained for HCE used in this study are presented in the last three columns in Table 2.

The lower average values of Herschel-Bulkley coefficients (τ_y, k and n) follow the trend: PIBSA-MEA > PIBSA-MEA/POSS AM0275 > PIBSA-MEA/Span 80 > PIBSA-Tween 80. This means that the use of POSS AM0275 as a co-surfactant could improve the pumpability of emulsion explosives prepared with PIBSA alone by reducing the required pressure drop to transfer the same amount of emulsion through a pipeline. However, the level of improvement observed with this co-surfactant is lower than the one associated with conventional ones.

It is seen that the low-amplitude plateau modulus G_p (rigidity of the structure) pursues the same trend as for the yield stress (strength of the structure), decreasing in the sequence: PIBSA-ME

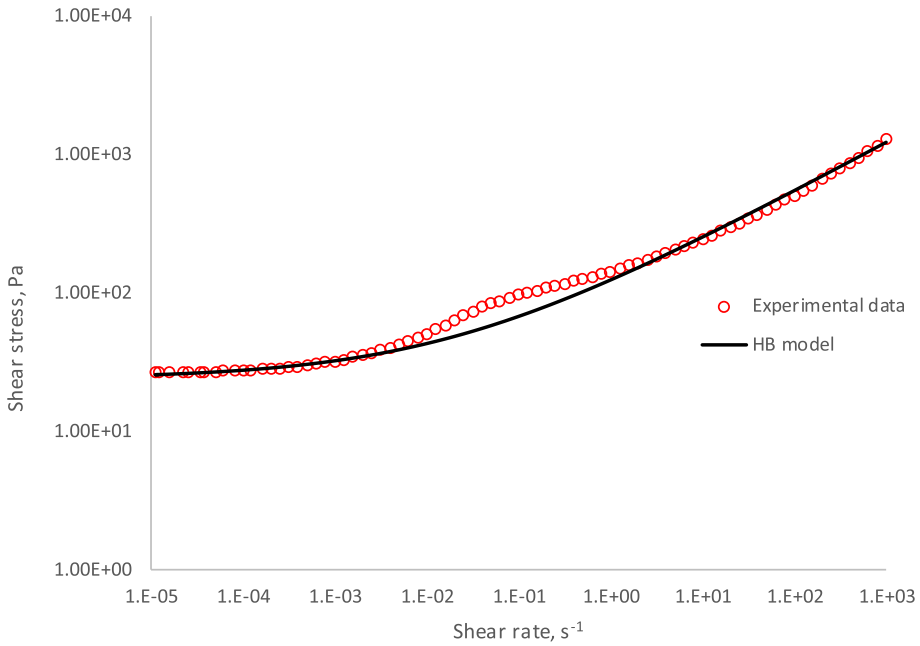


Fig. 3. Flow curve of the PIBSA-MEA/POSS AM0275 emulsion fitted by Herschel-Bulkley model.

A > PIBSA-MEA/POSS AM0275 > PIBSA-MEA/Span 80 > PIBSA-MEA/Tween 80. This means that both the strength and the rigidity of the emulsion's structure are obliged to the same physical source-interfacial rigidity and inter-droplet interaction. Although the maximum rigidity or strength (τ_y) of the emulsion structure is observed for samples with PIBSA-MEA alone, it is difficult to deform or break up a drop in emulsions prepared using PIBSA-MEA/POSS AM0275 mixture (highest B_n and El). The latter is in line with the interfacial elasticity results presented earlier. It seems reasonable to assume that the contribution of the inter-droplet interaction to the bulk rheological properties of PIBSA-based emulsions is higher than the one associated with samples prepared with PIBSA-MEA/POSS AM0275 mixtures.

3.3.1.3. Shear-induced crystallization. The emulsion stability under high shearing in technological operations was modeled by subjecting fresh emulsion to pumping under pressure of three bars supplied by a double cylinder pumping system where samples were forced to flow through a 4 mm diameter orifice. Typical microscopic images of sheared emulsions associated with 5 shearing cycles (N = 5) for PIBSA-MEA in combination with different co-surfactants are presented in Fig. 4. Data for emulsions stabilized by PIBSA-MEA solely are added for comparison purpose.

It is clear from Fig. 4 that POSS AM0275 significantly improves PIBSA-MEA based emulsions stability under shearing during pumping in comparison with conventional co-surfactants Span 80 or Tween 80. The trend is: PIBSA-MEA/POSS AM0275 (>45 days) > PIBSA-MEA/Tween 80 (≈ 10 days) > PIBSA-MEA/SMO (<3days) > PIBSA-MEA (0 day).

3.3.2. Emulsion stability against crystallization of the internal phase during storage

Emulsion stability with time was qualitatively assessed by a visual observation done with the aid of an optical microscope Leica equipped with a digital camera. The results of the crystallization of emulsions associated with all formulations used in this study are presented in Fig. 5.

The results in Fig. 5 clearly show that conversely to conventional mixtures (PIBSA-MEA/Span 80 or PIBSA-MEA/Tween 80), emulsion explosive stabilized with PIBSA-MEA/POSS AM 0275 mixture demonstrates a higher stability against crystallization of an internal phase as compared to the emulsions prepared with PIBSA-MEA alone. The trend of ageing is PIBSA-MEA/POSS AM0275 > PIBSA-MEA > PIBSA-MEA/Tween 80 > PIBSA-MEA/SMO. Once again, a strong synergism exists between PIBSA-MEA and POSS AM0275 enhancing emulsion stability (>45 days) in contrast to PIBSA –MEA alone (<45 days) or to complete instability for emulsions with POSS AM0275 alone (emulsion crystallized during manufacturing).

It is evident from these results that unlike conventional co-surfactants, POSS AM0275 improves the stability of PIBSA based emulsions not only under high shearing but more importantly during ageing. Moreover, the time to the start of crystallization of sheared as well as unsheared emulsion explosives has been significantly improved in presence of POSSAM0275 compared to conventional co-surfactants. If this outstanding emulsion stability in presence of POSS AM0275 results from a change in the stabilization mechanism of PIBSA based emulsion (which relies mainly on reverse micelles' ability to resist the spreading of crystallization throughout the system), needs to be answered. To discover this, two sets of experiments were carried out. An investigation into the stabilisation of emulsion explosives using different concentrations of PIBSA-MEA was first conducted, with the primary objective being to define the minimum concentration of surfactant required to make stable emulsion. This critical point is associated with a surfactant concentration where the reverse micelle's steric barrier is no longer able to guarantee the stability of the emulsion against spreading of crystallization from one drop to another (only few reverse micelles present in the inter-droplet layer) (Reynold et al., 2010). An emulsion explosive was then prepared using PIBSA-MEA/POSS AM0275: 10:1 mixture in which this critical concentration was considered as the total surfactant concentration and the shear stability of the emulsion during the emulsification process as well as its stability during ageing (for sheared and unsheared) were evaluated.

3.3.3. Determination of minimum surfactant concentration

The experimental data on the effects of PIBSA-MEA concentration on the kinetics of refinement showed that the minimum

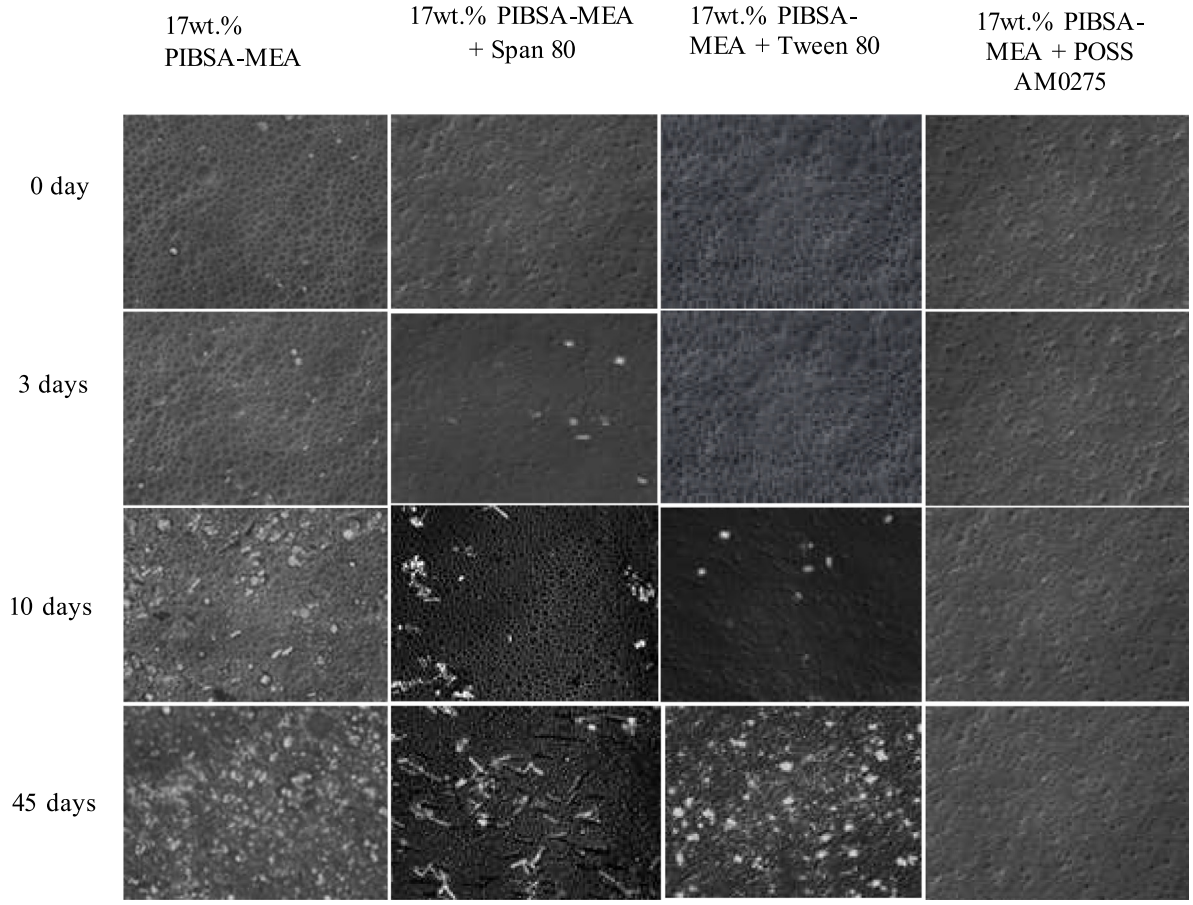


Fig. 4. Effect of a co-surfactant on the crystallization (shelf life) of sheared (N = 5) emulsion stabilized with PIBSA-MEA (17 wt% total surfactant concentration).

surfactant concentration required to make a stable emulsion explosive is 10 wt%. This agrees with the microscopic pictures (Fig. 6). Below this critical concentration, regardless of PIBSA-MEA concentration, the emulsions crystallized during the emulsification process prior to reaching the desired drop size (d_{32} = 10 μm).

On the other hand, as illustrated in Fig. 7, ageing of the emulsion reveals that at 10 wt% PIBSA-MEA in oil, crystals are predominantly needle-like in shape and importantly they are not confined to their original droplet size and shape; they break through the films separating droplets (conversely to the case where 17 wt% PIBSA-MEA were used). This could be considered indirect proof that at this critical concentration, only few reverse micelles are present in the thin film between droplets.

3.3.4. Emulsion stabilized using reduced surfactant concentration

3.3.4.1. Refining and stability under shearing. The experimental data demonstrated that first, reducing the total surfactant concentration from 17 wt% to 10 wt% increases the refinement time of emulsions prepared using PIBSA-MEA alone (from 45 to 55 min) as well as the emulsions stabilized with PIBSA-MEA/POSS AM0275 mixture (from 40 to 50 min). This is in line with the concomitant reduction of the diffusion rate of surface active species (surfactant or POSS AM0275) toward the newly formed droplet surfaces. Second, similarly to the case with 17 wt% total surfactant concentration, a synergism exists between POSS AM0275 and PIBSA-MEA, which enhances emulsion stability (50 min) as compared to the emulsion stabilized solely with PIBSA-MEA (55 min) or POSS AM0275(emulsion crystallized during the emulsification process).

Once again, similarly to the case with 17 wt% total surfactant, the observed synergism between PIBSA-MEA and POSS AM0275 was clearly expressed during the investigation on shear induced crystallization and shelf-life.

3.3.4.2. Shear-induced crystallization. The main results of the experiments on the stability against crystallization of sheared emulsions associated with 5 shearing cycles (N = 5) for PIBSA-MEA alone and PIBSA-MEA/POSSAM0275 mixture, at reduced total surfactant concentration (10 wt% in oil), are presented in Fig. 8. Data from samples prepared using 17 wt% total concentration of PIBSA-MEA in mixtures with conventional co-surfactants (SMO and Tween 80) are also shown for comparison.

Two observations can be made. First, unlike the case where emulsions were prepared using PIBSA-MEA alone, the reduction of the total surfactant concentration does not affect the stability of sheared emulsion stabilized with PIBSA-MEA/POSS AM0275 mixture in our experimental window. Second, the stability of sheared emulsion stabilized using PIBSA-MEA/POSSAM0275 mixture at reduced total concentration is higher than the one associated with 17 wt% total surfactant concentration when PIBSA-MEA is used alone or with conventional co-surfactants.

3.3.4.3. Stability with time. The main results of the experiments on the stability against crystallization of un-sheared emulsions prepared using PIBSA-MEA alone and PIBSA-MEA/POSS AM0275 mixture are presented in Fig. 9. Data from samples prepared using 17 wt% total concentration of PIBSA-MEA in mixtures with conventional co-surfactants (SMO and Tween 80) are also shown for comparison.

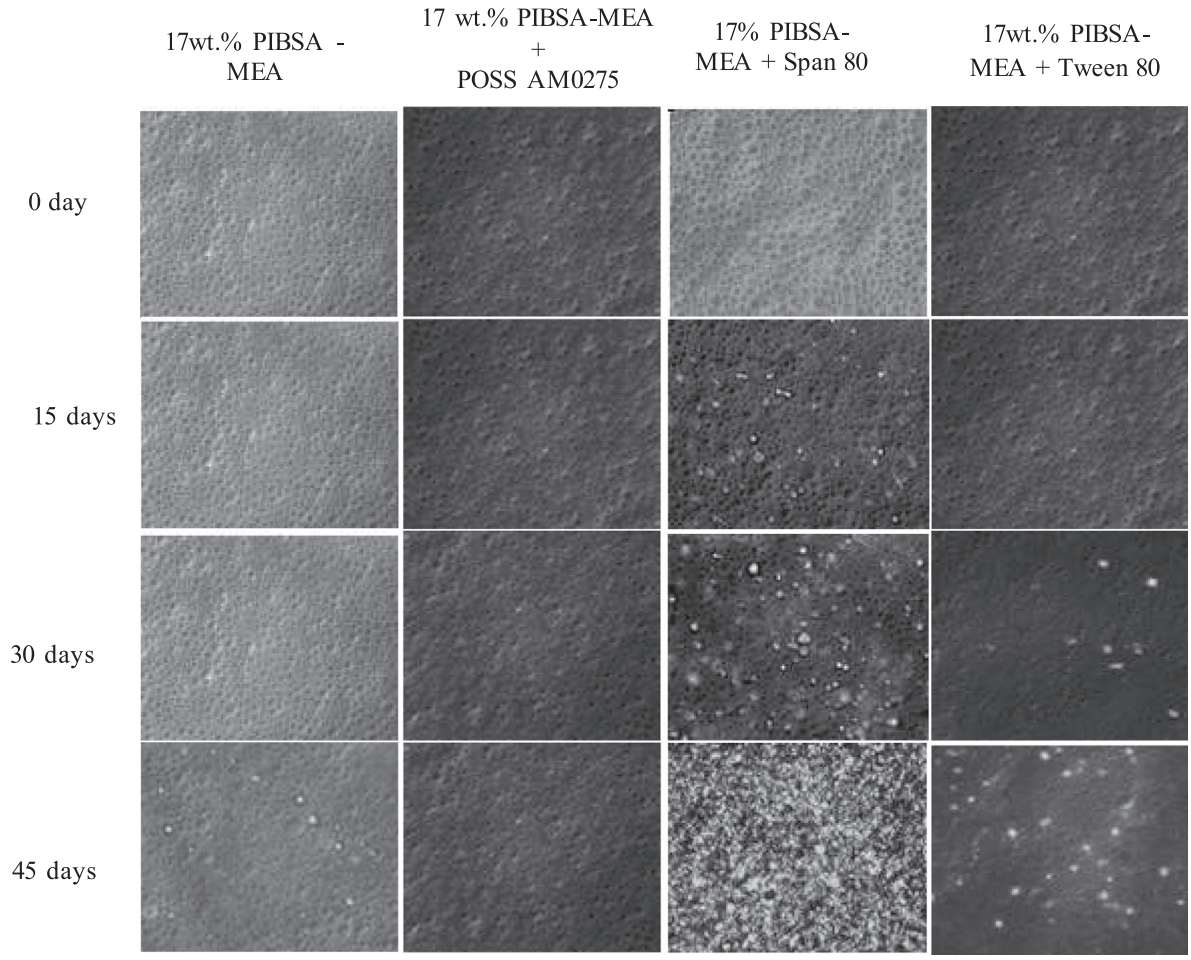


Fig. 5. Effect of a co-surfactant on the crystallization (shelf life) of HCE with an overcooled dispersed phase stabilized with PIBSA-MEA (17 wt% total surfactant concentration).

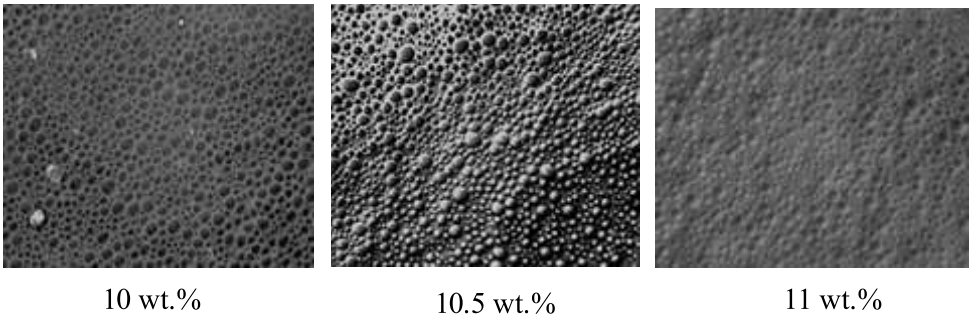


Fig. 6. Microscopic images depicting emulsions prepared with different surfactant concentrations.

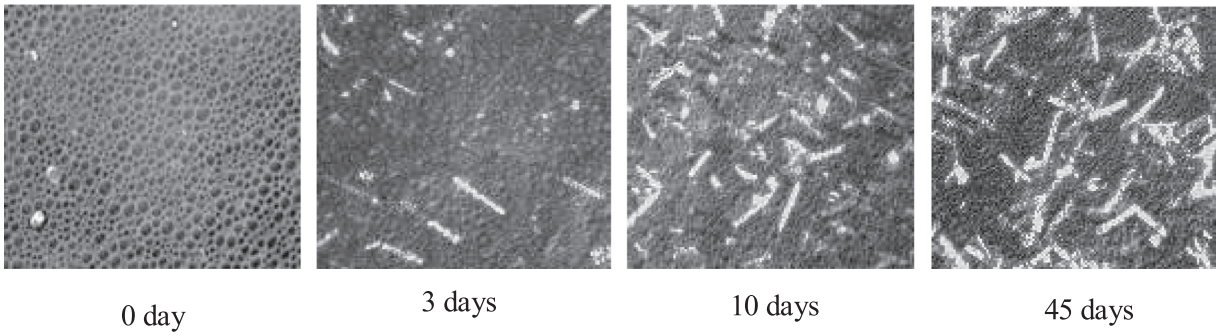


Fig. 7. Ageing of HCE with an overcooled dispersed phase stabilized with PIBSA-MEA (10 wt% total surfactant concentration).

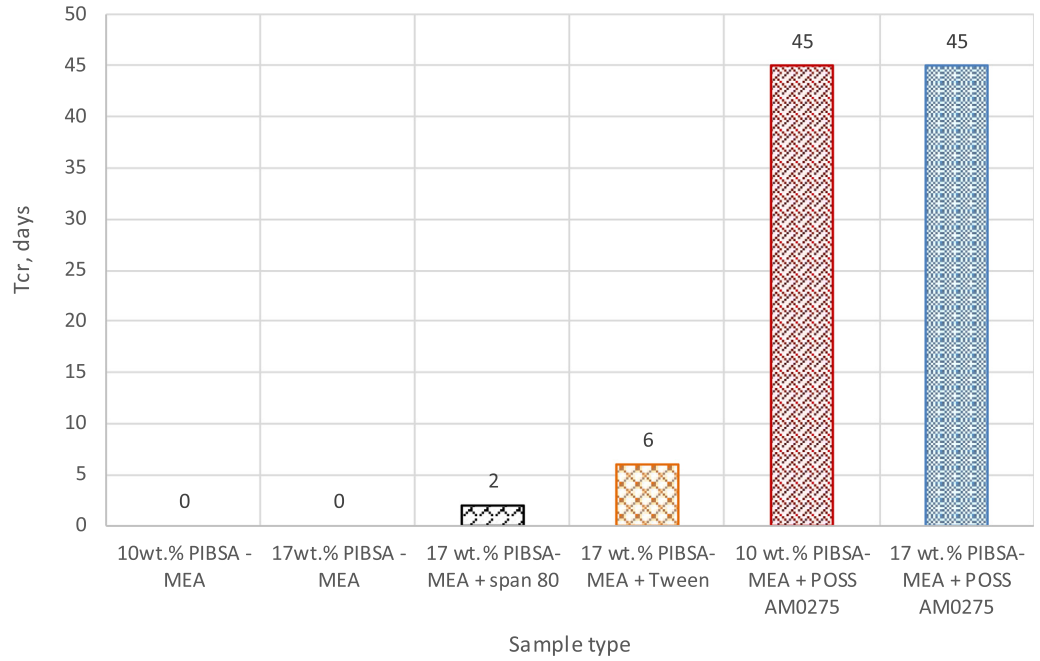


Fig. 8. Effect of reducing the total surfactant concentration on the crystallization (shelf life) of sheared (N = 5) emulsions stabilized with PIBSA-MEA alone and PIBSA-MEA/POSS AM0275 mixture.

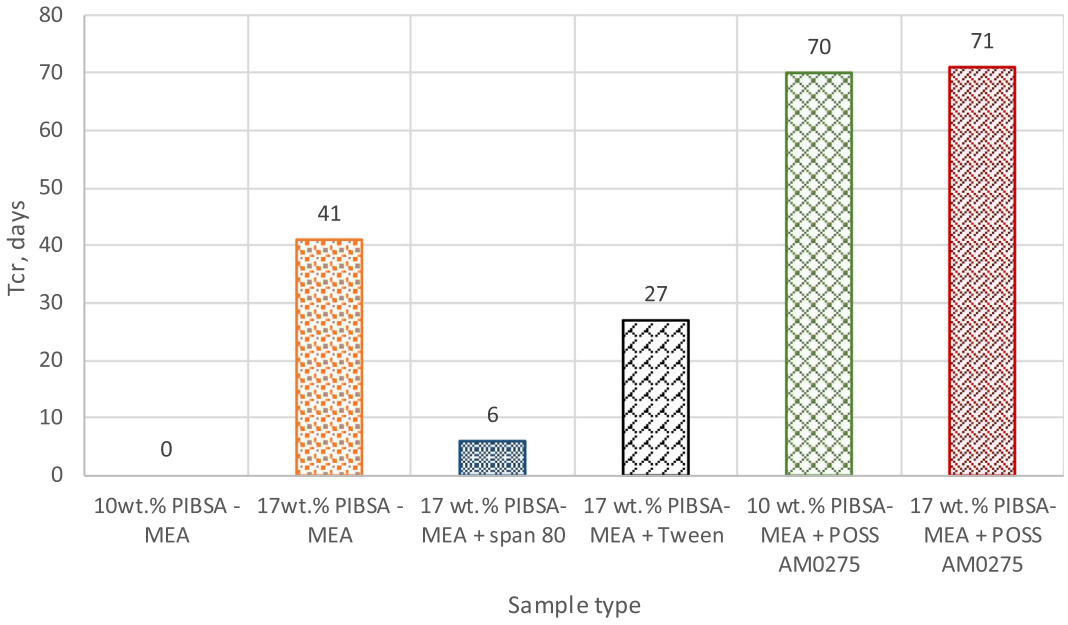


Fig. 9. Effect of reduction of the total concentration on the crystallization (shelf life) of un-sheared emulsions stabilized with PIBSA-MEA alone and PIBSA-MEA/POSS AM0275 mixture.

The results in Fig. 9 further confirm the strong synergetic interaction between PIBSA-MEA and POSS AM0275. Addition of POSS AM 0275 to PIBSA-MEA based emulsions at a reduced total concentration of 10 wt% demonstrated a higher stability against crystallization of an internal phase as compared to the emulsions prepared with either PIBSA-MEA alone or any mixture between PIBSA-MEA and conventional co-surfactants. This is deemed a critical finding for both scientific interest and technological applications of these systems.

The following arguments can be advanced to explain the source of the outstanding emulsion stability in presence of POSS AM0275. The fact that POSS AM0275 has an ability to maintain the emulsion stability when only few reverse micelles are present in the inter-droplet layer suggests that either these nanoparticles stabilize the emulsion by reinforcing the interfacial skin around droplets or by creating a 3D network in the thin film between droplets. The latter has been ruled out since rheological investigation demonstrated that both the oil phase with and without POSS AM0275 are Newtonian (not shown here) with similar viscosities; 4.7 Pas and 3.5 Pas respectively. We propose that through the synergetic interaction POSS AM0275 occupy the free spaces between the bulky polymeric PIBSA molecules and create a condensed layer

at the interface and thus reinforcing the rigidity of PIBSA-MEA monolayer. In this sense the interfacial layer could become able to strongly oppose crystal rupturing and thus prevent or slow down the spreading of crystallization through the sample.

4. Conclusion

Current study has investigated the new and unexplored field of using POSS nanoparticles as PIBSA-MEA's co-surfactant for stabilisation of water-in-oil (w/o) super-concentrated emulsions used as pumpable explosives. Thus, the primary goal of this research was to investigate the synergetic (or antagonistic) effect of the mixture between PIBSA-MEA and POSS AM0275 in stabilizing highly concentrated w/o emulsions with a supercooled dispersed phase, in comparison with one of the best surfactant mixtures PIBSA-MEA/Tween80 as well as the standard mixture PIBSA-MEA/Span80. It has been found that first, unlike conventional co-surfactants, POSS AM0275 improves the stability of PIBSA based emulsions not only under high shearing and more importantly during storage. Second, POSS AM0275 induces a change in the stabilization of mechanism of PIBSA based emulsion explosives by reinforcing the interfacial film rather than the usual mechanical barrier of reverse micelles. The new mechanism is much more effective than the conventional one; 10 wt% total concentration in the presence of POSS AM0275 gives rise to a more stable sheared as well as un-sheared emulsion than any formulation at 17 wt% total concentration without POSS AM0275. We propose that through the synergetic interaction POSS AM0275 occupy the free spaces between the bulky polymeric PIBSA molecules and create a condensed layer at the interface and thus. reinforcing the rigidity of PIBSA-MEA monolayer.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We would like to acknowledge Prof Irina Masalova (1955 – 2020) who provided academic leadership for many years to the research team. She is sincerely missed.

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