

Physio-Chemical Analysis of Amide and Amine Poly(dimethylsiloxane)-Modified Defoamer for Efficient Oil–Water Separation

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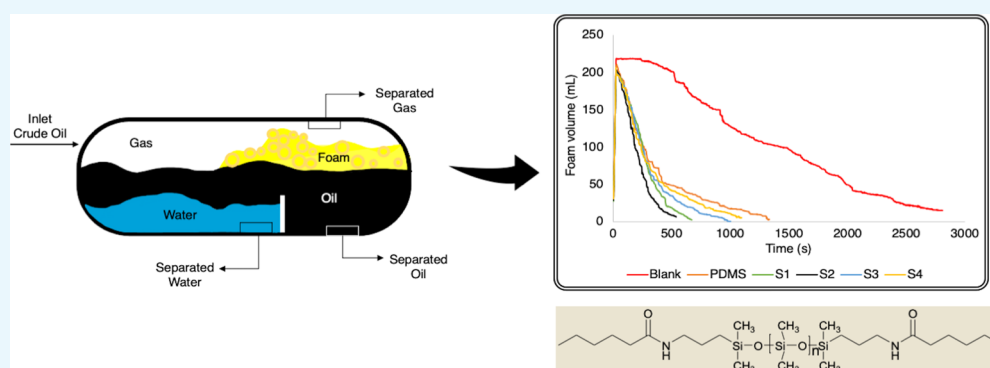
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ABSTRACT: The formation of foam due to the injection of surfactant foam in FAWAG causes significant problems in the oil well production and separation facilities. The excessive foam can lead to the reduction of the separator capacity as well as its efficiency. A defoamer is needed to break and destroy the foam in the separator. There are many commercially available defoamer agents in the market, but not all defoamers are suitable for every application. For this reason, four modified silicone-based defoamers were successfully synthesized and characterized based on the data obtained from the screening process using various commercial defoamers. The performance of modified defoamers was evaluated using TECLIS FoamScan that imitate real conditions of treatment. The results show that all four of the modified silicone-based defoamers, especially amide-terminated-modified defoamers (S2) showed excellent performance as a defoaming agent to mitigate foam in specific conditions. The best-case condition for the modified defoamer to perform was at a high temperature (60 °C), gas flow rate of 1.0 L/min, and low ration concentration of the surfactant to brine (30:70). The study on the bubble count and distribution using a KRÜSS Dynamic Foam Analyzer revealed that S2 excellently contributes to the formation of unstable foam that can fasten foam destruction in the foaming system.

1. INTRODUCTION

The water alternating gas (WAG) is one of the gas injection methods used in the enhanced oil recovery process to improve the mobility of the flooding system, provide better sweep performance, and improve oil recovery efficiency.^{1,2} Foam-assisted WAG (FAWAG) is one of the WAG injections that creates a foam barrier forcing gas to spread in the upward passage to combine with the previously unsweep parts.³ However, one of the significant downfalls is the use of surfactant foam in the process causing excessive foam formation in crude oil, affecting separation facilities and can cause severe operational problems. Foam formation causes a reduction in the capacity equipment as its excessive production will occupy most of the vessel spaces leading to spilling in tanks and equipment. Besides, the separation capacity and efficiency reduces tremendously as it is impossible to remove the separated gas or liquid oil from the separator without

entraining some of the materials resulting in wet oil or oily water phases.⁴

As reported by Juprasert and Davis,⁵ the best approach to overcome this problem is by disrupting the foam either chemically or hydraulically or both. The defoamer is a chemical additive that is widely used to disrupt the surface of the bubbles and break the existing foams. When the defoamer is added into a foaming system, a defoamer droplet will emerge from the aqueous phase into the gas–water interface during the process called entering. As the foam and defoamer interact, some oil from the droplet spreads on the

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foam surface forming lenses. The spreading of oil on the one film side of foam causes a significant difference between the tension of the two film sides, which destabilizes the foam film causing foam rupture.⁶

Many different types of defoamers have been introduced in the O&G industry, such as organic siloxane, polyether, silicon, ether graft, amines, imines, and amide siloxane. The development of the defoamer can be divided into four generations. The first generation mainly refers to the mineral oil defoamer, such as a water-soluble traditional defoamer, which is applied universally but less effective. The second generation is the polyether defoamer, where it possesses the characteristic of poison-less, tasteless, no irritation, and power dispersion in water. The third generation belongs to polysiloxane (i.e., silicone), which has a low surface tension, better thermal stability and chemical stability, nonphysiological toxicity, and high-foaming ability. Polydimethylsiloxane is one of the commercially used polysilicone defoamers that has a highly flexible backbone made of strong and very polar Si—O bonds but shielded by the low interacting methyl group, thus leading to low intermolecular forces and properties such as low surface tension.⁷ Besides, polydimethylsiloxane exhibits properties such as nonionic, insoluble in water, and hydrophobic in nature, which enables it to perform very well as an antifoaming agent. The silicone antifoaming agent usually disrupts the foam stabilizing mechanism by displacing it with silicone that does not exhibit any hydrogen bonding. This displacement causes the electric double-layer effects to be destroyed and removes the resistance to gas diffusion between bubbles and allow the bubble breaking mechanism to operate. However, one of the downfalls of this generation is the difficulty to be emulsified due to the poor utilization effect.

Modified silicone defoamer belongs to the fourth generation defoamer. The modification of the silicone defoamer usually involves the modification of the chemical structure and composition between a parent chain, typically the polysiloxane group with a side chain containing different types of a functional groups. The modified silicone defoamers mainly have improved emulsified performance of the polysiloxane defoamer by introducing a hydrophilic group of polyorganosiloxane, thus exhibiting excellent foaming properties and water solubility.⁸ Besides, studies show that polysiloxane cannot be used directly as a defoamer in an oily system.^{9,10} Therefore, the structure and performance of polysiloxane are typically modified when applied in an oily system. This is due to certain solubility in an oily system, which may have a toxic impact on the catalyst in the subsequent petroleum process. Furthermore, by modifying the polysiloxane structure and composition, its capability in heat resistance can be improved for the application in more extreme and harsh conditions.^{9,10}

Different researchers have different approaches in modifying the polysiloxane-based defoamer to improve its ability in breaking foams at certain conditions. Han et al.⁸ stated that the nature of the silicone-based defoamer, the structure of the polymer, the type of terminal group, the ratio and the conjunction way between the polymer and silicone are the factors affecting the performance of the modified defoamer. The polyether-modified polysiloxane defoamer is one of the widely used modified silicone defoamer in the O&G industry. One of the many methods in synthesizing a polyether-modified polysiloxane was introduced by Ni et al.,¹¹ in 2009. The reaction involved an addition reaction between low hydrogen silicone oil and allyl-terminated polyoxyalkylene in the

presence of chloroplatinic acid as a catalyst. The modified defoamer was then compounded with silica, emulsifiers, and a thickener in water to give a high-performance defoamer for crude oil. Based on this study, the synthesized defoamer shows an excellent defoaming capability of 75–91% for high water cut conditions at a chemical dosage of 20–80 mg/L. The results also show that the synthesized defoamer's defoaming capability increases as the chemical dosage increases from 40 to 80 mg/L compared to the control defoamer used in the study. Most of the polyether-modified polysiloxane defoamer has better antifoaming performance than polydimethylsiloxane because it disperses quickly in the antifoaming system, at a much higher efficiency than antifoam. This antifoam's performance is influenced by the nature of polysiloxane, the structure of the polyether, the type of the terminal group, the ratio, and the conjunction way between polyether and polysiloxane. The viscosity of silicone oil also plays a vital role in water solubility and surface activity of polyether-modified polysiloxane antifoaming agents.^{4,8}

Other modified silicone-based defoamers, known as PPG-*b*-PDMS-*b*-PPG and PEG-*b*-PDMS-*b*-PEG, is a combination of poly(ethylene glycol) (PEG) and poly(propylene glycol) of different molecular weights (200, 400, and 1200) bonded to polysiloxane to produce tri-block copolymers. These modified silicone-based copolymers were synthesized by Kekevi et al.¹² through a polycondensation reaction between chloride-terminated polysiloxane and polyethers, which showed a low surface tension values, fast liquid drainage, and efficient foam destruction. The spectroscopic analysis of this copolymer confirmed the bonding of polyether to polysiloxane. In this research, the Ross–Miles test method was used to determine the foam height, foaming properties, and antifoaming efficiency of the copolymer. According to the results obtained, the antifoaming efficiency of these copolymers tends to increase with an increase in the hydrophilic character of the copolymer chains as a decrease in foaming was observed during the gas purging process. The study concluded that all the tri-block copolymer has the same foam destruction mechanism. However, a tri-block copolymer with the shortest PEG molecular weight, PEG 200-*b*-PDMS-*b*-PEG 200 shows a faster foam collapse and is the most effective antifoaming agent among all.

A recent study by Wang et al.⁹ showed a modification of polysiloxane by introducing fluoroalkyl and polyether groups in the structure to form a modified polysiloxane defoamer known as fluoroalkyl and polyether co-modified polysiloxane (FPEPS). This modification aimed to improve oleophobicity, hydrophobicity, heat resistance, and foam-inhibiting ability of defoamers. The foam breaking and inhibiting performance of the modified FPEPS defoamer were tested using self-assembled equipment and compared with three commercially oily defoamers. The prepared simulated foaming oily system was kept under a circulating water bath of 50 °C, and nitrogen gas purging at 80 mL/min with 0.01 g of the defoamer added once foam produced. Based on the results obtained, the new FPEPS defoamer gives better foam breaking and inhibiting performance than the commercial products with the shortest defoaming time of 15.1 s. Moreover, the ability of the modified defoamer in higher heat resistance was much improved due to the modification and addition of 1,3,5-tris(3,3,3-trifluoropropyl) methylcyclotrisiloxane (D₃F) and polyether in the structure.

Therefore, our research is aimed to solve an issue in the oil treatment industry and enhance defoamer's performance in mitigating foam for WAG treatment. In this study, a series of commercially available silicone-based defoamers underwent a screening test to evaluate their performances in conditions that imitate real condition treatment. The best performing commercial defoamer was modified to further enhance its efficiency. The modified silicone-based defoamers were characterized using modern spectroscopic techniques, and the effects of the modification were investigated. The performance aspect of the modified defoamers for foam mitigation was also covered to ensure that the synthesized modified defoamers can perform well compared to the commercial parent chain in the condition that mimics gas/oil separator treatment.

2. MATERIALS

Crude oils were obtained from the PETRONAS Peninsular field (PETRONAS, Terengganu, Malaysia). EFOMAX 2.0 (16%) was obtained from PETRONAS Research Sdn. Bhd., and was used as a polymer in the surfactant–polymer (SP) solution. Calcium chloride pentahydrate (purity 99%), magnesium chloride hexahydrate (purity 99%), potassium chloride (purity 99%), barium chloride dihydrate (purity 99%), strontium dichloride hexahydrate (purity 99%), sodium sulfate (purity 99%), sodium chloride (purity 99%), and sodium bicarbonate (purity 99%) used for the preparation of the brine solution were obtained from Aldrich (Darmstadt, Germany). Table 1 shows the composition and properties of the brine

Table 1. Brine Composition and Properties

compounds (brands)	weight (g) for 1.0 L brine solution
CaCl ₂ ·2H ₂ O (R&M Chemicals)	0.0997
MgCl ₂ ·6H ₂ O (R&M Chemicals)	0.0820
KCl (Merck)	0.3098
BaCl ₂ ·2H ₂ O (Merck)	0.0011
SrCl ₂ ·6H ₂ O (Merck)	0.0014
Na ₂ SO ₄ (R&M Chemicals)	0.3844
NaCl (Bendosen)	17.3742
NaHCO ₃ (Fischer Scientific UK)	3.1570

solution. For the screening test, a wide range of chemical defoamers were used, as listed in Table S1 (see Supporting Information).

3. EXPERIMENTAL WORK

3.1. Screening of Commercially Available Defoamers Using a Foam Tester. The screening test was performed using a foam tester by Anton Paar (Graz, Austria) at 30 °C under atmospheric pressure. In Stage 1, 48 mL of surfactant polymer, 32 mL of brine solution (ratio of 60:40), and 20 mL of Dulang crude oil were added into a 1000 mL graduated cylinder followed by 50 μL of chemical defoamer in five different active concentrations (10, 20, 40, 60, and 80%) and then placed in a water bath at 30 °C. The cylinder was inserted with an air inlet tube, which was fastened with a gas diffuser. The time taken for foam to collapse was recorded.

Meanwhile in Stage 2, the same procedure was applied. However, the ratio of the surfactant polymer-to-brine was increased from 60:40 to 90:10. Thus, 72 mL of the surfactant polymer and 8 mL of the brine solution was mixed. The test was conducted at the same temperature of 30 °C. The

temperature and pressure for these tests were maintained at 30 °C under atmospheric pressure. It is the minimum temperature and pressure for the operation value of the chemical defoamer to perform in a separator. The test was also performed using crude oil from the Dulang field.

3.2. Modification of the Selected Silicone-Based Defoamers. Based on the screening test results obtained, the silicone-based defoamer was selected for further modification due to its high performance in rupturing foam with the shortest duration. Four different functional groups were then introduced to the parent chain of the selected defoamer, namely, Poly(dimethylsiloxane), bis(3-aminopropyl) terminated, also known as APPDMS consisting of long, short, branch chains and an amine group to produce modified defoamers. The synthetic pathway followed the method reported by Lin et al.¹³

For the synthesis of the long-chain modified defoamer (S1), APPDMS (2.0 mmol, 5.0 g) and 30% NaOH aqueous solution (0.1 mol, 1.0 g) were placed into a 250 mL three-necked reaction flask equipped with a magnetic stirrer and a thermometer. The mixture was then heated to 70 °C until a homogenous solution was obtained. Then, 1-octanol (4.0 mmol, 0.52 g) was added and left to react for 7 h. Once the reaction completed, the product underwent purification using solvent extraction in acetone (150 mL) and was extracted twice with saturated Na₂CO₃ solution to remove any unreacted fatty alcohol. The final product was dried overnight in an oven to remove moisture, appearing as a clear liquid at room temperature.

For the amide-modified synthesis (S2), DMF (1.0 g) was added into the reaction as a catalyst as well as an aprotic solvent in a reaction prone to polar group formation. The same procedure was applied, except 1-octanol was replaced with hexanoic acid (4.0 mmol, 0.46 g). The final product was obtained as a white solid. For the synthesis of short-chain modified (S3), 1-octanol was replaced with 1-hexanol (4.0 mmol, 0.41 g). The same procedure was also applied. The final product obtained as a clear liquid. Lastly, for the synthesis of the branched modified (S4), the same procedure was also applied, with 3,3-dimethyl-1-butanol (4.0 mmol, 0.46 g) replacing the addition of 1-octanol. The final product obtained as clear liquid.

3.3. Characterization. The FTIR spectra of the modified defoamer were recorded using a Perkin Elmer Spectrum 65 FT-IR spectrometer with Universal ATR sampling, from 10 to 4500 cm⁻¹ spectral regions. The spectra were obtained by measuring the bulk samples directly with the ATR instrument to avoid the absorption of atmospheric water during the traditional grinding process for pellets with KBr. The ACD/Labs software was used to analyze the presence of the functional group. Proton (¹H) and carbon (¹³C) NMR spectra of the each modified defoamer were recorded on Bruker 400 MHz SB Ultra Shield spectrometer, using TMS as a standard. Around 10 mg of each modified defoamer was dissolved in 600 μm of deuterated chloroform (CDCl₃) and transferred into a 5.0 mm NMR tube. All of the NMR spectra obtained were analyzed using Mestrelab software.

3.4. Performance Evaluation Using TECLIS Foamsan. The modified defoamers were tested using the TECLIS Foamsan instrument (TECLIS, France) to investigate the collapse time, half-life, and stability of foam produced. Initially, foam was generated using NO₂ gas purging through a glass chamber, containing the mixture of the surfactant polymer,

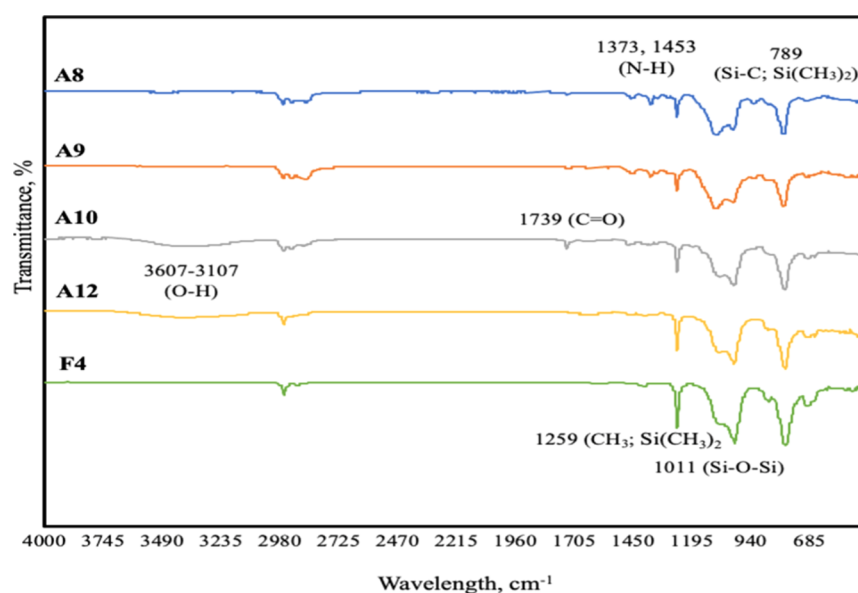


Figure 1. FT-IR spectrum for all the five selected commercial defoamers.

brine, and crude oil, heated at 60 °C. The gas stopped purging when the foam reaches the maximum pre-set volume of 200 mL. The foam collapse profile was measured via a CCD camera placed near the chamber, and the foam stability was determined based on the half-life time.¹⁴ In this test, a mixture of 64.8 mL of the surfactant polymer and 7.2 mL of brine solution were prepared in a beaker, followed by the addition of 40 μ L of the modified defoamer was first prepared. The crude oil (8.0 mL) was injected into the chamber, followed by the addition of the first mixture. Then, the pressure was set up to 4.0 bar, and a flow rate of 0.5 L/min. The pressure was set at 4.0 bar to stimulate the real pressure in the separator.

To investigate the effect of the concentration, mixtures of the surfactant polymer and brine solution were prepared at different ratios of the surfactant polymer-to-brine ratios of 30:70 and 90:10. The mixture of 30:70 refers to 21.6 mL of the surfactant polymer and 50.4 mL of the brine solution, while 90:10 is a mixture of 64.8 and 7.2 mL of the surfactant polymer and brine solution, respectively. Then, 8.0 mL of crude oil was added to each ratio. The effect of flow rate and the effect of temperature on the performance of modified defoamers were also studied. The modified defoamers were tested at two different flow rates of 0.5 and 1.0 L/min and two different temperatures (30 and 60 °C). Two different crude oils, Dulang and Baronia, were used in this study.

3.5. Bubble Count and Distribution Study Using KRÜSS Dynamic Foam. The bubble size and distribution of foam in the modified defoamers were studied using a KRÜSS dynamic foam analyzer DFA100 (KRÜSS GmbH, German), using a precise and high-resolution optic sensor and camera attached to the instrument to monitor the bubble count (BC) and distribution. In this test, a ratio of the surfactant polymer-to-brine of 90:10 was selected as it is the maximum ratio for foam production using the surfactant polymer. A 28.8 mL of the surfactant polymer, 3.2 mL of the brine solution, and 8.0 mL of crude oil were mixed in a 250 mL tempered glass column with a 40 mm diameter followed by the injection of 20 μ L of the modified defoamer into the column. Then, air was purged through a 16–40 μ m porous filter plate with a constant flow rate of 0.5 L/min at atmospheric pressure.¹⁵ The gas

purging was stopped after reaching the maximum foam height (200 mL) or maximum time of purging (120 s). The foamability of liquid and the foam stability were obtained by measuring the foam height and foam decay over time. The optic sensor and camera attached to the instrument was used to monitor the BC and distribution during the maximum foam height and minimum foam height.

4. RESULTS AND DISCUSSION

4.1. Screening of the Commercially Available Defoamer (Foam Testing Analysis). Foam testing analysis using a foam tester by Anton Paar was performed as a screening tool to study the performances of the chemical defoamers in condition specific to FAWAG application. Thirty-four commercial defoamers were selected based on several factors such as their chemical and physical properties, family types, and their ability to perform as an antifoaming agent specific to oil application. Figure S1 (see [Supporting Information](#)) shows the time taken for generated foams to collapse for all commercial defoamers in Stage 1 of the screening test. Based on the results obtained, only 13 defoamers showed a deficient foam collapse time below 3000 s (50 min). Silicone-based defoamers displayed the most excellent performance among all the commercial defoamers tested. Defoamer A9 (Silcolapse C585) gave the shortest foam collapse time (1 s), followed by defoamers A8 (Poly-(dimethylsiloxane), bis (3-aminopropylterminated)), and A10 (Silcolapse C550) at 31 and 43 s, respectively.

Meanwhile, the time taken for foam to collapse for the 13 selected defoamers during Stage 2 of the screening test is illustrated in Figure S2 (see [Supporting Information](#)). All the selected chemical defoamers were tested using a higher concentration of surfactant polymers (90:10) compared to the first stage (60:40). The higher ratio of the surfactant polymer indicates more foam produced during the process caused by the surfactant polymer. As observed, only five defoamers, A8 (poly(dimethylsiloxane), bis(3-aminopropyl)), A9 (Silcolapse C585), A10 (Silcolapse C550), A12 (Bluesil SP3304), and F4 (Airase 5100), resulted in foam breakage below 16,000 s (267 min) with the highest defoamer

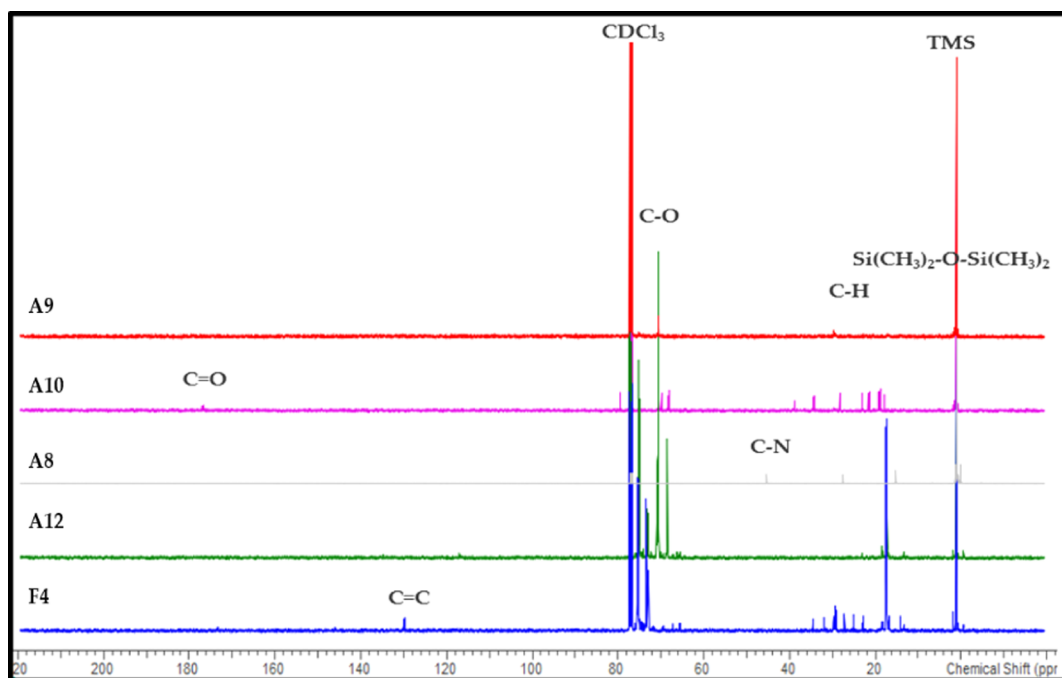


Figure 2. ^{13}C NMR spectrum for all the five selected commercial defoamers.

percentage (80%) giving faster foam breakage. Among all the selected defoamers, four out of five (A8, A9, A10, and A12) belong to the silicone-based, while F4 is an unknown formulated commercial defoamer.

4.2. Characterization of Selected Defoamers from the Screening Test (Stage 2). Figure 1 shows the Fourier transform infrared (FT-IR) spectra for all five selected commercial defoamers. Based on the spectra, all defoamers exhibit similar peaks, indicating the presence of identical functional groups except for the occurrence of a medium and broadband of the hydroxyl ($-\text{OH}$) or secondary amide ($-\text{NH}$) group at 3107 to 3607 cm^{-1} in defoamers A10 and A12, respectively. Also, the band at 1739 cm^{-1} indicates the presence of a carbonyl ($-\text{C}=\text{O}$) group in A10, A12, and F4. The stretching vibration for CH_2 and CH_3 for all five defoamers can be observed from 2825 to 3000 cm^{-1} . The adsorption band at 789 , 1011 , and 1259 cm^{-1} shown in all defoamers were due to $\text{Si}-\text{C}$; $\text{Si}(\text{CH}_3)_2$, $\text{Si}-\text{O}-\text{Si}$, and CH_3 ; $\text{Si}(\text{CH}_3)_2$ groups, respectively.

As depicted in Figure 2, the ^{13}C NMR spectrum for all defoamers showed peaks in the region of δ 0 – 2 and δ 14 – 40 due to the $\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2$ and $-\text{C}-\text{H}$ carbon, resulting from the same polydimethylsiloxane parent chain, respectively. The presence of $-\text{C}-\text{O}$ carbon can be seen in a region of δ 60 – 80 in all defoamers except for defoamer A8. Defoamer A10 only shows a peak at δ 177 that indicates the $-\text{C}=\text{O}$ carbon. The FT-IR and ^{13}C NMR spectra conclude that most of the defoamers have similar functional groups in their chemical structure, as it is believed to have resulted from the same polydimethylsiloxane parent chain. However, only A10 shows the presence of $\text{C}=\text{O}$ and $-\text{OH}$ groups in the structure giving the best performance among all the selected defoamers. Hence, the presence of these specific functional groups is believed to increase the performance of the defoamer to mitigate foam more effectively.

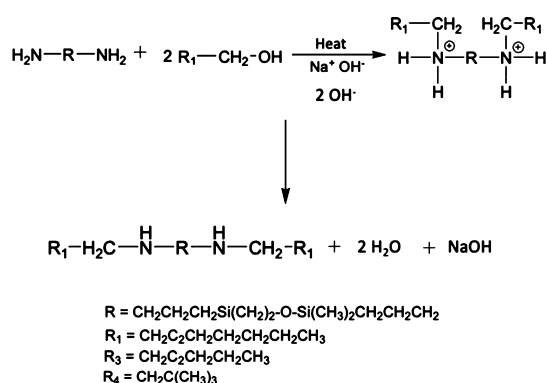
4.3. Modification and Characterization of the Silicone-Based Defoamer. Defoamer A8, or also known as

poly(dimethylsiloxane), bis(3-aminopropyl) terminated (APPDMS) was selected to be the parent chain for the modification. A8 is the only compound that has a known chemical structure while the other chemicals were in the form of formulation and mixture with an unknown composition. The modification of the selected parent chain consists of the addition of short, long, and branched alkyl chains, and an amide functional group in the terminal chain of the parent structure. The amide functional group was selected based on the previous characterization results, which indicate that the defoamer with the presence of $\text{C}=\text{O}$ gave faster foam drainage compared to the others without $\text{C}=\text{O}$. Meanwhile, the addition of long, short, and branched chains is aimed to study the effect of the alkyl chain length on the performance of the defoamer in mitigating the foam.

The modified defoamers were successfully synthesized through alkylation for long, short, and branched modified defoamers (S1, S3, and S4) and acylation with carboxylic acid for the amide-modified defoamer (S2). Each of the modified defoamer exhibits a clear viscous liquid as the final product, except for S2 with a white waxy solid appearance. The percentage yields for S1, S2, S3, and S4, is 89, 93, 72, and 42%, respectively. The low yield was obtained due to weight loss during purification and drying process. Schemes 1 and 2 illustrate the reaction synthesis of all the modified defoamers.

The FT-IR spectra of the $\text{Si}-\text{O}-\text{Si}$ stretching vibration show an intensity band at 1099 cm^{-1} , followed by $\text{Si}-\text{C}$ group stretching, and CH_3 rocking in $\text{Si}-\text{CH}_3$ at 810 and 1266 cm^{-1} , respectively, attributed to the parent chain of all the modified defoamers (Figure 3). The polysiloxane backbone parent chain remained unchanged as the bonds were unbroken by acid throughout the synthesis process. When the modified products were formed, a $-\text{NH}$ stretch band represents the secondary amine (single peak) produced at 3317 cm^{-1} , due to the linkage of the parent chain and side chain in the synthesis pathway indicating the formation of new molecular bonding by the modified products. This was further confirmed by the presence

Scheme 1. Reaction of APPDMS with Alcohol through Alkylation for S1, S3, and S4 Defoamers



Scheme 2. Reaction of APPDMS with Carboxylic Acid through Acylation for S2 Defoamer

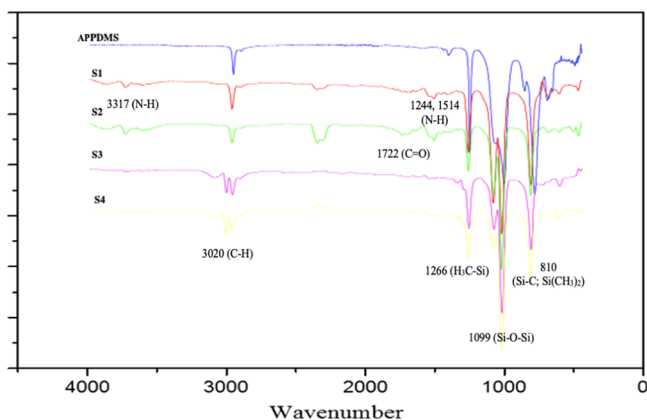
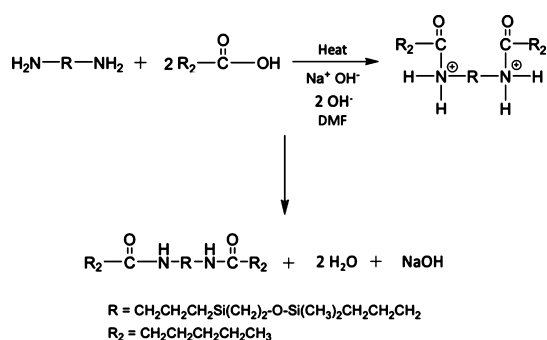


Figure 3. FT-IR spectrum for all four modified defoamers.

of a medium band appearing in the region of 1244 and 1514 cm^{-1} , indicating N–H stretching and bending.¹⁶ In addition, the disappearance of the –OH stretching medium broadband in the range of 3400–3650 cm^{-1} strongly suggests the completion of the modified products.¹⁷ For the amide-modified defoamer, a strong, prominent, and stack-shaped band around 1710–1720 cm^{-1} in the middle of the spectrum represented the formation of the amide group. However, only a weak peak of the C=O stretch was observed at 1722 cm^{-1} due to the high-density of the polymer compound (APPDMS). The absorption band of C–H for all the modified defoamers was observed in the range of 2698–3020 cm^{-1} .¹⁶

Figure S3 (see Supporting Information) shows the ^1H NMR spectrum for all four modified silicone-based defoamers. The first two peaks labeled H1 and H2 at a chemical shift of 0.1–

0.6 ppm indicate the dimethyl siloxane repeating units obtained from the parent chain.¹⁸ Meanwhile, peaks in the downfield region at a chemical shift of 0.8–1.8 ppm were attributed to the proton at the terminal chain of the modified defoamers. These peaks are assigned based on the position of each proton and the chemical environment. The peaks labeled H4 and H5 at a chemical shift of 2.6–3.7 ppm corresponded to the –CH₂ groups, which were located at adjacent to the nitrogen atom. For modified defoamer S2, the peak detected in the most downfield region is referred to the proton of the amide group labeled H5. Figure S4 (see Supporting Information) shows the ^{13}C NMR of all four modified defoamers. The first two peaks, labeled C1 and C2, represent the carbon atoms of the dimethyl siloxane repeating unit from the parent chain of APPDMS.¹⁹ Peaks at the chemical shift of 47–63 ppm labeled C4 and C5 for S1, S3, and S4, refer to the carbon located within the amine group. However, in the S2 spectrum, the carbons located within the amine group labeled C4 and C6, were observed around δ 36 to 40 ppm, due to the different chemical environment caused by the presence of the carbonyl group, marked as C5 at δ 178 ppm. The C5 peak shifted to the upfield region due to the de-shielding effect of the nitrogen atom.

4.4. Performance of Modified Silicone-Based Defoamers.

Figures 4 and 5 show the foam height generated and

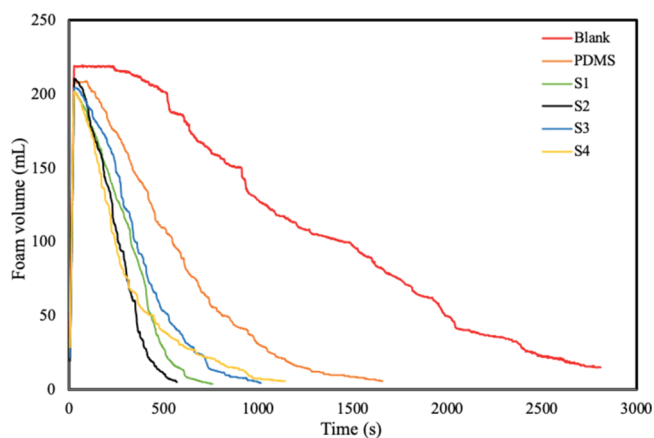


Figure 4. Foam volume as a function of time for all systems (first trial).

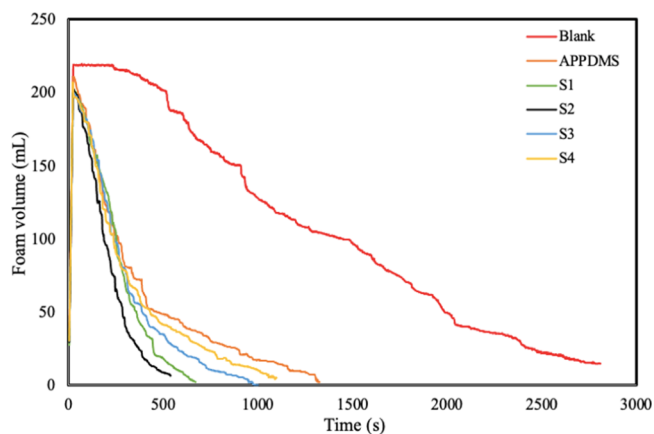


Figure 5. Foam volume as a function of time for all systems (second trial).

Table 2. Maximum and Minimum Foam Height, Foam Collapse Time, and Slope Value of all Systems at 60 °C and 4.0 bar^a

system	trial	time of foam (s)						slope value (m)
		max height of foams (t_{\max})	min foam height after foam breakage (t_{\min})	collapse time (t_{\min}) – (t_{\max})	average collapse time (t_{Avg})	foam half-life ($t_{1/2}$)	Average half-life ($t_{1/2 \text{ avg}}$)	
blank	1	28	2809	2781	2781	1390.5	1309.5	–0.0839
APPDMS	1	27	1655	1628	1451.5	814	838	–0.1348
	2	25	1300	1275		862.5		–0.1239
S1	1	24	757	730	684	365	342	–0.3145
	2	22	660	638		319		–0.3354
S2	1	28	571	543	526.5	271.5	263	–0.4442
	2	25	535	510		255		–0.4115
S3	1	28	1013	985	980	492.5	490	–0.2266
	2	25	1000	975		487.5		–0.1951
S4	1	24	1138	1114	1094.5	557	547	–0.1574
	2	25	1100	1075		537.5		–0.1559

^aThe slope values (m) were obtained from linear functions.

the time taken for each sample to collapse after reaching the maximum height at the first and second trials, respectively. As can be seen from both figures and data tabulated in Table 2, the degeneration of foams based on the collapse time of each sample follows the order of S2 < S1 < S3 < S4 < APPDMS < blank. The amide-modified defoamer (S2) gave the most rapid foam collapse time of 526 s on average, followed by long-chain modified (S1), short-chain modified (S3), and branched modified (S4) at 684, 980, and 1094 s, respectively. The parent structure, A8 or APPDMS, required an average of 1451 s to break foams, which was much longer compared to all modified defoamers but faster than the blank system which takes about 2781 s to degenerate all foams. The addition of the amide functional group and carbon chain length has a great effect on foam degeneration and helps to increase the ability of modified defoamers to aid foam breakage. The possible reason was the addition of carbonyl to the parent chain to form the amide-modified defoamer (S2) has increased its polarity and its hydrophilic–lipophilic balance compared to the other modified defoamers. This is because a higher polarity compound will have lower solubility in oil, thus hindering the diffusion of their molecules to the oil surface. This means that the defoamer will act more within the foam liquid film and rupture the foams than the surface of oil. Besides, increasing the hydrophilic–lipophilic balance in the polar compound has favored the efficiency of the defoamer antifoaming action via the formation of the heterogeneous phase in the oil medium. This finding was in agreement with the study conducted by Fraga et al.²⁰ that also revealed a similar observation when comparing both defoamers with different polarities in crude oil. In a study by Fraga et al., it was reported that the most polar polyester silicone defoamer performed the best in breaking down the foam while the defoamer that has lower polarity turned out to be the least efficient foam inhibitor.

The results also show that the carbon chain length has affected the performance of the antifoaming agent in degenerating foams. As seen in Table 2, the modified defoamer with a longer alkyl chain (S1) has faster foam breakage compared to the one with a shorter alkyl chain (S3). This is due to the fact that S1 has a longer alkyl chain and thus exhibits a stronger hydrophobic interaction. The increase in the hydrophobic chain interaction can cause a greater destabilizing effect on the pseudo-emulsion film and accelerates drop-entry or film thinning via subsurface fluid which causes the foam film to rupture more quickly.^{21–23}

Besides, the increase in molecular weight due to the increase of the alkyl chain caused the defoamer to become increasingly effective due to the van der Waals cohesive forces.²⁴ El-Sukkary et al.²⁵ observed that the foam stability and foam half-life decreased with the increase of alkyl chain length.

The slope value (m) obtained from the linear function represents the foam drainage of each system. As can be seen in the data obtained in Table 2, S2 shows the highest rate of foam drainage, while the blank system shows the lowest drainage rate. The relative order of the drainage rate is as follows: S2 > S1 > S3 > S4 > APPDMS > blank. These results agree with the earlier finding that the presence of the amide functional group helps to increase the performance of the defoamer in mitigating foam due to the increase of polarity in the modified compound. Hence, defoamer molecules act more on a foam liquid film by allowing more liquid to flow out of the foam, causing the foam to dry out and rupture more quickly. Table 2 also shows that the average foam half-life decreases as the ability of the defoamer to mitigate the foam increases. This is due to foam stability (represented by the foam half-life) declines rapidly in the system with the presence of defoamer molecules such as S2. The ability of S2 in penetrating foam film more effectively caused foams to have a greater destabilizing effect breaking foam more rapidly, thus a shorter foam half-life. On the other hand, the longest foam half-life was observed in the blank system, which indicates that the stability of foam was at the highest. Moreover, the presence of foam surfactants also promoted the stability of the produced foams in the system. Overall, all modified defoamers gave better performance in degenerating foams compared to the commercial defoamer, with S2 showed the best performance.

4.5. Factors Affecting the Performance of Modified Defoamer S2. As S2 showed a promising result among all the modified defoamers, a further evaluation test was conducted to investigate and understand the best-case condition for the said defoamer to perform at different parameters while the others were not tested further. Defoamer S2 was studied at variable temperatures, concentrations, flowrates, and crude oil compositions. The series of experiments were conducted at a fixed pressure of 4.0 bar, as the assumed pressure condition at the separator facilities.

4.5.1. Effect of Temperature. Temperature is well known as one of the factors affecting defoaming action in breaking down foams as foam stability depends on temperature. In this study, the S2 defoamer was tested in two different temperatures, 30

and 60 °C, with the pressure maintained at 4.0 bar, the ratio of polymer and brine solution was 90:10 in 20% of crude oil, and the gas flow rate was 0.5 L/min. Only two temperatures were selected for the evaluation as the previous study stated that the extremely high temperature can lead to the decomposition of the surfactant foam that is present in the foaming system.^{26–28} Because this study is focusing on the application in the FAWAG treatment, the temperature was set at a low range. Furthermore, there is a high-temperature instrument limitation for the application with a pressure of 4.0 bar. The performance of the modified defoamer was evaluated based on the measurement of foam degeneration over time, foam drainage, and foam stability. Figure 6 illustrates the foam height at two

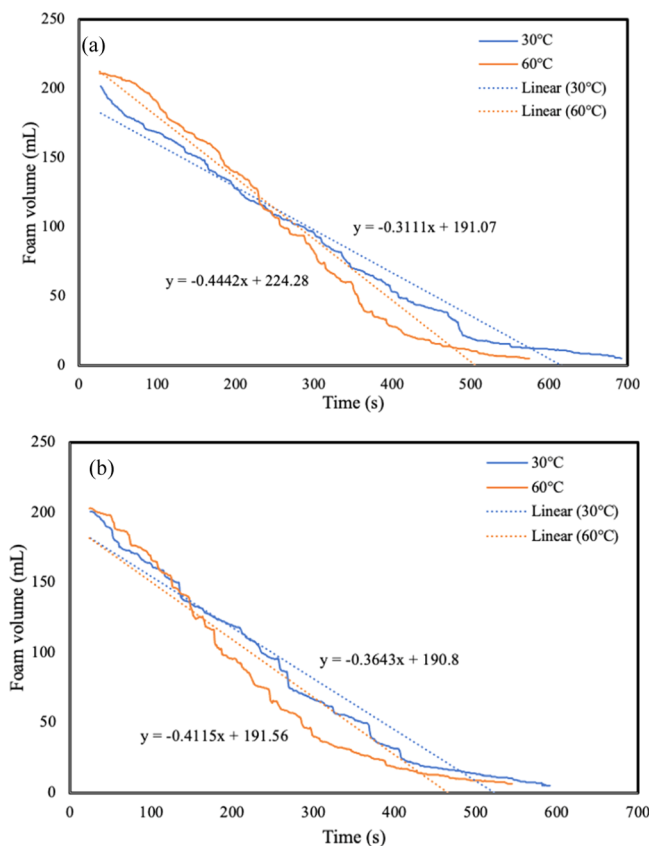


Figure 6. Foam volume at two different temperatures, 30 and 60 °C as a function of time, (a) trial 1 and (b) trial 2. The slope values (m) were obtained from linear functions.

different temperatures as a function of time. The rate of foam degeneration was determined based on the time taken of foams to collapse once it reached the maximum height. The slope value (m) of the linear function indicates the foam drainage. Based on the results obtained, the foam degeneration and foam drainage increased as the temperature increased. The foaming system in the condition with a higher temperature showed faster foam collapse and smaller m value, which indicates speedier foam drainage compared to the lower temperature foaming system.

Theoretically, a higher temperature can cause the average energy of gas molecules and the collision frequency of gas molecules to increase tremendously. As a result, more gas molecules would overcome the energy barrier and pass through the foam film, therefore aiding foam destruction by the defoamer. Besides, the increase in temperature causes the

viscosity of the foam system to decrease. Consequently, the strength of the foam film reduces; thus, it is easier for the defoaming action to break down foams.²⁶ Overall, it can be concluded that a higher temperature is the best-case condition for the defoaming action. This is due to the fact that defoamer molecules can react more effectively as the foams produced in higher temperatures are less stable due to the higher kinetic velocity and lower surface viscosity of foaming system, therefore resulting in rapid foam drainage.

4.5.2. Effect of Concentration. The effect of concentration of the surfactant polymer (SP) and brine solution (B) in mitigating foams was investigated. The test was conducted using two different ratio concentrations of the surfactant polymer and brine solution, 30:70 and 90:10. The total water-cut (SP/B) was 80% with 20% of Dulang crude oil. The pressure and flow rate were maintained at 4.0 bar, and 0.5 L/min, respectively, and the temperature was set to 60 °C, based on the previous finding. The rate of foam degeneration was determined based on the time taken of foams to collapse once it reached the maximum height. The slope value (m) of the linear function indicates the foam drainage.

Referring to Figure 7, a rapid foam rupture was observed in the system with a 30:70 ratio of the surfactant polymer to brine and smaller m value compared to the system with a 90:10 ratio. This showed that the defoamer action occurred more effectively in a system with a lower concentration of the surfactant foam. The lower concentration of surfactant foam

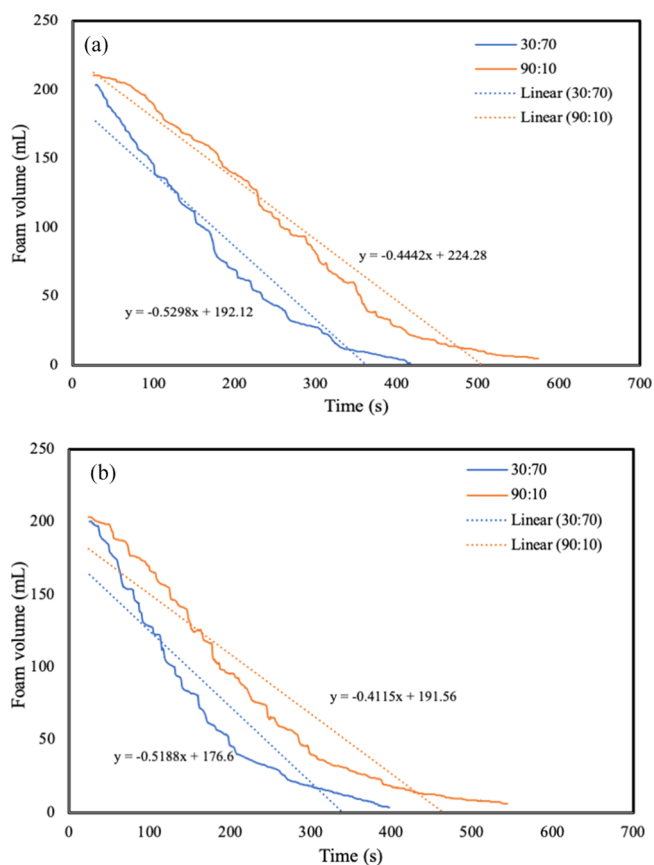


Figure 7. Foam volume in two different concentrations of the surfactant polymer-to-brine (SP/B), 30:70 and 90:10 as a function of time for (a) trial 1 and (b) trial 2. The slope values (m) were obtained from linear functions.

will reduce the availability of the foaming agent in the solution, hence reducing the volume of foam generated in the system. Moreover, the higher concentration of the brine solution assisted the action of the defoamer molecules to ruptured foam.²⁹ On the other hand, the increase of the surfactant concentration led to an increase in the number of foams produced as well as the foamability of foams.^{30,31} This contributes to the increase of the disjoining pressure and the network of micelles in foam lamella,¹⁹ which resist the lamella rupture as the stability of foam increases.³² Furthermore, the reduction in the surface elasticity of foams also caused difficulty in breaking the foam lamella.¹⁷

4.5.3. Effect of the Flowrate. The effect of gas flow rates was conducted using nitrogen gas at two different gas flow rates, 0.5 and 1.0 L/min. The other parameters were maintained at 4.0 bar and 60 °C, while the ratio of the surfactant polymer and brine solution was fixed at 30:70 in 20% of Dulang crude oil. Figure 8 illustrates the foam volume

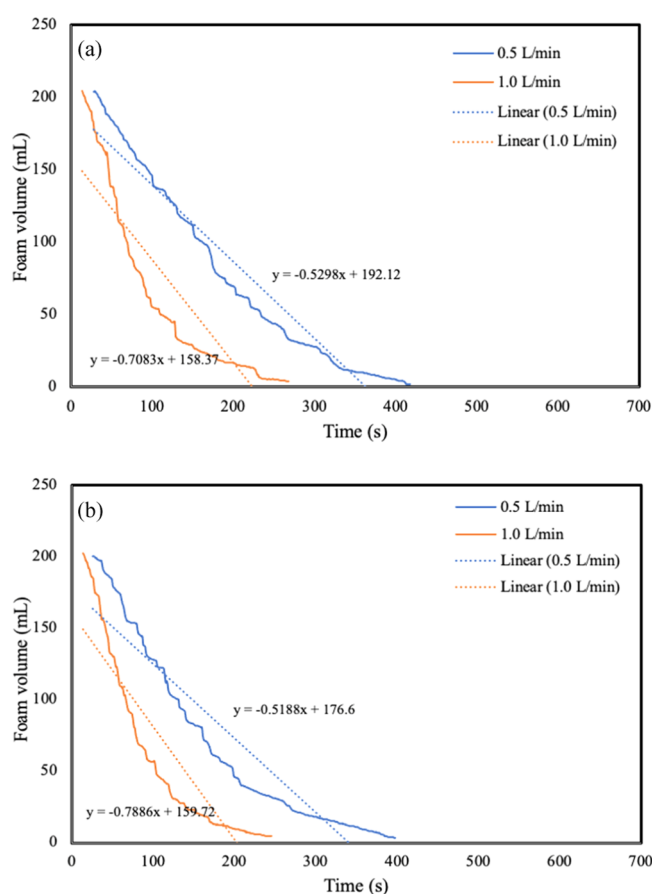


Figure 8. Foam volume in two different flow rates, 0.5 and 1.0 L/min, as a function of time for (a) trial 1 and (b) trial 2. The slope values (m) were obtained from linear functions.

as a function of time at different flow rates for both trials. The rate of foam degeneration was determined based on the time taken for foams to collapse once it reached the maximum height. The slope value (m) of the linear function indicates the foam drainage. Based on the presented linear functions, the slope value for 1.0 L/min has a smaller value compared to 0.5 L/min, indicating faster foam drainage. Similarly, the rate of foam degeneration observed in 1.0 L/min also had a smaller value, which means rapid foam collapse. Wang et al.³¹ has also

proved a similar finding. Their study showed that the increased in the gas flow rate caused the foaming time to decrease while the liquid content of foam increased. The increase in the liquid content of foam indicates faster liquid drainage, which contributes to rapid foam breakage. In a study by Chang and Grigg³² on the effects of the foam quality and flow rate, it was found that the quality of foam declines as the flow rate increases. With declining foam quality, gas bubbles can move freely with a little restriction from adjacent bubbles, resulting in a low surface viscosity. The lower the viscosity, the smaller the stabilizing effect on the foam films,³³ hence, allowing more defoaming mechanisms to occur.

4.5.4. Effect of the Crude Oil Composition. Different oil fields have different percentages of the composition. Hence, it will affect the behavior of the oils in foaming and defoaming action. This study focused on crude oil from two oil fields in Malaysia, namely, Dulang and Baronia. Both oils were obtained from the PETRONAS oil fields. Dulang is a significant oil field in the Malay Basin while Baronia is located at Baram Delta, Lutong Sarawak. In this test, the ratio of surfactant polymer-to-brine was fixed at 30:70, while pressure and temperature were maintained at 4 bar, and 60 °C, respectively and the gas flow rate was set to 1.0 L/min. These conditions were established based on the previous finding that is the best-case condition for the defoaming action. As presented in Figure 9, both crude oils showed almost the same trend in foam degeneration. There was only a small difference in the time taken of each foam to collapse. However, the difference in the slope value proved that

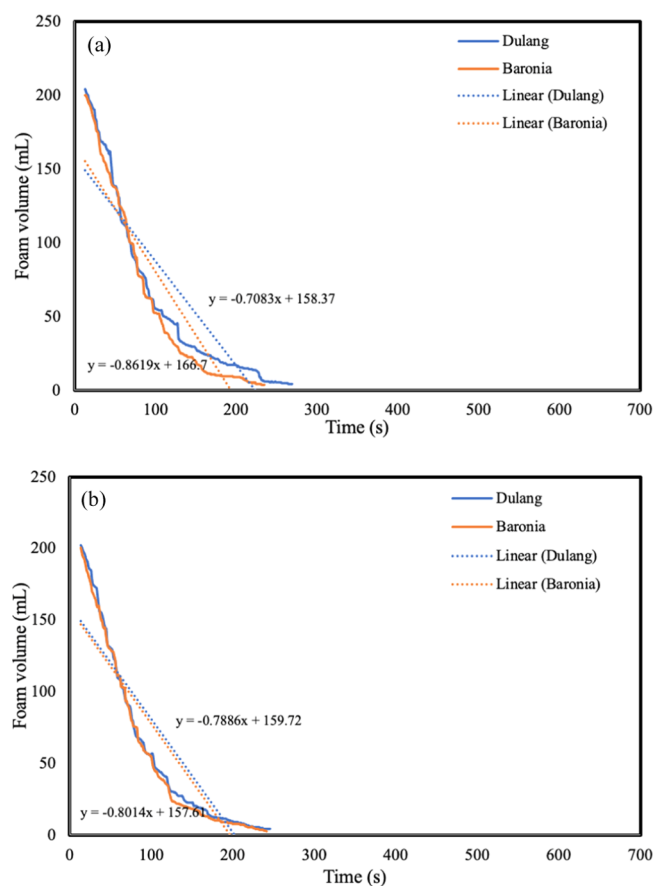


Figure 9. Foam volume in two different crude oils, Dulang and Baronia, as a function of time for (a) trial 1 and (b) trial 2. The slope values (m) were obtained from linear functions.

Baronia has faster foam drainage compared to Dulang. This can be explained by comparing the properties and composition of each crude oil, focusing on the viscosity, density, and wax contents as the foaming and defoaming characteristics are greatly affected based on these properties.³⁴

As tabulated in Table 3, Dulang has a higher viscosity, density, and wax content than Baronia. Higher viscosity and

Table 3. Composition of Dulang and Baronia Crude Oils Obtained from PETRONAS Research Sdn. Bhd., Malaysia with Permission.^{38,39}

composition	properties of crude oils	
	Dulang	Baronia
viscosity, cP	0.6	0.3
density, at 15 °C	0.858	0.817
wax content, wt %	25.5	1.86
saturates, wt %	82.15	71.43
aromatics, wt %	17.85	26.37
resins, wt %	2.26	1.92
asphaltene, wt %	0.18	0.28

wax content contribute to the formation of more stable and waxy foams. The higher the viscosity and stability of foams, the more challenging for defoamer molecules to penetrate and rupture foam films as the resistance of liquid drainage increases, resulting in the delays of defoaming time.^{33,35,36} This finding agreed with the study conducted by Osei-Bonsu et al.³⁷ They show that the increase in oil viscosity and density led to a longer foam half-life. This is due to the reduction of oil droplet dispersion in the bulk foam with the rise in oil viscosity and density. Thus, it increases the foam stability as the contact between oil and foam network reduces and slows down the foam destabilization. Furthermore, as the viscosity increases, the wax content increases too, leading to a lower rate of liquid drainage as stated by Zhang et al.³⁶ in their study. Overall, the properties of crude oils have a significant effect on the defoaming action.

4.5.5. BC and Distribution. Ideally, in order for a foam system to be stable, the arrangement of bubbles needs to possess a minimal surface area as well as an equal distribution of surface tension forces along with the liquid films of the bubbles.^{40,41} Stable foams usually have thick films and small in radius. Smaller foams are harder to break as the foam is entrained within the liquid film and stabilized.^{41,42} In contrast, bubbles with a broad radius have a thin film thickness, which contributes to a rapid coalescence of the bubbles due to easy penetration and destabilizing of the foam lamella.⁴³ Therefore, foam is more likely to burst rapidly. The primary purpose of this test is to study the effect of the defoaming action on the foam texture and distribution of the bubbles and how it affects the foamability.

Three different sets of foaming systems were prepared: Blank, APPDMS, and S2 for the comparison study. All foaming systems composed of surfactant polymer-to-brine (90:10) in 20% of Dulang crude oil. The temperature and pressure in all systems were maintained at 30 °C under atmospheric pressure with a constant flow rate of 0.5 L/min. These conditions were established based on the instrument limitation and not the best-case condition. Figure 10 represents foam volume, BC, and average bubble size, for all three systems. Foams are generated when air was purged into the systems and foam height (h_{foam}) starts to increase, indicating foam generation.

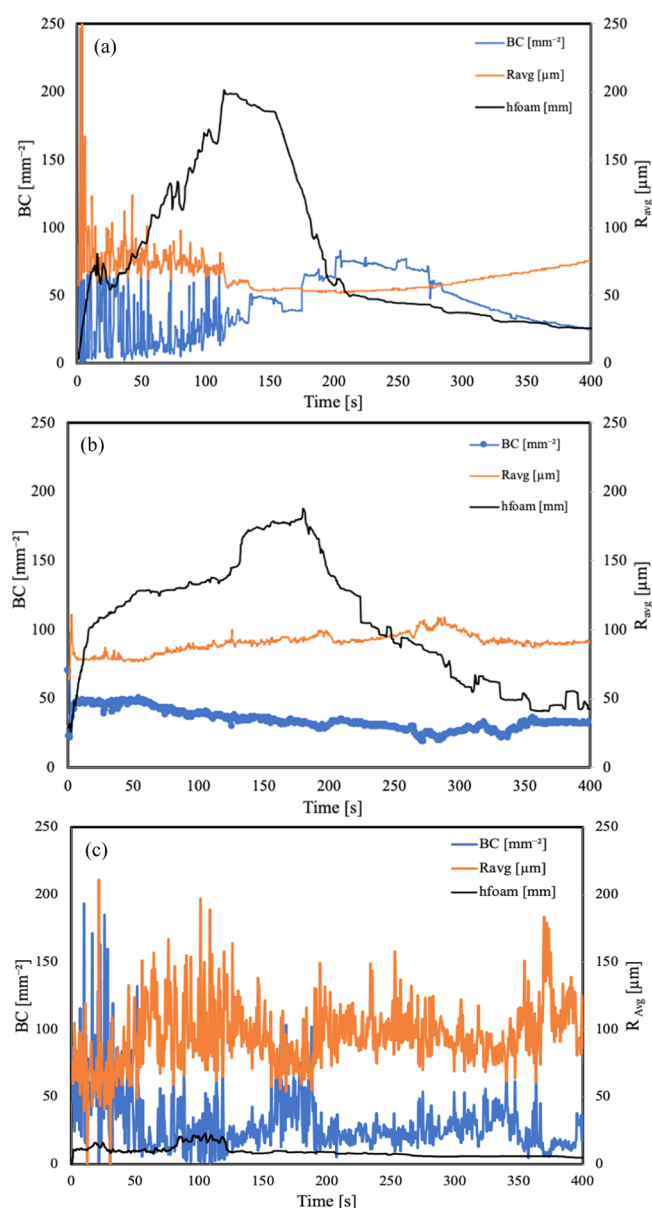


Figure 10. Foam volume, BC and average bubble size (R_{avg}) as a function of time for (a) blank, (b) APPDMS, and (c) S2 modified defoamer.

Once foam reached maximum height, gas purging was stopped, and foam degeneration was observed over time. The bubble count (BC) and average bubble size (R_{avg}) were observed at three different points, the moment foam started to generate (t_{min}), when foam reached maximum height (t_{max}) and after 400 s of foam generation in the system ($t_{400\text{s}}$). Table 4 tabulates all the data obtained on BC and R_{avg} for all systems.

Overall, the trends showed that the total BC decreased as the R_{avg} increased in a system with the presence of a defoaming agent. The observation also showed that the foamability of foam declined in the system with the presence of a defoamer. As shown in Figure 10c, the S2 foaming system had difficulties in generating foams and can only reach a maximum height of 20 mm compared to 200 mm achieved in the blank system with the same gas flow rate. This proved that the defoaming agent has a significant effect on preventing and disturbing the formation of foams and also the distribution of bubbles. The addition of the defoamer caused a disturbance in the foaming

Table 4. BC and Average Bubble Radius (R_{Avg}) in Various Systems

system	min foam height (t_{min})		max foam height (t_{max})		foam height at 400 s (t_{400} s)	
	BC (mm ²)	R_{Avg} (μm)	BC (mm ²)	R_{Avg} (μm)	BC (mm ²)	R_{Avg} (μm)
blank	87	57	58	57	24	75
APPDMS	69	67	31	90	31	91
S2	46	76	25	94	20	110

system as well as the foamability, which led to the formation of low-quality foams with thinned film radius. As a result, the foams film ruptured more quickly as they are more susceptible to internal (a defoaming mechanism) and external disturbances such as vibration, shock, and condition change.⁴⁴

This finding was in agreement with a study conducted by Narsimhan and Ruckenstein⁴³ on the effect of bubble distribution on the enrichment and collapse in foams. Their findings proved that bubbles with a broad radius have a thin film thickness which contributes to a rapid coalescence of the bubbles causing foams to collapse. Similarly, a few studies have shown the same observation on the ability of antifoams in enhancing bubble coalescence and bubble size.^{36,42,45–47} Moreover, results showed that the size of the average bubbles produced in S2 were more than 100 μm , which indicates macrofoam properties. According to Hallack et al.⁴¹ macrofoam takes a shorter time to burst compared to microfoam because the latter is more stable compared to macrofoam. All in all, the defoaming agent S2 caused a significant destabilizing effect on the foaming system, which contributes to the formation of unstable foams leading to rapid foam destruction in the system.

5. CONCLUSIONS

All four modified defoamers were successfully synthesized based on the parent APPDMS structure and characterized. The modified defoamers were tested for the performance in mitigating foams at specific parameters in order to stimulate and mimic the industrial conditions in the real separator facility. All measurements were performed under the conditions of a surfactant polymer-to-brine solution ratio of 90:10 in 20% of crude oil, gas flow rate of 0.5 L/min, and 4.0 bar pressure at 60 °C. The results show that the amide-modified defoamer (S2) gave the most rapid foam collapse time of 526 s on average, followed by long-chain modified (S1), short-chain modified (S3), and branched modified (S4) at 684, 980, and 1094 s, respectively. The parent structure, A8 or APPDMS, required an average of 1451 s, threefold compared to S2 to degenerate all foams. While the blank sample took about 2781 s, which was fivefold compared to S2. Intensive performance evaluation focusing only on S2 was conducted at different parameters to investigate and understand the best-case conditions. The findings showed that the performances of S2 to suppress the foam were profoundly affected by several factors such as temperature, ratio of surfactant polymer-to-brine, flow rate, and the viscosity of crude oil used. The amide-modified defoamer (S2) showed higher performance at higher temperatures. The increase of the surfactant concentration led to an increase in the number of foams produced and the foamability of foams, thus reducing the performance of S2 in mitigating foams. At a high flow rate of 1.0 L/min, S2 exhibits a smaller slope value compared to 0.5

L/min, indicating faster foam drainage. The increase of the flow rate caused a destabilizing effect on the foams, contributing to the defoaming action to initiate foam destruction more effectively. The finding also showed that the S2 performed best in Baronia crude oil with low viscosity.

The higher the viscosity and stability of foams, the more challenging for defoamer S2 molecules to penetrate and rupture the foam films as the resistant of liquid drainage increases, resulting in the delay of defoaming time. The results obtained conclusively proved that all the synthesized modified silicone-based defoamers, especially S2, exhibited excellent performance as a defoaming agent in mitigating foams compared to its commercial structure and blank sample. It is believed that the findings of this study will contribute to the benefits of the oil and gas industry, considering that there is a rising demand for petroleum and petrochemical products, which leads to the increase refinery capacity demand for oil and gas defoaming separators.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c00350>.

Chemical defoamers for the screening test, foam collapse time for all 34 commercial defoamers at different percentages of chemical concentrations at 30 °C (stage 1), foam collapse time for 13 selected commercial defoamers from stage 1 at different percentages of chemical concentrations at 30 °C, ¹H NMR spectra of long chain modified (S1), amide modified (S2), short chain modified (S3), and branched chain modified (S4) in CDCl₃, and ¹³C NMR spectra of long chain modified (S1), amide modified (S2), short chain modified (S3), and branched chain modified (S4) in CDCl₃ (PDF)

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Author Contributions

The manuscript was written through contributions of all the authors.

Notes

The authors declare no competing financial interest.

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