Comparative study of the tribological behaviour of emulsions and demoulding oils at the concrete/formwork interface

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ABSTRACT. To ensure a performing demoulding, a release agent must resist the friction of concrete on the formwork. Emulsions are interesting alternatives that leads to a reduced consumption of oil on construction sites. The behaviours of two commercial emulsions are compared with two conventional demoulding oils. The adhesion energy calculated were favourable to the emulsions. The water evaporation kinetics leads to the measurements of film thickness. Tests with the tribometer have shown that the films produced from the emulsions generate a friction reduction of 30% and 40% at the concrete / formwork interface. Such performance can be explained by Wenzel's state of wettability, which facilitates the film fit into the formwork roughness.

KEYWORDS: tribometer, friction, emulsion, adhesion energy, interface, demoulding oil

Highlights:

Adhesion energies are higher for films generated from emulsions

Films from emulsions have specificities in term of thickness and uniformity.

The vegetable-based films generate a reduction of friction on concrete.

Tribological tests confirms a Wenzel state for emulsions on the formwork

1. Introduction

In the building industry, concrete formwork removal has always been a complex part of construction operations. Current regulations limit the use of formwork release oils to two hours per day and per user, which represents severe constraints for the on-site organisation. Users attempt to make this step easier by implementing new techniques, namely: the polarisation [1], the creation of self-lubricating surface coatings [2], or even the application of a controlled permeable formwork liner at the interface [3]. The adhesion of concrete on the formwork remains an open subject. Permeable coatings still need to develop their re-use to become competitive. The mechanical characteristics of waterproof polymer coatings limit their use. The use of release agents remains the most used process despite its repeatability and costs, as evidenced by the number of published works [4]. Due to environmental and health impacts, the market for vegetable-based products has significantly grown. In order to classify these products, the SYNAD (National Union of Admixtures for Concrete and Mortar) built an abacus [5] based on the product composition and the use-related criteria (safety, health, environment). While the compositions of vegetable-based formulations contribute to an effective concrete setting in the formwork, defects (variation in hues, micro-bubbling) can nonetheless appear in the event of an overconcentration [6,7]. Emulsions contains about 70 % of water, which makes it possible to apply a reduced amount of oil on the formwork surface. Previous works [4,16] have already studied the configuration of films composed of mineral and vegetable oils at the surface of a metal formwork, in connection with their mode of action. In contrast, the behaviour of emulsions has not received much attention in the civil engineering field [8]. Therefore, it seems interesting to investigate the characteristics of the film after the water evaporation. To identify the specificities of the resulting film, comparisons are done between four commercial demoulding agents: two emulsions and two conventional oils. The resistance of the film to the moving concrete was determined by a plane/plane tribometer that represents concrete casting conditions in a formwork.

2. Emulsions characterization

An emulsion is the dispersion of a liquid in small droplets into another immiscible liquid [9]. Thus, for an oil-in-water emulsion, the oil is the dispersed phase in the water, the continuous phase. The oil

dispersion requires a mechanical action (homogeniser) in order to form minuscule droplets [10]. The addition of an emulsifier that lowers the interfacial tension between the two phases, improves the physical stability of the mixture by forming micelle [8] (Fig. 1). Creaming or sedimentation refers to a process leading to a phase separation. Emulsions are widely used in the cosmetics, food processing, paint and construction industries.

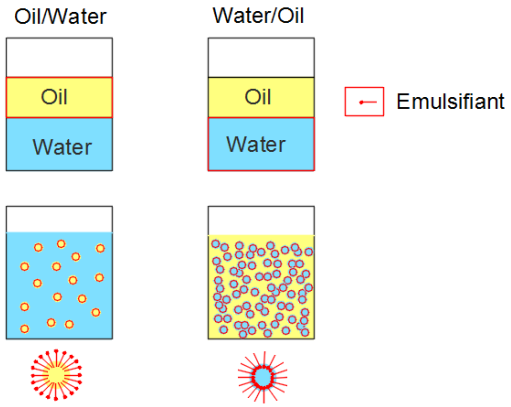


Fig. 1. Diagram of the direct emulsion O/W and invert W/O

Table 1 lists the characteristics of the four demoulding oils supplied by a manufacturer. An invert mineral emulsion (IME) and direct vegetable emulsion (DVE) are compared to a vegetable oil-based product (V) and a mineral oil-based product (M).

Table 1 Properties of release agents

	DVE	**IME**	**V**	**M**
Type	Direct emulsion	Invert emulsion	Oil	Oil
Composition	Vegetable esters	Paraffinic wax	Vegetable esters	Paraffinic hydrocarbons
Oily phase	Vegetable	Mineral	Vegetable	Mineral
Content of water (%)	80	70	0	0
Flash point °C	> 100	96	>100	>100
Viscosity (mPa.s)	38.5±1.5	60.6±3.4	66.6±2.8	24.5±1.7
Density	< 1	< 1	0.93	0.86

The dynamic viscosity is determined using a HAAKE VT550 single-speed viscometer, fitted with a 1° (PK5) cone. A constant volume of oil (v = 0.6 cm^3) is deposited on the plate, and the cone is lowered

toward the plate. As expected, the direct emulsion has a lower viscosity than for invert emulsion, due to a lower content in oil. The contents of water were given by the supplier.

2.1. Surface state of formwork

Metal formwork is extensively present in the building trades; it serves to streamline concrete setting and enhance worksite productivity. The potential for formwork reuse is substantial for these structural elements repeated throughout a project, i.e. vertical shear walls, floors and columns. A new steel formwork was chosen, and its surface roughness was measured. Samples were cut from the formwork surface to perform microscopy tests and to measure film thicknesses. The parameters (Fig. 2) chosen to evaluate roughness are as follows [11]:

Ra: arithmetic mean of profile deviations relative to the average line.

Rp: average depth over an evaluation length.

Rt: peak height at the maximum profile valley.

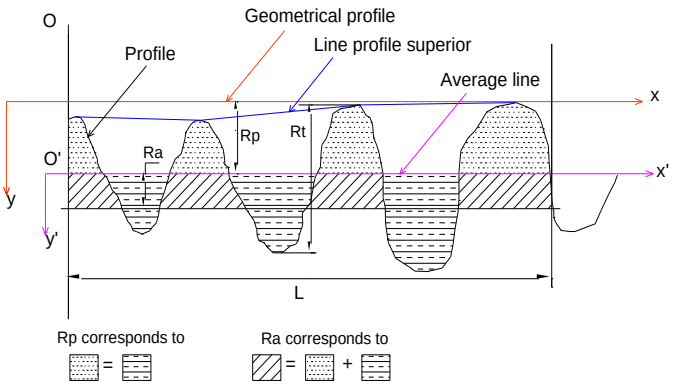


Fig. 2. Scheme of the roughness profile (height vs. length).

Figure 3 displays a 3D view of the roughness profile of the formwork sample using a white-light interferometry microscope (WLIM) VEECO NT3300 over a 4×4 mm² area [2]. The surface was sampled at 2052 × 2052 points with a 1.9 µm step scale along X- and Y-directions. For this sample, an average roughness value Ra of 1.34 µm, a maximum Rt profile deviation of 18.31 µm, a Rp value of 3.28 µm, and a value dispersion on the image of +/-0.02. The profile values between 8 and - 10 µm and the low deviation, indicated that the formwork surface has a low roughness, uniform on the sample.

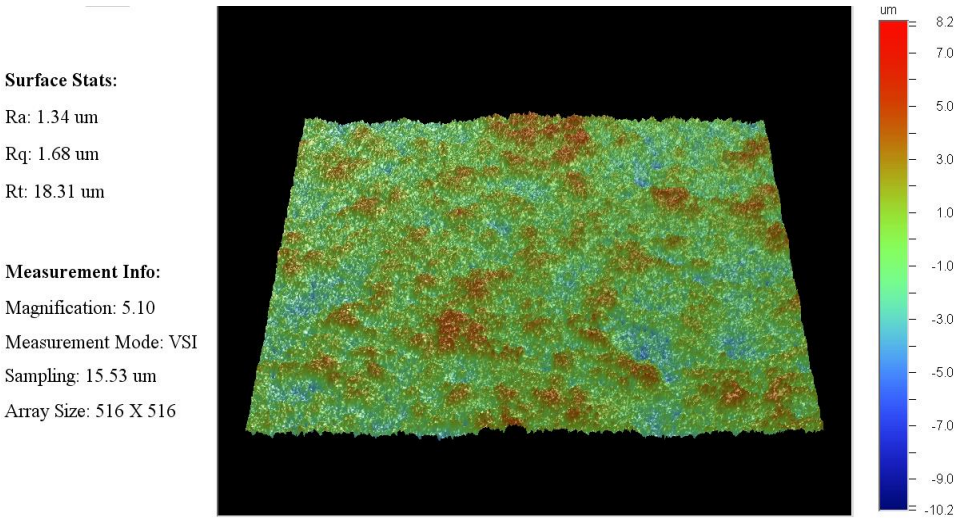


Fig. 3. 3D image of the new formwork roughness profile

Further measurements have been made on a roughness meter [11] on ten measuring points to obtain a more precise representation of the formwork roughness. The average values are given in Table 2. The dispersion value is ±0.02 µm.

Table 2. Roughness parameters of the formwork sample.

Test	1	2	3	4	5	6	7	8	9	10	Average
Ra (µm)	1.32	1.23	1.35	1.13	1,41	1.18	1.18	1.38	1.26	1.15	1.26
Rt (µm)	13.53	13.23	15.54	12.53	15.67	13.87	13.65	18.56	16.98	13.23	14.68
Rp (µm)	2.69	3.17	3.76	3.08	4.05	3.45	2.98	3.65	4.12	3.07	3.40

Roughness values obtained by the two methods are in agreement with those of a new formwork surface used on site. [6].

2.2. Interfacial properties

The assessment of release agent performances implies the characterization of the interface in contact with the support. The affinity of oil with the support is a significant property since the oil film acts as a protective coating for the formwork and plays the role of a lubricant during the concrete casting step [6].

As a matter of fact, the liquid/vapor surface tension of a liquid is correlated with the value of the contact angle formed by a drop on a support [12]. Contact angles are a readily observed physical phenomenon related to the more fundamental concepts of energy and surface tension. This insight helps determine

the properties of wettability and adhesion of a film, which in turn makes it possible to predict the properties of a coating or detect traces of surface pollutants. As part of a theoretical approach, adhesion energy values are calculated based on contact angle data. It may be considered that the liquid/solid adhesion energy value is representative of the adhesive strength between the liquid and the support.

The liquid/solid adhesion energy value also represents the adhesive force between a liquid and a support. Adhesion energies are calculated according to Zisman's Equation [13]:

$$\omega_{LS} = \gamma_{LV} \times (1 + \cos\theta) \quad (1)$$

The liquid/vapor surface (γ_{LV}) tension was measured using Wilhelmy's plate method at 20°C. The device employed is a tension meter manufactured by the CAD firm and fitted with a platinum blade. The surface tension is indicated by the meniscus formed along the plate boundary. The material contact angle (θ) was then determined by a PGX type of mobile goniometer. This device measures the contact angle at the interface between a liquid drop and the substrate surface where the drop has been deposited [14].

Table 3 summarises adhesion energy values at 20°C. We can observe that emulsions have higher adhesion energies than oils, which is a necessary condition to reduce frictions. Higher adhesion energy corresponds to higher surface tension and lower drop angle.

Table 3. Interfacial properties of release agents at 20 °C

	Surface tension L/V (mN/m)	**Contact angle** (°)	**Adhesion energy L/S** (mN/m)
DVE	40.0	33.1	73.50
IME	37.1	22.5	71.35
V	33.4	32.8	61.5
M	30.6	18.5	59.6

2.3. Formation of the oil film

Demoulding oils were applied in a regular manner at a distance of 15cm from the surface of a formwork sample (disk with a diameter of 5 cm) using an Ecospray sprayer fitted with a conical nozzle of 1 mm diameter (Fig. 4).

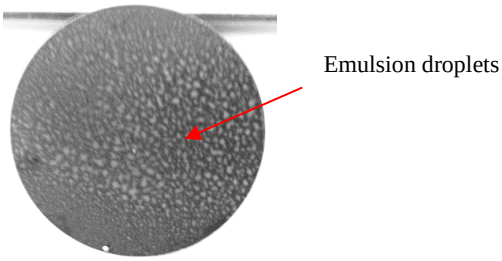


Fig. 4. Surface state after spraying on the formwork

A cloud of white droplets fell on the surface. Then, a latency period occurs during the evaporation of water. The time elapsed has been estimated by the supplier at 15-20 min. During this latency period, the emulsion film formation was in progress and was analysed by means of optical microscopy (Figs. 5 and 6). As the water gradually evaporated, the emulsified medium became structured. On the emulsion micrographs, the white colour denotes the emulsified phase, which tends to disappear in favour of the oily phase. The observations conducted under optical microscopy of a single drop showed that, for the invert emulsion, water disappeared more quickly compared to direct emulsion water (white colour no longer visible). Similarly, the reverse emulsion drop diameter increased rapidly (+20% after 5 min), which indicates that the film began to form at the surface.

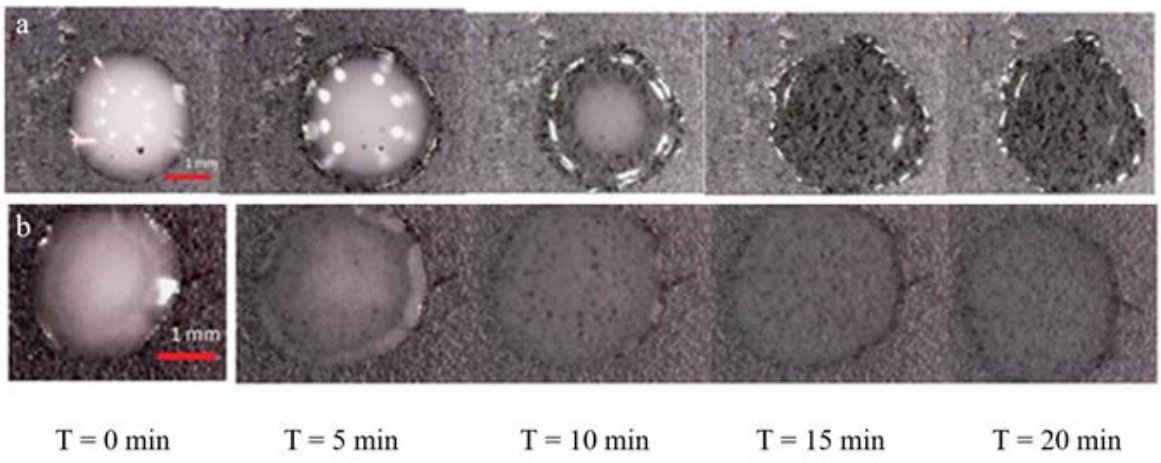


Fig.5. Evolution of a drop of (a) DVE and (b) IME emulsions during the latency period

Micrographs were taken 20 min after spraying of DVE emulsion and vegetable oil (V) on two formwork samples. After the oil droplets has merged, DVE emulsion has generated a film with a uniform distribution over the formwork surface (Fig. 6). We can observe that the vegetable oil film has a lesser

coating rate. In fact, previous works have shown that it was necessary to scrape the vegetable oil film to improve its homogeneity [15].

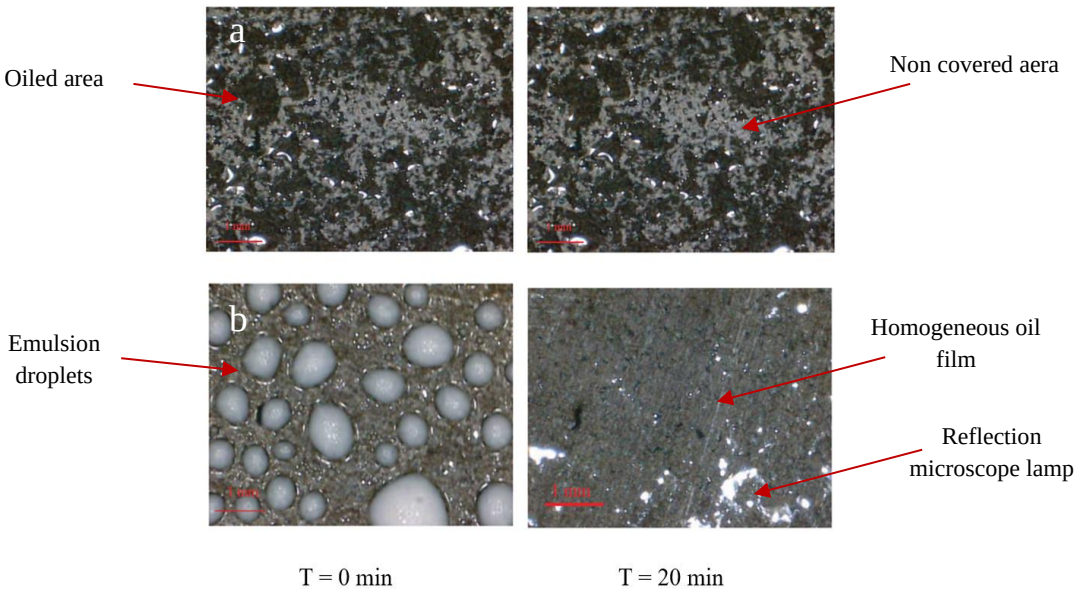


Fig. 6. Film micrographs after spraying (a) the V oil and (b) the DVE emulsion

During the latency period, a monitoring of the emulsion deposited onto the new formwork samples was carried out

The thickness of film (e) depends on the mass (m) of product on the plate, its density (ρ) and the plate surface (S). Weighing was performed with a precision scale of 10^{-4} g [6].

$$V = S \times e \Leftrightarrow e = \frac{V}{S};\ V = \frac{m}{\rho};\ \text{then} \quad e = \frac{m}{\rho \times S} \tag{2}$$

with S (m^3), ρ (kg/m^3), m (kg), and e the thickness (m).

Previous works have shown that values obtained by the weighing method were very close to measurements carried out by PIXE [16]. It was found that the film thicknesses for conventional oils are typically between 3 and 4 µm for a mineral oil and between 2 and 3 µm for a vegetable oil [4].

A monitoring of film thickness variation over time was carried out. (Fig. 7). The reproducibility of measurement is based on four tests.

One test was conducted by spraying 0.0168 g of DVE and 0.0101 g of IME on two formwork samples. The lower viscosity of DVE led to deposit a slightly higher mass of DVE.

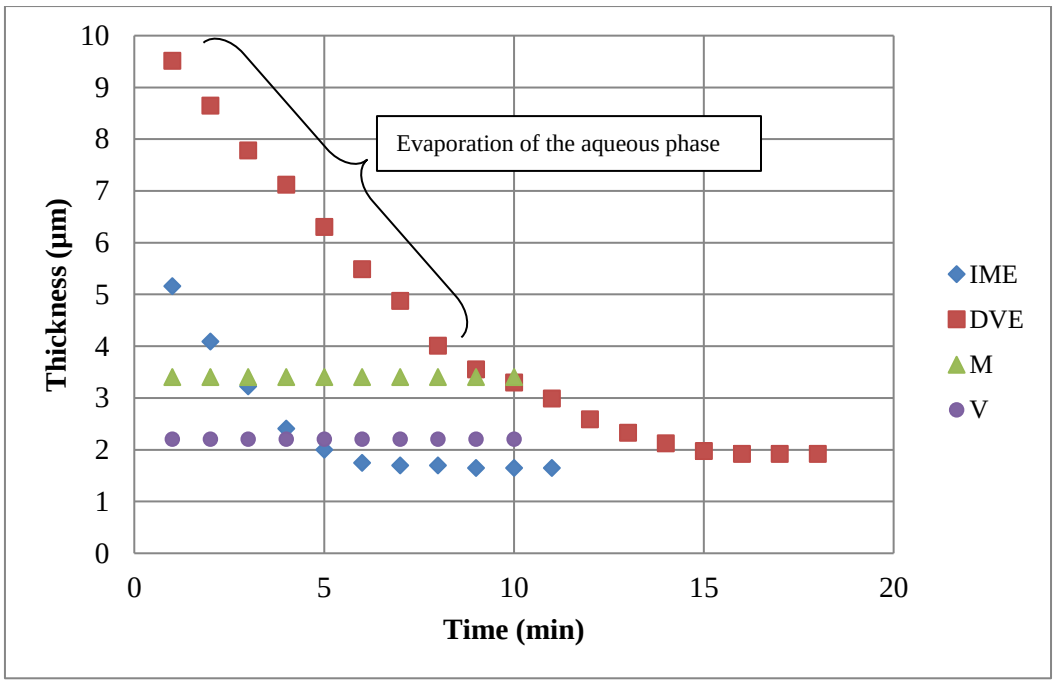


Fig. 7. Water evaporation kinetics for the deposited emulsions

The final thickness of the oil film after complete water evaporation was determined by weighing. The aqueous phase is completely evaporated when the film mass remained constant, which corresponds to the final oil film thickness. Seven minutes were required for the film formation with the invert emulsion and 16 minutes with the direct emulsion, which is in agreement with their water content (table 1). Thus, the direct emulsion lost 79% of its initial mass, whereas the decrease of mass was close to 67% for the invert emulsion. The direct emulsion film reached an average thickness of 1.9±0.2 µm, while the invert emulsion film was 1.7±0.2 µm thick (averaged over 4 tests). The difference between the two initial masses was 39.9%, but the final film thicknesses were very close, because of the higher evaporation rate of the direct emulsion. For the mineral emulsion, the reduction in thickness was 47% compared to the mineral oil, whereas the reduction was 14% for vegetable emulsion compared to the conventional vegetable oil. Indeed, the active fractions in VDE is lower compared to that of IME. Finally, in both cases, emulsions generated thin oil films with high adhesion energies, especially for the mineral oil.

3. The friction of the concrete on the formwork

An experimental campaign has been conducted in order to assess the resistance of these films to concrete friction using a plane/plane tribometer. Previous studies [4,15] have shown that this level of resistance is connected to the aesthetic quality of concrete facing and depends on the mechanisms at the interface

and on the type of oil. The performances of a mineral film are driven by its thickness. A vegetable-based film contains fatty acids contributing to an interfacial organization in layers.

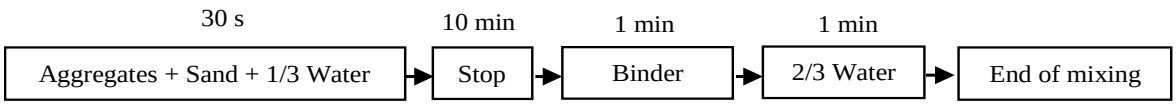
3.1. The concrete

The concrete used is a traditional mix with a water-to-binder (W/B) ratio of 0.57 and a gravel-to-sand (G/S) ratio equal to 1.27. The workability measured with the Abrams cone, is between 12 and 14 cm, which corresponds to the S3 consistency class (according to Standard NF EN 206-1). The relevant mix design is given in Table 4.

Table 4. Concrete formulation

Concrete	(kg/m^3)
Cement CEM I 52,5 CP2	265
Fillers	88
Sand 0/4	792
Gravel 4/8	271
Gravel 6/20	734
Water	201

The concrete production requires a well-defined mixing protocol. Standard NF P 18-404, entitled "Concretes - Design, suitability and inspection testing - Specimen production and conservation", was implemented. The mixing procedure was performed with dry materials according to this protocol:



Tests were carried out at a temperature of 20°C.

3.2. The plane/plane tribometer

A plane/plane tribometer was developed by our team and was patented under the number PCT/EP 2017068017. The principle behind this test set-up (Fig. 8) is as follows [4]: an interchangeable plate slides between two fresh concrete samples, with the movement being carried out using a motor coupled to an auger. The plate speed is controlled by a programmable controller. The samples are pressurised by

means of jacks, with the pressure lying between 50 kPa and 500 kPa. A force sensor connected to the plate measures the tangential stresses acting on the plate due to the concrete.

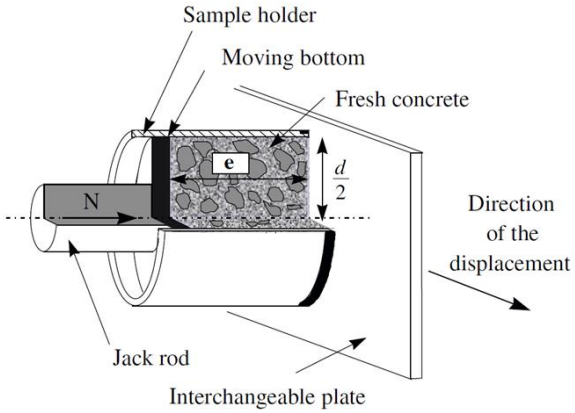


Fig 8. Concrete tribometer principle [4]

3.2.1. Experimental conditions

For the experimental campaign, the test parameters replicated worksite conditions in order to approximate the stresses being exerted on the oil film by the concrete. The casting speed and pressures at the formwork base constitute the key parameters of the study. Tests were conducted on a plate cut-out from a formwork wall with roughness values of Ra = 1.34 µm. The emulsions were applied by spraying in full compliance with the supplier recommendations.

3.2.2. Casting speed

The plate displacement speed corresponds to the casting speed of a concrete shell extending over a certain height. For our testing campaign, a speed of 3 m/h (0.84 mm/s) was used, which corresponds to the speed most commonly practiced on worksites [18].

3.2.3. Contact pressure

The contact pressure of the selected jack corresponds to the concrete pressures being exerted at the formwork base for a given height. The vertical formwork elements are subjected, as a result of the fresh concrete, to a thrust perpendicular to the shuttering surface. The factors capable of influencing this

pressure exerted on the formwork consist of: specific gravity of the concrete, workability measured using Abrams' cone, height of fresh concrete, minimum formwork dimension, and filling speed.

Considering fresh concrete as a fluid, the distribution of the pressure is triangular. The hydrostatic thrust (P) is given in Pascal by the following formula:

$$P = \gamma \times h \quad (3)$$

with γ the concrete density estimated at 25 kN/m^3 and h the height of the formwork (m)

Shell heights ranging from 2 to 6 m have been evaluated; they correspond to pressures in the range of 50 to 150 kPa.

4. Analysis of the formwork/concrete interface

Friction stresses vs. contact pressure for the fresh concrete and for formwork release agents are shown in Figure 9. A Coulomb law is applied in this pressure range:

$$\tau_f = \mu \times P \quad (4)$$

with τ_f the tangential stress (Pa) and P the contact pressure (Pa).

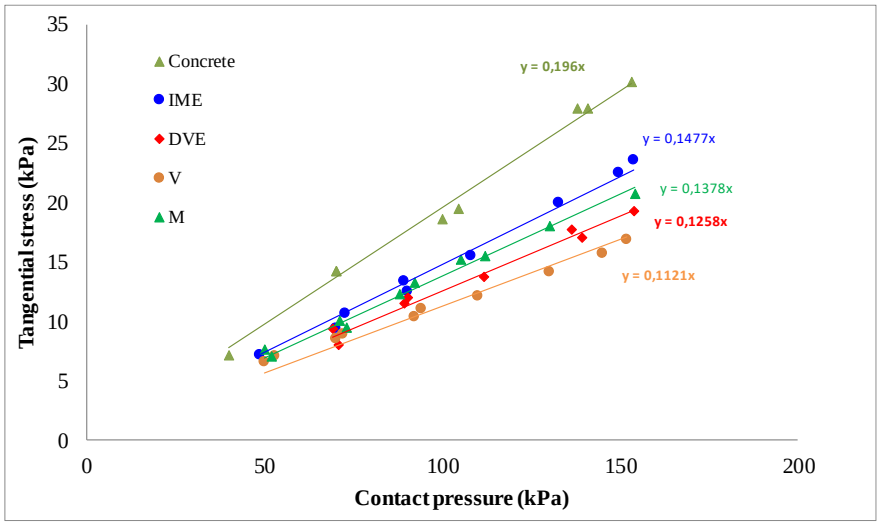


Fig 9. Dynamic friction constraints according to the pressure (v = 0.84 mm / s)

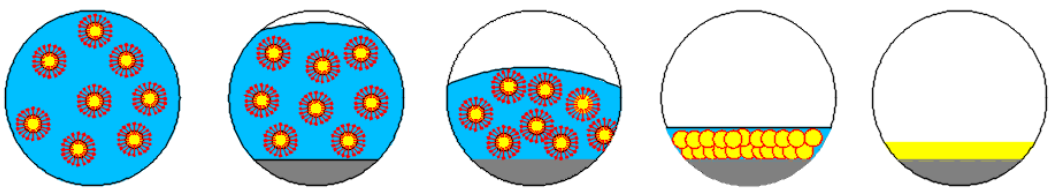
The stress variations vs. contact pressure indicate an average decrease in friction stresses of 30% for IME and up to 40% for VDE, compared to the interface without any demoulding agent. The oil films from emulsions thus contribute to a significant reduction in concrete friction against the formwork, even

despite thin films (between 1.5 and 2 µm). We can note that the vegetable-based films (oil or emulsion) prove to be more efficient in contact with concrete, compared to the both mineral films.

A previous study of the oil/concrete interface has described two behaviours: a lubricating effect mainly due to a physical action for mineral oils and a chemical action of the vegetable-based formulations [15]. Thanks to triglycerides, fatty acids and other esters as ingredients in a vegetable formulation, carboxylates (soap) are formed in contact with concrete (basic medium), which can explain the lower frictions observed.

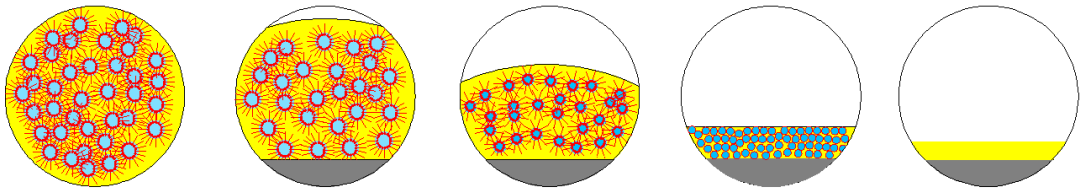
5. Discussion

This study describes the film formation generated from an emulsion and its main characteristics. Before spraying, protected from the air, the direct emulsion (DVE) is stable (Fig. 10), and the oily micelles are dispersed in the emulsion (Fig. 10a). After spraying, a set of droplets forms on the formwork surface; water is still present in a large quantity, and the micelles are still mobile (Fig. 10b). As the water gradually evaporates, the film becomes reconfigured and the micelles are directed towards the formwork surface. Due to their chemical adsorption, the film can adhere to the surface (Fig. 10c). In conclusion, the polarity of the metal surface makes it possible to correctly direct the micelles (Fig. 10d); meanwhile, the droplets combine to form a homogeneous oil film on the surface (Fig. 10e) [17]. In the case of the invert emulsion (IME) (Fig. 11), the aqueous phase is composed of smaller-sized and more numerous water micelles compared to the direct emulsion (Fig. 11a). Over time, the water micelles occupy less volume (Figs. 11b, 11c). This process forces the oily phase to move towards the formwork (Fig. 11d). Ultimately, the water contained in the micelles evaporates and the film becomes homogeneous (Fig. 11e).



(a) (b) (c) (d) (e)

Fig. 10. Evolution diagram of the direct emulsion over time



(a) (b) (c) (d) (e)

Fig. 11. Evolution diagram of the invert emulsion over time

To understand the phenomena at the emulsion/formwork interface, it is necessary to focus on the roughness of the plate. In fact, a sprayed oil tends to remain at the surface of the formwork asperities [11]. In contrast, the micelles (whether direct or invert) in emulsion have a size (0.02 and 0.2 µm) facilitating their insertion into the plate surface roughness (Fig. 2). In this case, the Wenzel wettability state [19] has been reached, as opposed to the conventional oils, which are in a Cassie state [20] (Figure 12).

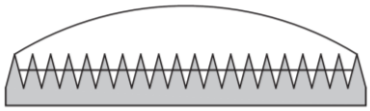


Fig. 12. Schematic representation of the Cassie state for conventional oil on a new formwork [11]

The measured surface tensions are greater than the conventional oils, this validates the Wenzel state for emulsions. According to Wenzel state, the film obtained after evaporation of the aqueous phase is totally inserted into the roughness of the plate, thus generating a homogeneous film, covering the whole surface. According to the work of Bormashenko [21, 22], figure 13 illustrates the Wenzel state for an emulsion. The film of IME is anchored more quickly in the formwork asperities in fact, the micelles of water evaporate faster. In both cases, despite a lower weight, the consequence of this configuration is the formation of an oily film, more resistant to the contact with the concrete.

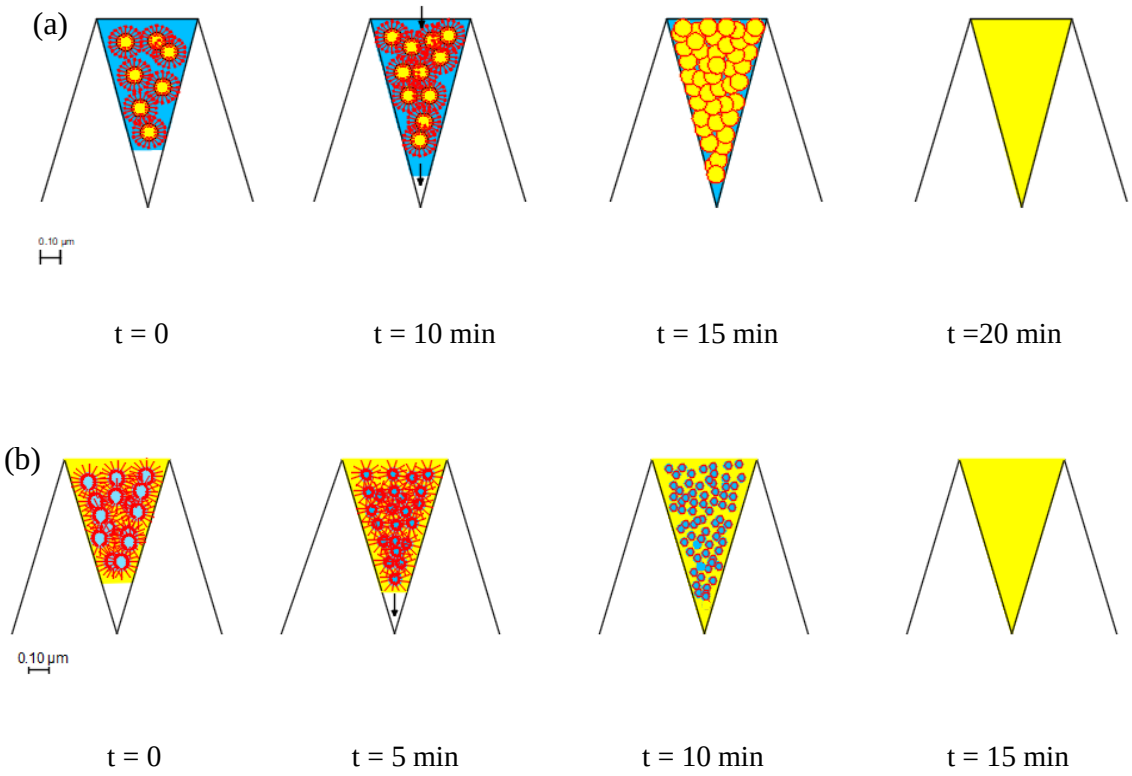


Fig. 13. Schematic evolution of (a) DVE and (b) IME emulsion films towards Wenzel state [21]

6. Conclusion

Emulsions exhibit a set of specific physicochemical properties. Their spraying on a formwork surface is followed by a water evaporation phase, along with the oily phase organization, leading to the formation of a rather thin oil film. The water evaporation profile indicated that the latency period may vary from 6 to 15 min, which is in agreement with the time period mentioned by the manufacturers. The film micrographs (20 min after spraying the emulsion) showed that the film formed as the oil droplets merge displayed a homogeneous distribution of oil on the formwork. Furthermore, the emulsions demonstrated a tribological behaviour similar to that of the conventional oils, i.e. resulting in a significant stress reduction. The formation of the lipophilic film as the aqueous phase evaporated is most likely related to micelle migration into the formwork roughness. This process helps improve the lubricating effect between concrete and formwork, as the oil film is reconfigured by interacting with the formwork roughness and do not need to be scrapped. The use of emulsions as a formwork release agent represents an efficient alternative to combine technical performance with a lower content of active ingredients. Vegetable formulations remain more effective compared to mineral formulations. They

306 should continue to develop on worksites over the near term. Other tests could bring further data about
307 the appearance of concrete facings demoulded with emulsions, or by involving other techniques (CPF
308 film, wood formwork, …).

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