



Research article

Synthesis of new defoamer agents and characterization of cementitious formulations

Francesco Taddeo^a, Rosa Vitiello^{a,*}, Michela Ruocco^a, Rosa Turco^a,
Vincenzo Russo^a, Riccardo Tesser^{a,b}, Martino Di Serio^a

^a University of Naples Federico II, Department of Chemical Sciences, Complesso Universitario di Monte Sant'Angelo, 80126, Naples, Italy

^b Consorzio Interuniversitario per le Reattività Chimiche e la Catalisi, CIRCC, Italy

ARTICLE INFO

Keywords:

Sustainable materials
pH-responsive esters
Cementitious formulations
Antifoams
Bubbles reduction

ABSTRACT

The production of cementitious formulations involves the addition of chemical additives essential for the optimization of many properties. Superplasticizers are considered additives of great interest but when mixed with concrete they lead to an undesirable increase of air content, with the consequent development of foam. This can adversely affect both mechanical properties and workability, therefore, the use of an antifoam agent is also necessary which should be able to prevent or destroy the foam. This work aims to synthesize esters derived from the reaction of glycine betaine with saturated and unsaturated fatty alcohols of different chain lengths. The reaction products were analyzed by ¹H NMR analysis, and the stability of antifoam agents in a superplasticizer solution was studied through foaming tests according to the Ross-Miles method. At the same time, their effectiveness in the cementitious systems was evaluated through flow Table tests. Finally, the effectiveness of the antifoam agents was quantified through an image analysis software, *Image J*, which allowed the investigation of the contents of the bubble in concrete samples. All synthesized antifoams showed properties superior to the commercial product, especially defoamers containing saturated fatty alcohols. It has been found that alcohols with too small or too long carbon chains were not effective. In particular, it was verified the optimal range of carbon atoms number contained in the antifoam chain which included between 12 and 14.

1. Introduction

Additives play a fundamental role in cement paste production in order to optimize their properties. They are substances that are dispersed in water and when added to the cement, they modify and improve its performance [1,2]. Additives for concrete are classified in agreement with the role UNI-EN 934-2 [3] which determines the requirements needed for their function in the cement pastes. The additives are divided into four categories: (i) accelerators, (ii) setting and hardening retarders, (iii) aerating, and (iv) water-reducing agents. In particular, water-reducing additives are able to increase the workability of the concrete, reducing the water/concrete ratio (w/c) without significant changes in their properties [4]. The effects of the use of water-reducing additives are mainly the formation of concrete with the same workability as the standard product and with similar mechanical properties. Based on the reduction of the water amount, two different classes of water-reducing additives can be defined: plasticizers can reduce the w/c ratio in a range

* Corresponding author.

E-mail address: rosa.vitiello@unina.it (R. Vitiello).

<https://doi.org/10.1016/j.heliyon.2024.e33164>

Received 22 February 2024; Received in revised form 27 May 2024; Accepted 14 June 2024

Available online 18 June 2024

2405-8440/© 2024 Published by Elsevier Ltd.

This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

List of symbols

C_0	Aqueous solution and/or cementitious formulation made with only the superplasticizer
C_x	Aqueous solution and/or cementitious formulation made with the commercial antifoam
C_{10}	Aqueous solution and/or cementitious formulation made with the antifoam derived from capric alcohol
C_{12}	Aqueous solution and/or cementitious formulation made with the antifoam derived from laurilic alcohol
C_{14}	Aqueous solution and/or cementitious formulation made with the antifoam derived from myristic alcohol
C_{18}	Aqueous solution and/or cementitious formulation made with the antifoam derived from stearic alcohol
u- C_{11}	Aqueous solution and/or cementitious formulation made with the antifoam derived from undecenyl alcohol
u- C_{18}	Aqueous solution and/or cementitious formulation made with the antifoam derived from oleic alcohol
MSA	Methane sulfonic acid

between 5 and 15 % and superplasticizers from 15 to 30 % [5,6]. Different superplasticizers can be used and among these polycarboxylates (PCE), which are synthetic polymers with flexible chemical structures, are of particular interest allowing water reductions up to 40 % [4]. Due to the surface properties of superplasticizers, an excess of air is trapped in the concrete mixture. This air amount can increase the workability but an air content higher than 3 % leads to worse performance, hence it should be avoided [7]. For this reason, defoamers are needed since they can enhance the mechanical properties and durability of concrete by reducing bubbles and optimizing pore structure [8]. However, the addition of the antifoam agent to a superplasticizer aqueous solution leads to phase instability. In particular, when mineral oils and silicones are used, a phase separation occurs over time leading to storage for a limited period due to an inhomogeneity in the composition of concrete admixtures. This implies the need to place them in different tanks and mix them a short time before the addition in the concrete or it is necessary the continuous mixing of the two elements. Both alternatives show problems from an economic and practical point of view. On the other hand, polyether defoamers have demonstrated better water solubility and compatibility with other admixtures [9,10]. Therefore, two aspects are important for an antifoam agent: the first one is related to the dispersion in the superplasticizer aqueous solution while the other one is the effectiveness to prevent or destroy the occluded air [11–14]. Antifoam agents are widely used to reduce the volume of foam in several applications [15]. Antifoams developed in recent years contain numerous components to satisfy different requirements. The active components can be classified based on their composition, in particular non-polar or polar components such as oil-based, silicon-based antifoams, and surfactants [16–18]. Antifoam agents act by replacing or modifying the active stabilizers on the surface; therefore, they must be more active on the surface. Most of the antifoams have surface tensions in a range between 20 and 30 mN m⁻¹ while a great number of organic surfactants solutions and other aqueous foaming media show a surface tension between 30 and 50 mN m⁻¹ [19]. Furthermore, antifoam agents must be insoluble in the medium and at the same time easily dispersible in the medium itself [15]. More durable antifoams can destroy a higher amount of foam and keep its volume below a specific value for a longer period. The effectiveness of an antifoam agent is usually referred to as its performance both concerning its activity and duration [16]. Patents were proposed for the synthesis of a new antifoam and its stability in a cementitious formulation [20,21]. This antifoam is an ester of fatty alcohol and betaine which is soluble in an aqueous medium at acidic pH, as in the case of the superplasticizer aqueous solution, and at the same time, it is hydrolyzable in a basic medium as the cementitious water. In these conditions, the hydrolysis of the afore-mentioned ester occurs, releasing in situ the fatty alcohol which acts as the antifoam agent [20]. The synthesis of the esters with properties suitable to be used as antifoam agents provides the acid-catalyzed esterification reaction of the glycine betaine with saturated or unsaturated fatty alcohols [21]. In this study, antifoams were synthesized using sustainable raw materials through the esterification of glycine betaine, a feedstock obtainable from biomass, with fatty alcohols of different chain lengths, both saturated and unsaturated.

Their effectiveness was assessed using foaming tests based on the Ross-Miles method. The focus then turned to the application of the synthesized antifoams in cement formulations, which is particularly important due to the increased air bubble content from the use of superplasticizers, resulting in fragile concrete, especially when dried. The use of antifoams significantly reduced the air bubble content, as confirmed by flow table tests. Furthermore, concrete samples were analyzed using image processing software to assess the number, size, and shape of the bubbles formed.

2. Materials and methods

2.1. Materials

Glycine betaine anhydrous (GB) from Alfa Aesar (purity 98 wt%) and methane sulfonic acid (MSA) in water (70 wt%) from Merck were used for the synthesis of all the esters. Capric alcohol (purity 98 wt%) was purchased from Merck, Laurilic alcohol (purity 98 wt%) from Acros Organics, Myristic alcohol (purity 97 wt%) was purchased from Fluka, Stearic alcohol (purity 99 wt%) from Merck. Unsaturated fatty alcohols are: Undecenyl alcohol (purity 99 wt%) was purchased from Alfa Aesar while Oleic alcohol (purity 85 wt%) from Merck. Commercial superplasticizers and antifoam agents were used as references. Portland limestone cement CEM//B-M (V-LL) 32.5 R was used for the cementitious formulation.

2.2. Reactor setup and esters synthesis procedure

The experimental setup used for synthesizing the ester involved a magnetically stirred glass flask with two necks. The reactor was connected from one neck to the condenser to remove the water formed during the reaction using a vacuum pump while on the other neck, a thermometer was placed to control the reaction mixture temperature. A heating plate together with an oil bath allows to heat the system and maintain the temperature to the set value. Alcohol was added to a suspension of glycine betaine in methane sulfonic acid and the reaction mixture was gradually heated up to the desired temperature equal to 130 °C. The reaction conditions used for each test are reported in Table 1.

2.3. Ester purification procedure

The ester obtained from Test 2, which resulted in the best one from characterizations explained in the next paragraphs, was neutralized with a sodium bicarbonate solution weighing 510 mg of NaHCO₃ in 70 mL of water. Diethyl ether was then added to the reaction mixture and finally, the extraction with 1-butanol/ethyl acetate (1:1 mol/mol) was made. The organic phase was evaporated under reduced pressure and to the obtained product, a solution of ethanol/ethyl acetate (1:1 mol/mol) was added and finally, a recrystallization of the pure compound was obtained in the freeze [22].

2.4. ¹H NMR analysis

Samples were analyzed by ¹H NMR with a Bruker Avance Ultrashield operating at a proton frequency of 400 MHz using CDCl₃ as solvents depending on the compound. The signals of the spectra of each product are assigned as follows and an example is reported in Fig. 1. The spectra of all the other synthesized antifoams are reported in the Supplementary materials file.

Test 1. δ_H(400 MHz; CDCl₃) 0.85 (3H, t, CH₃), 1.33 (14H, m, (CH₂)₇CH₃), 1.65 (2H, q, CH₂CH₂O), 2.92 (3H, s, CH₃SO₃⁻), 3.50 (9H, s, (CH₃)₃), 3.70 (2H, t, CH₂O), 4.35 (2H, t, CH₂O), 4.45 (2H, s, CH₂CO).

Test 2. δ_H(400 MHz; CDCl₃) 0.88 (3H, t, CH₃), 1.30 (18H, m, (CH₂)₉CH₃), 1.55 (2H, t, CH₂CH₂O), 1.68 (2H, q, CH₂CH₂O), 2.90 (3H, s, CH₃SO₃⁻), 3.50 (9H, s, (CH₃)₃), 3.67 (2H, t, CH₂O), 4.24 (2H, t, CH₂O), 4.50 (2H, s, CH₂CO)

Test 3. δ_H(400 MHz; CDCl₃) 0.88 (3H, t, CH₃), 1.28 (22H, m, (CH₂)₁₁CH₃), 1.55 (2H, t, CH₂CH₂O), 1.60 (2H, q, CH₂CH₂O), 2.85 (3H, s, CH₃SO₃⁻), 3.50 (9H, s, (CH₃)₃), 3.65 (2H, t, CH₂O), 4.35 (2H, t, CH₂O), 4.50 (2H, s, CH₂CO).

Test 4. δ_H(400 MHz; CDCl₃) 0.88 (3H, t, CH₃), 1.35 (30H, m, (CH₂)₁₅CH₃), 1.55 (2H, t, CH₂CH₂O), 1.65 (2H, q, CH₂CH₂O), 2.90 (3H, s, CH₃SO₃⁻), 3.50 (9H, s, (CH₃)₃), 3.65 (2H, t, CH₂O), 4.35 (2H, t, CH₂O), 4.48 (2H, s, CH₂CO).

Test 5. δ_H(400 MHz; CDCl₃) 0.88 (3H, t, CH₃), 1.25 (14H, m, CH₂), 2.10 (4H, m, CH₂CH[CH₂]), 2.90 (3H, s, CH₃SO₃⁻), 3.50 (9H, s, (CH₃)₃), 3.65 (2H, t, CH₂O), 4.35 (2H, t, CH₂O), 4.50 (2H, s, CH₂CO), 5.00 (4H, m, CH[CH₂]), 5.80 (2H, m, CH[CH₂]).

Test 6. δ_H(400 MHz; CDCl₃) 0.83 (3H, t, CH₃), 1.37 (22H, m, CH₂), 1.55 (2H, m, CH₂CH₂O), 1.60 (2H, m, CH₂CH₂O), 2.10 (8H, m, CH₂CH[CH₂]), 2.81 (3H, s, CH₃SO₃⁻), 3.50 (9H, s, (CH₃)₃), 3.65 (2H, t, CH₂O), 4.35 (2H, t, CH₂O), 4.50 (4H, s, CH₂CO), 5.45 (4H, m, CH₂CH[CH₂]).

The conversion of the glycine betaine was calculated by the integration of the signal of CH₂O of the product resonating at 4.24 ppm (I₁), reported in red in Scheme 1,2, and the signal of the methyl groups of the glycine betaine resonating at 3.50 ppm (I₂), highlighted in blue.

$$X_{GB}[\%] = \frac{9I_1}{2I_2} * 100 \quad (1)$$

2.5. Foaming tests

Foaming tests were made according to the Ross-Miles method in order to measure the foam produced from the surfactant over time following ASTM D 1173-07 role [23]. The experimental setup is constituted by a glass pipet and a glass receiver. The pipet was made by a bulb and a lower stem with an outside diameter respectively of 45.0 ± 1.5 mm and 7.0 ± 0.5 mm. The lower stem length is 60 ± 2 mm, and the total capacity of the foam pipet is 200.0 ± 0.2 mL. Finally, on the upper stem, a stopper is placed. The receiver is made of a jacketed tube with an internal diameter of 50.0 ± 0.8 mm and a length of 90.0 ± 0.5 cm. All the details of the above-described apparatus can be found in the ASTM D 1173-07 role [23].

Table 1
Operative conditions for esters synthesis.

Test	Reactants			Molar ratio	Time [h]
1	Capric alcohol	Glycine betaine	MSA	1.5/1.0/2.5	8
2	Laurilic alcohol	Glycine betaine	MSA	2.0/1.0/2.0	5
3	Myristic alcohol	Glycine betaine	MSA	1.5/1.0/2.5	10
4	Stearic alcohol	Glycine betaine	MSA	1.2/1.0/2.6	7
5	Undecenyl alcohol	Glycine betaine	MSA	1.5/1.0/2.5	10
6	Oleic alcohol	Glycine betaine	MSA	1.4/1.0/2.5	10

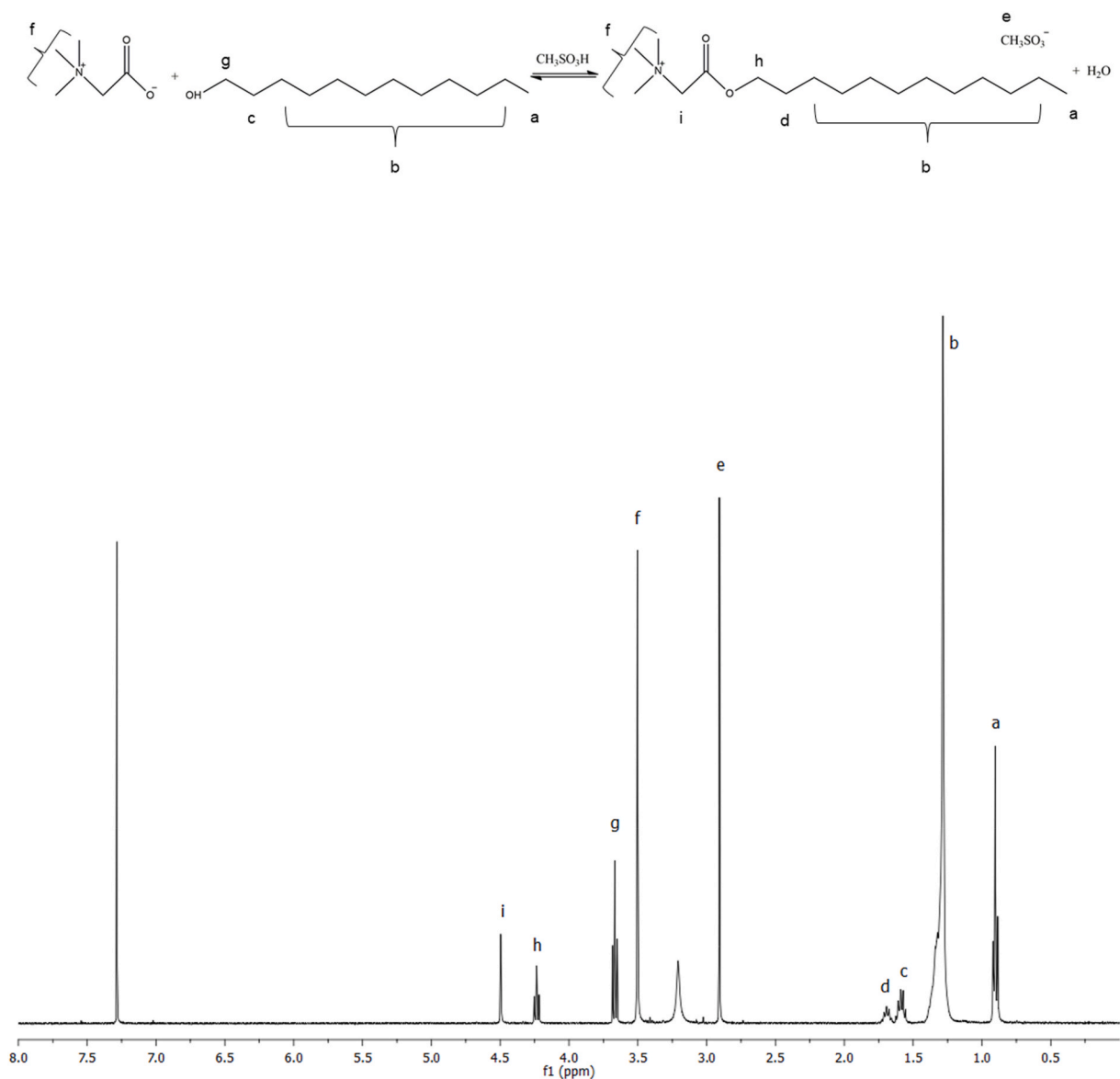
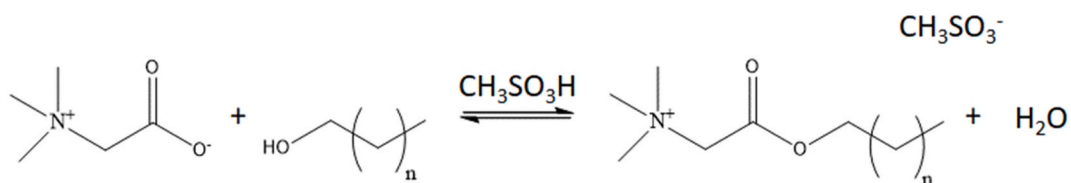


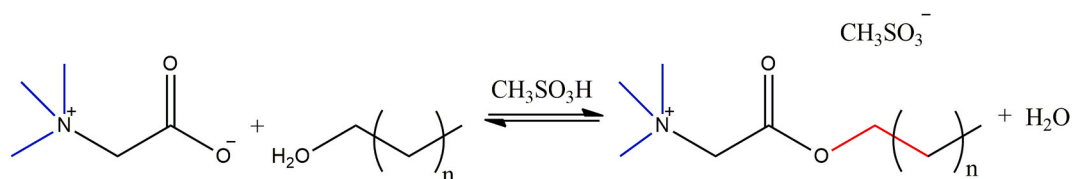
Fig. 1. ^1H NMR of C_{12} ester (Test 2).



Scheme 1. Glycine betaine esterification with fatty alcohols.

All the synthesized antifoam agents were used in the foaming tests, and they were compared with a commercial one. 250 mL of solution was prepared for each case by mixing water and antifoam agents. In particular, the amount of the antifoam agent involved in the preparation of the solution was 0.05 g, equal to the high amount added in the cementitious formulations.

The receiver was loaded with 50 mL of solution while the remaining part was inserted into the pipet. The pipet was placed on the receiver and the 200 mL of the solution was loaded, too. When the total amount of the solution was in the receiver, the height of the formed foam was monitored over time, in particular at $t = 0$ min, $t = 1$ min, $t = 3$ min, and $t = 5$ min.



Scheme 2. Identification of groups considered for the conversion calculation of the glycine betaine esterification with fatty alcohols.

2.6. Cementitious formulation

Cementitious formulations were prepared by mixing water and concrete, firstly sieved with a 710 μm sieve, and adding a determined amount of a commercial superplasticizer and the antifoam agent. In particular, all the synthesized antifoam agents were tested, and their performances were compared to those of the commercial ones. It was verified that the optimal w/c ratio was 0.35 and the superplasticizer amount was 0.1 wt % with respect to the concrete mass. In the literature, it was reported that the amount of antifoam agent to be added could vary in a range between 0.01 wt % and 5 wt % with respect to the superplasticizer [11–13]. Hence, all the formulations were prepared using 1000 g of concrete, 350 g of distilled water, 1 g of superplasticizer, and a variable mass of antifoam agent (respectively 0.01 g, 0.03 g, and 0.05 g) by using a planetary mixer for 360 s.

2.7. Flow-table tests

The experimental apparatus is made of a cast rigid iron frame and a circular table top with a diameter of 255.0 ± 2.5 mm which ensures 25 drops in 25 s, as reported in the ASTM C 230/C 230M – 03 role [24]. The conical mold in which the cementitious formulation is placed has a bottom diameter of 100.0 ± 0.5 mm. The conical mold together with the funnel is placed in the middle of the table top and the cementitious formulation is inserted up to fill the cone. In this way, when the conical mold is removed, the cementitious formulation has a conical shape with a bottom diameter equal to 10 cm. At this point, the flow table is activated and after 25 drops, the final diameter of all the formulations is measured to evaluate the difference in the widening [25].

2.8. Image processing

The image processing software used is *ImageJ* [26] which allows the analysis of the characteristic parameters in terms of number, dimension, and shape of the bubbles present in the cementitious formulation after the flow table test. Firstly, the concrete sample was photographed to be subjected to an image processing analysis. Each bubble was manually selected, and the software was able to give information about all the above-mentioned parameters, in particular number, area, major and minor axis, and the shape factor.

3. Results

3.1. Ester synthesis

As reported in paragraphs 2.2 and 2.4, several fatty alcohols were involved in the esterification reaction. In the following Table 2, the reached conversion in each test, obtained through Equation (1), is reported.

It is possible to see from the data reported in Table 2 that the reached conversion is always higher than 95 %. Since an excess of fatty alcohol was used in each test, it was still present in the obtained products and for this reason, it was decided to purify one of the synthesized esters (C₁₂, Test 2 in Table 1) to evaluate the effect of the alcohol itself on its performances.

3.2. Foaming tests

Foaming tests were made according to the Ross-Miles method [23] as explained in paragraph 2.5. Tests were performed with each synthesized and commercial antifoam agent and the results are compared with those obtained with the solution of superplasticizer without antifoam. The height of the foam monitored over time is reported in Table 3 and Fig. 2.

Table 2
Glycine betaine conversion.

Test	X_{GB} [%]
1	99
2	95
3	99
4	98
5	97
6	98

Table 3
Foaming test results.

t [min]	Foam height [cm]							
	C_0	C_x	C_{10}	C_{12}	C_{14}	C_{18}	u- C_{11}	u- C_{18}
0	4.5	3.5	1.5	0.6	0.5	1.5	2.5	3.0
1	4.5	3.3	1.3	0.5	0.3	1.2	2.1	2.9
3	4.3	3.0	1.1	0.3	0.2	0.9	2.0	2.7
5	4.3	2.8	0.9	0.0	0.0	0.9	1.9	2.6

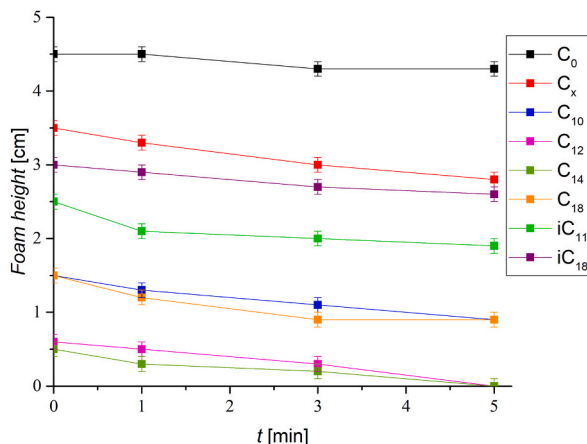


Fig. 2. Foaming test results.

As it is possible to observe from the data reported in Fig. 2, in the case of C_0 solution a high foam amount is formed, and it is stable over time. This behavior is expected since this test was made only with the superplasticizer without the antifoam agent. With the C_x solution, instead, a lower amount of foam was formed with respect to the C_0 solution, but the height was higher than those obtained in the case of all the synthesized antifoam agents. Therefore, it is possible to see that the commercial antifoam can eliminate part of the foam, but it is less effective compared to the synthesized ones. It was verified that the best results were reached with C_{12} and C_{14} solutions since the height of the foam at t_0 time was 4 cm lower than the C_0 solution and the foam is characterized by a fast decay up to disappearing after 5 min (t_3), index of a less stable foam. Good results were found also with C_{10} and C_{18} solutions where the initial height was 3 cm lower than the C_0 solution and a decreasing trend of the foam over time was observed reaching a value of 0.9 cm at t_3 time. Finally, with the solutions u- C_{11} and u- C_{18} a lower foam formation was visible with respect to C_0 , but it is rather stable since the height remains constant in the time.

In Fig. 3, a comparison between C_0 and C_{12} solutions is reported, where the better results reached with the antifoam agent obtained from laurilic alcohol are clearly visible.

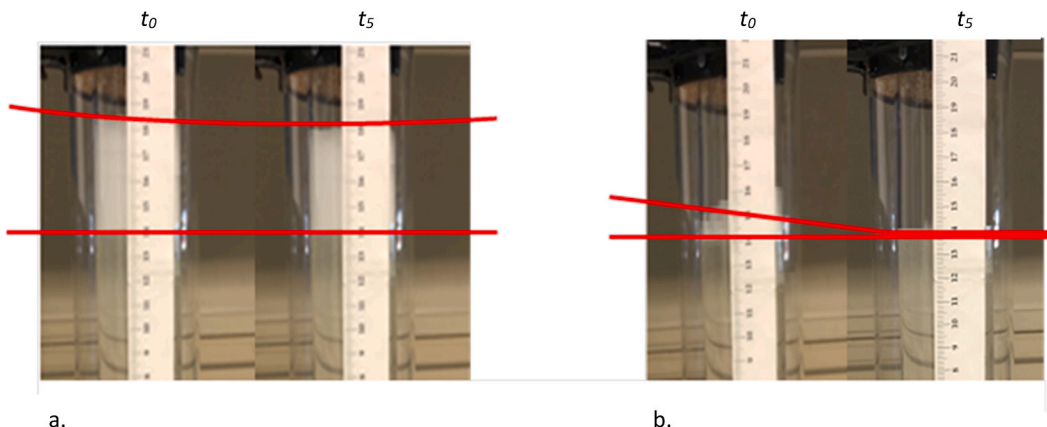


Fig. 3. Comparison between a. C_0 and b. C_{12} solutions.

3.3. Flow-table tests

All the samples showed the same widening after the flow-table test reaching a final diameter of about 18 cm. This result can be expected since the widening phenomenon is mainly due to the amount and the nature of the superplasticizer. In all the formulations, these two elements are always added in the same amount therefore, the widening is constant. On the contrary, the number, size, and shape of the bubbles formed in the samples depend on the nature and the amount of the antifoams which is the only component varied in the formulations. For this reason, the attention was focused on this aspect, which was investigated through the image processing, tool discussed in the next paragraph.

4. Discussion

4.1. Image processing

As reported in paragraph 2.6, the percentage of antifoam agents in the cementitious formulation varied from 1 wt% to 3 wt% and 5 wt% respect to the superplasticizer. The first set of tests consisted of a standard formulation made by concrete, water, and the superplasticizer without adding the antifoam (C₀) and seven further formulations prepared in the same way above-mentioned with the addition of the 5 wt% of the antifoam agent. The antifoam agents used in the formulations are the esters obtained from the reaction of glycine betaine with the six fatty alcohols and the commercial defoamer. All the samples were analyzed with ImageJ software after the flow-table test. Data obtained from the software were processed and the results are reported in Table 4.

The number of bubbles represents the sum of all the bubbles of the considered sample. The total bubble area was obtained from the sum of the area of each bubble while the percentage of the occupied area was calculated with Equation (2).

$$\%_{\text{occupied area}} = \frac{\text{total bubbles area}}{\text{total area}} * 100 \quad (2)$$

where total area is referred to the whole sample.

The average diameter of each bubble was calculated through Equation (3):

$$\text{Average diameter} = \frac{\text{Major axis} + \text{minor axis}}{2} \quad (3)$$

where the major and minor axis were measured by the ImageJ software. From the average diameter of each bubble, a cumulative average value was calculated (Equation (4)).

$$\text{Cumulative average diameters} = \frac{\sum_{i=1}^n \text{average diameter}}{\text{total bubbles number}} \quad (4)$$

where n is the number of bubbles.

Shape factor was obtained from the software according to Equation (5) [27] and an average value, reported in Table 4, was calculated.

$$\text{Shape factor} = 4 \pi \frac{\text{bubble area}}{\text{perimeter}^2} \quad (5)$$

The experimental tests were repeated three times under the same conditions to estimate the error in the experimental data, expressed as the standard deviation.

To study the efficiency of the antifoam agents, the results obtained were compared based on the number of carbons in the chain, indeed, it's the alcohol that performs the anti-foaming action. The measured parameters were related to the length of the chain for different cases.

- (i) formulation without antifoam agent (C₀);

Table 4

Results obtained from the image processing.

	Bubbles number	Total bubbles area [cm ²]	Percentage of occupied area [%]	Average diameters [cm]	Shape factor
C ₀	128 ± 2	49.0 ± 0.2	8.4 ± 0.1	0.48 ± 0.01	0.7 ± 0.1
C _X	70 ± 1	11.0 ± 0.2	3.7 ± 0.1	0.57 ± 0.01	0.6 ± 0.1
C ₁₀	38 ± 2	6.0 ± 0.2	2.1 ± 0.1	0.64 ± 0.02	0.7 ± 0.2
C ₁₂	37 ± 1	2.0 ± 0.1	0.9 ± 0.1	0.41 ± 0.01	0.8 ± 0.1
C ₁₄	35 ± 1	2.0 ± 0.1	0.7 ± 0.1	0.37 ± 0.01	0.8 ± 0.1
C ₁₈	48 ± 2	8.0 ± 0.2	2.7 ± 0.1	0.66 ± 0.02	0.7 ± 0.2
u-C ₁₁	47 ± 2	10.0 ± 0.2	3.5 ± 0.1	0.69 ± 0.02	0.6 ± 0.2
u-C ₁₈	60 ± 2	11.0 ± 0.2	3.8 ± 0.1	0.73 ± 0.02	0.6 ± 0.2

- (ii) formulation with commercial antifoam agent (C_x);
- (iii) formulation with esters synthesized from saturated fatty alcohol (C_{10} , C_{12} , C_{14} , C_{18});
- (iv) formulation with esters synthesized from unsaturated fatty alcohol ($u-C_{11}$, $u-C_{18}$).

In Fig. 4, the number of bubbles as a function of the carbon atoms number for each formulation above mentioned is reported.

From Fig. 4, it can be seen that for the formulation with the antifoam agent characterized by small chain alcohols (C_{10} – C_{14}) a great decrease in the bubbles number occurred, less than 1/3 concerning the formulation made only with the superplasticizer and less than 1/2 with respect to the formulation made with the commercial antifoam. In the case of the formulation with 18 carbon atoms of alcohol, a decrease in the number of bubbles can be observed even if this effect is less evident if compared with the previously mentioned case. It is also verified that for both unsaturated fatty alcohols, there is a decrease in the number of bubbles, above all in the case of $u-C_{11}$ alcohol but they are overall less efficient with respect to the saturated alcohols. In Fig. 5 the percentage of occupied area by the bubbles as a function of chain length is reported. This parameter is important for evaluating the overall performance of an antifoam because the number of bubbles alone is not indicative of a good antifoam.

Also in this case, the best performances are reached by using antifoams characterized by saturated fatty alcohols with several carbon atoms between 10 and 14. In particular, the percentage of occupied area is much lower in the case of the saturated C_{12} and C_{14} alcohol formulations. The obtained results showed that the used antifoams can eliminate almost completely the foam produced by the superplasticizer. In Fig. 6 the average diameters as a function of carbon atoms number can be observed.

The investigation of this parameter underlines that the formulation made using only the aqueous solution of superplasticizer is characterized by small bubbles. In fact, in Fig. 6, it can be seen that the average value of the bubble's diameter is 0.48 cm. This product is characterized by a high number of bubbles and consequently a high fraction of the area occupied by the bubbles, and they have a small diameter. Also, the formulations obtained from antifoam agents with good performances are characterized by small bubbles and the derived average value of the diameters in the cases of C_{12} and C_{14} fatty alcohols are respectively 0.41 cm and 0.37 cm. On the contrary, bubbles with higher average diameters were found for both smaller and longer chains with respect to the above-cited ones and in the case of unsaturated alcohols (Fig. 6). Finally, the shape factor related to the chain length is reported in Fig. 7.

A shape factor value approaching the unity is an index of the presence of circular bubbles. The highest value was obtained with C_{12} and C_{14} formulates which also in this case showed the best performances. As it can be possible to note from the performed tests, antifoams characterized by short chains showed too little hydrophobic behavior while those with long chains stabilize the foam hence in both cases their action is not optimal. Based on the results obtained from foaming tests and image analysis, antifoam agents synthesized with C_{12} and C_{14} saturated fatty alcohols showed the best antifoam performances, and they were taken into account to perform further investigations. For this purpose, other cementitious formulations were prepared reducing the antifoam content and using the same amount of other components. These formulations were compared with the standard formulation (C_0) and with those obtained with the commercial antifoam (C_x). The percentage of the antifoam agent was reduced from 5 wt% respect to the superplasticizer (which represents the highest percentage useable) respectively to 3 wt% (Formulations A) and 1 wt% (Formulations B). In Table 5 their characteristics are reported.

Flow table tests were made on the formulations and after that, they were analyzed through *Image J* software using the same approach previously described.

In Table 6 the results obtained for Formulations A are reported.

The efficiency of the synthesized antifoam agents resulted to be higher than the commercial ones even when a lower weight percentage was used. In fact, the formulate with the commercial antifoam showed a bubble number and an occupied area of almost 1/2 with respect to the formulate made only with the superplasticizer while the formulates made with the synthesized antifoam agents

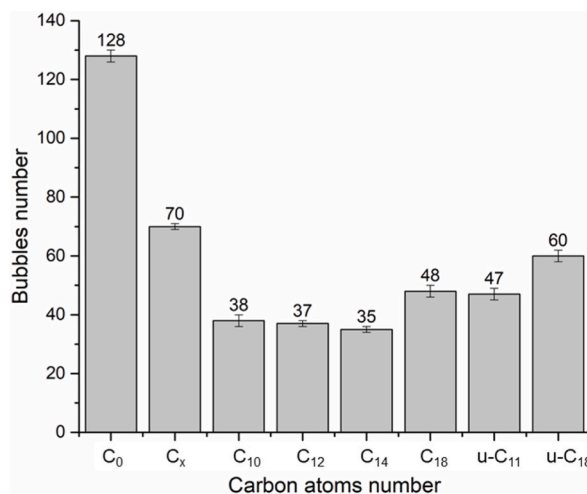


Fig. 4. Number of the bubbles as a function of carbon atoms number for saturated and unsaturated fatty alcohols.

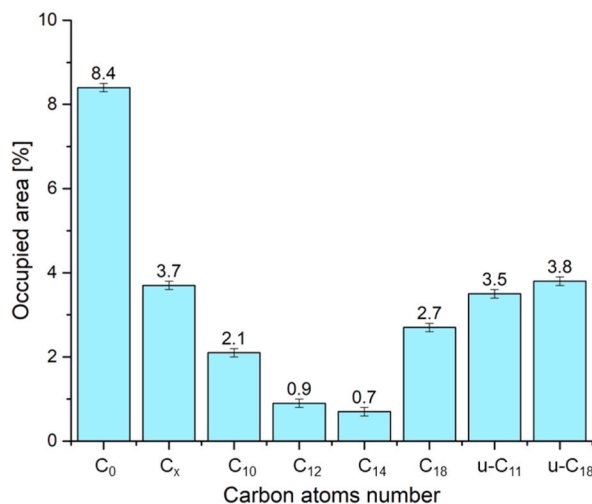


Fig. 5. Percentage of occupied area as a function of chain length for saturated and unsaturated fatty alcohols.

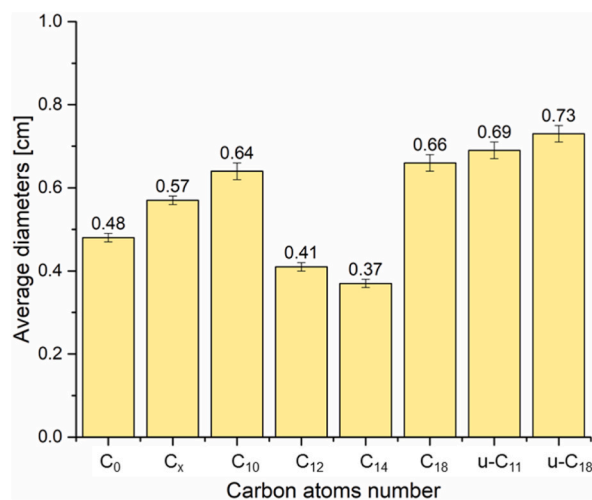


Fig. 6. Average diameters as a function of carbon atoms number for saturated and unsaturated fatty alcohols.

showed parameters value equal to 1/3 with respect to the formulate made only with the superplasticizer. In Table 7 the results for Formulations B are reported.

Decreasing the concentration of the antifoam agent down to 1 wt%, their performances get worse even if the synthesized antifoams continue to be better than the commercial one. Great attention was devoted to the area occupied by the bubbles since it gives us a clear idea of their activity. This parameter was investigated as a function of alcohol chain length for the formulations made by three different concentrations (5 wt%, 3 wt%, and 1 wt%). The comparison is reported in Fig. 8.

As it is possible to see, the synthesized antifoam agents showed better properties compared to the commercial ones in all three cases. The antifoam agent synthesized with C₁₂ alcohol was purified as explained in section 2.3. The foaming test was made on the purified product obtaining an excellent result since no foam formation was observed.

Finally, a cementitious formulation was prepared by using the purified product at the maximum useable percentage (5 wt%) and the results were compared with those obtained in the case of the same antifoam agent before the purification and the commercial one. In Table 8 the results obtained from the *Image J* analysis are summarized showing the improvement of the antifoaming properties of the considered product.

In Fig. 9, the comparison between the cementitious formulation made without the antifoam agent and with the purified antifoam is reported where the improved properties can be appreciated.

5. Conclusions

The synthesis of antifoam agents to be used in cementitious formulations was proposed and in particular, esters of glycine betaine

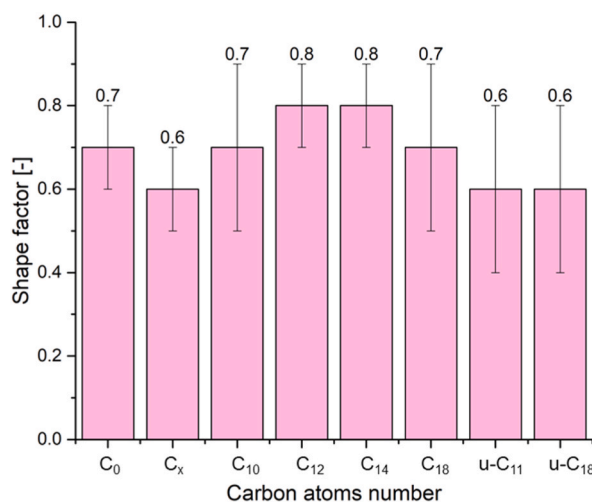


Fig. 7. Shape factor related to the chain length for saturated and unsaturated fatty alcohols.

Table 5

Cementitious formulatues characteristics.

Components	Standard formulation	Formulations A	Formulations B
Concrete	1000 g	1000 g	1000 g
Water	350 g	350 g	350 g
Superplasticizer	1 g	1 g	1 g
Antifoam agent ^a	/	0.03 g	0.01 g

^a it was prepared a formulation for each antifoam agent, both for the commercial one and the two chosen antifoams.

Table 6

Results obtained for Formulation A.

	Bubbles number	Total bubbles area [cm ²]	Percentage of occupied area [%]	Cumulative average diameters [cm]	Shape factor
C ₀	128 ± 2	49 ± 1	8.4 ± 0.1	0.48 ± 0.01	0.7 ± 0.1
C _x	71 ± 1	26 ± 0.2	4.3 ± 0.1	0.62 ± 0.01	0.7 ± 0.1
C ₁₂	40 ± 1	12 ± 0.1	3.3 ± 0.1	0.44 ± 0.01	0.8 ± 0.2
C ₁₄	42 ± 1	12 ± 0.1	3.2 ± 0.1	0.45 ± 0.01	0.8 ± 0.2

Table 7

Results obtained for Formulation B.

	Bubbles number	Total bubbles area [cm ²]	Percentage of occupied area [%]	Cumulative average diameters [cm]	Shape factor
C ₀	128 ± 2	49 ± 1	8.4 ± 0.1	0.48 ± 0.01	0.7 ± 0.1
C _x	78 ± 1	40 ± 0.2	7.9 ± 0.1	0.76 ± 0.01	0.7 ± 0.1
C ₁₂	60 ± 2	25 ± 0.1	5.8 ± 0.1	0.34 ± 0.01	0.8 ± 0.2
C ₁₄	65 ± 2	24 ± 0.1	5.6 ± 0.1	0.30 ± 0.01	0.8 ± 0.2

and fatty alcohols, both saturated and unsaturated, were considered. Antifoams need to remain stable when in contact with a superplasticizer. These esters are soluble in an acidic aqueous medium, such as in a solution of superplasticizer, and are also hydrolyzable in a basic medium, like the hydration water of the concrete. This hydrolysis releases alcohol, which acts as the antifoam molecule. Capric, laurilic, myristic, and stearic alcohols were used as saturated ones while undecenyl and oleic were the unsaturated alcohols. In all the different cases, the reached conversions were higher than 95 %. On the synthesized products, the antifoaming properties were tested through a foaming test according to the Ross-Miles method to evaluate the stability of the formed foam over time and a flow table test to examine the formation of the bubbles. The results were compared to those obtained with a solution made only with the superplasticizer without antifoam and with a commercial antifoam. The best results were obtained with the antifoam synthesized from C₁₂ and C₁₄ alcohols. In these cases, fewer foam was formed, and it was less stable since it decayed completely. Furthermore, the investigation of the bubble content in the cementitious formulations was made through an image processing software, *ImageJ*. All the synthesized antifoam agents showed better properties than the commercial ones, particularly the antifoams containing saturated fatty alcohols. It was observed that alcohols with shorter chains exhibited insufficient hydrophobic behavior,

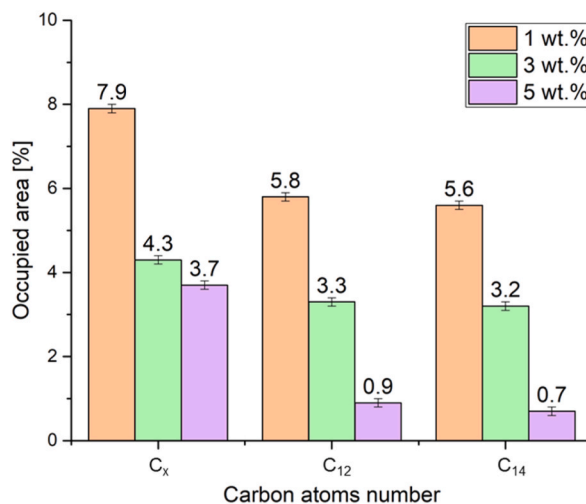


Fig. 8. Percentage of the occupied area as a function of chain length for the three different amounts of antifoams.

Table 8

Results obtained from the test with the purified antifoam agent.

	Bubbles number	Total bubbles area [cm ²]	Percentage of occupied area [%]	Cumulative average diameters [cm]	Shape factor
C ₁₂	28 ± 1	1 ± 0.1	0.2 ± 0.1	0.15 ± 0.01	0.8 ± 0.1

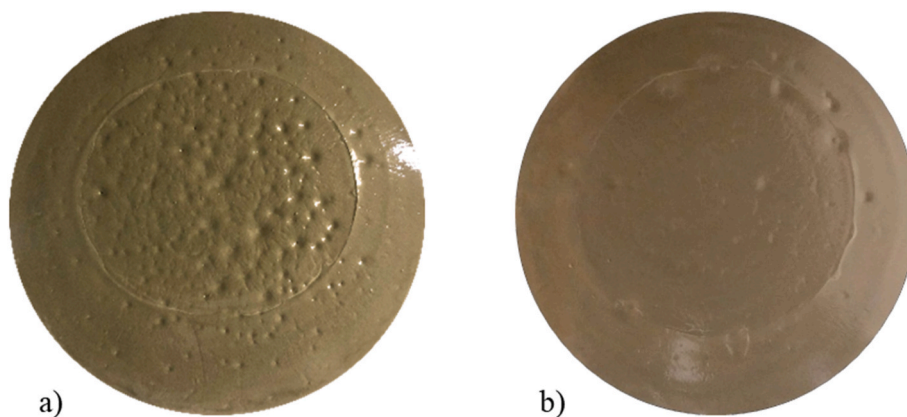


Fig. 9. Comparison between the cementitious formulation C₀ (a) and purified C₁₂ (b).

while alcohols with longer chains stabilized the foam. This outcome suggests that both classes of molecules have an ineffective impact on the formulation. Finally, a purification step was performed on the C₁₂ antifoam, leading to improved properties, including a reduction in the number of bubbles, a decrease in the percentage of occupied area, and a smaller average diameter for the bubbles.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data availability

Data are available from the authors.

CRediT authorship contribution statement

Francesco Taddeo: Writing – review & editing, Writing – original draft, Investigation. Rosa Vitiello: Writing – review & editing,

Methodology, Data curation, Conceptualization. **Michela Ruocco**: Writing – original draft, Investigation. **Rosa Turco**: Formal analysis, Data curation. **Vincenzo Russo**: Software, Data curation. **Riccardo Tesser**: Supervision, Methodology, Conceptualization. **Martino Di Serio**: Writing – review & editing, Supervision.

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

Mapei S.p.A. Italia is acknowledged for the supply of commercial products. The authors thank CIRCC (Progetto Competitivo 2022/CMPT222955, MIUR) for the financial support. This study was carried out within the MICS (Made in Italy–Circular and Sustainable) Extended Partnership and received funding from the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) –MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 –D.D. 1551.11-10-2022, PE00000004). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e33164>.

References

- [1] P. Hewlett, *Lea's Chemistry of Cement and Concrete*, fourth ed., Butterworth-Heinemann, New York, 2003.
- [2] R. Vitiello, M. Di Serio, P. Perrotta, R. Tesser, Effect of hydrophobic polymers (HASE) as additives on the cement paste flow behavior, *Results Mater* 17 (2023) 100370, <https://doi.org/10.1016/j.rinma.2023.100370>.
- [3] UNI EN 934-2, *Admixtures for Concrete, Mortar and Grout- Part 2: Concrete Admixtures – Definitions, Requirements, Conformity, marking and labelling*, 2012.
- [4] R.M. Rixom, *Chemical Admixtures for Concrete*, E & FN SPON, London, 1999.
- [5] Engineering Civil, Limitations of concrete or disadvantages of concrete. <https://engineeringcivil.org/articles/concrete/limitations-concrete-disadvantages-concrete-8-reasons/>. (Accessed 15 November 2023).
- [6] S. Erdogdu, Compatibility of superplasticizers with cements different in composition, *Cement Concr. Res.* 30 (2000) 767–773, [https://doi.org/10.1016/S0008-8846\(00\)00229-5](https://doi.org/10.1016/S0008-8846(00)00229-5).
- [7] V.S. Ramachandran, M.S. Lowery, T. Wise, G.M. Polomark, The role of phosphonates in the hydration of Portland cement, *Mater. Struct.* 26 (1993) 425–432, <https://doi.org/10.1007/BF02472943>.
- [8] M. Qiao, J. Wu, N. Gao, G. Shan, F. Shen, J. Chen, B. Zhu, Preparation and properties of different polyether-type defoamers for concrete, *Materials* 15 (2022) 7492.
- [9] J. Chen, G. Shan, J. Wu, M. Qiao, N. Gao, Q. Ran, Branched alkyl polyethers as novel defoamers for concrete, *Cement Concr. Res.* 157 (2022) 106821.
- [10] M. Qiao, J. Chen, N. Gao, G. Shan, J. Wu, Q. Ran, Synthesis and properties of different alkyl alcohol polyethers as the defoamers for concrete, *Colloids Surf., A* 646 (2022) 128998.
- [11] A. Mahmoudkhani, R.E. Wilson, L. Bava, J. Rucker, U.S. Patent No. 13036397, U.S. Patent and Trademark Office, Washington, DC, 2011.
- [12] D.C. Darwin, R.T. Taylor, A.A. Jeknavorian, D.F. Shen, U.S. Patent No. 6139623, U.S. Patent and Trademark Office, Washington, DC, 2000.
- [13] S. Mehalebi, A. Desmotz, U.S. Patent No. 20130291764, U.S. Patent and Trademark Office, Washington, DC, 2013.
- [14] E.M. Gartner, D.F. Myers, EU Patent No. 0519747A2, European Patent Office, Paris, France, 2012.
- [15] S.I. Karakashev, M.V. Grozdanova, Foams and antifoams, *Adv. Colloid Interface Sci.* 176–177 (2012) 1–17, <https://doi.org/10.1016/j.cis.2012.04.001>.
- [16] N.D. Denkov, Mechanism of foam destruction by oil-based antifoams, *Langmuir* 20 (2004) 9463–9505, <https://doi.org/10.1021/la049676o>.
- [17] A. Fabozzi, I. Russo Krauss, R. Vitiello, M. Fornasier, L. Sicignano, S. King, S. Guido, C. Jones, L. Paduano, S. Murgia, G. D'Errico, Branched alkyldimethylamine oxide surfactants: an effective strategy for the design of high concentration/low viscosity surfactant formulations, *J. Colloid Interface Sci.* 552 (2019) 448–463, <https://doi.org/10.1016/j.jcis.2019.05.052>.
- [18] R. Vitiello, C. Rossano, I. Russo Krauss, G. D'Errico, M. Di Serio, Hydrophobically modified alkali soluble emulsion polymers: literature review, *J. Surfactants Deterg.* 23 (2020) 5–19, <https://doi.org/10.1002/jsde.12361>.
- [19] W. Erwied, *Foams and Foam Control*, Ullman's Encyclopedia of Industrial Chemistry, Wiley-VHC, Weinheim, 2000.
- [20] S. Mehalebi, A.E. Desmotz, Water Soluble Antifoam Additive for a Cement Composition, Aqueous Solution Containing Same and Use Thereof in Mortars or Concretes, US 2013/0291764 A1, 2013.
- [21] M.E. Saint Victor, T. Benvegnu, H.F. Azira, *Green glycine Betaine Derivative Compounds and Compositions Containing Same*, US, 2018, 9,909,086 B2.
- [22] F. Goursaud, M. Berchel, J. Guilbot, N. Legros, L. Lemiègre, J. Marcilloux, D. Plusquellec, T. Benvegnu, Glycine betaine as a renewable raw material to “greener” new cationic surfactants, *Green Chem.* 10 (2008) 310–320, <https://doi.org/10.1039/B713429K>.
- [23] ASTM Standard: D1173, Standard Test Method for Foaming Properties of Surface-Active Agents.
- [24] ASTM Standard: C 230/C 230 M, Specification for Flow Table Use in Tests of Hydraulic Cement.
- [25] ASTM Standard: C 1437, Standard Test Method for Flow of Hydraulic Cement Mortar.
- [26] ImageJ, <https://imagej.nih.gov>. (accessed 15 November 2023).
- [27] <https://imagej.nih.gov/ij/docs/guide/user-guide.pdf>. (Accessed 15 November 2023).