Physicochemical and tribological characterization of release agents

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Summary

Release agents are a significant source of pollution in the construction and prefabrication industries. Conventional products are known to be toxic to humans and the environment. New formulations based on vegetable esters have appeared on the market to mitigate against this drawback, but more knowledge must be required about the properties and behaviour of these products, and their industry profile is raised. Understanding the phenomena that occur over the formwork-oil-concrete interface is a real challenge. This paper begins with a physicochemical survey of release agents by defining the formwork-oil and oil-concrete interfaces. It then characterizes the formwork-oil-concrete interface by dynamic studies (tribometer) and static studies (formwork) of the concrete.

Key words: Physicochemical characterization, release agents, interface, roughness, tribometry, formwork, concrete.

1. Introduction

After the Second World War, concrete was widely used for reconstruction and particularly in the 1960s for building social housing blocks. Its mechanical qualities, speed of execution and durability make it an exceptional product. Although a concrete's mechanical strength is of primary importance, the appearance of the material (facing) cannot be neglected.

Concrete adhesion to the formwork surface is due to two causes: engagement, and the forces of capillarity. The first is dominant in relatively soft or irregular-surfaced formworks, while the second only concerns formwork with hard, smooth surfaces.

Thanks to its extremely fine structure and great consistency at the start of casting, cement paste spreads over the formwork surface and becomes encrusted in the smallest asperities. Adhesion is thus significant. The forces of capillarity develop in the water-filled interstices, whose contact surfaces are very close. These forces can be considerable at the start of casting and decrease slowly as the concrete hardens.

To mitigate against these problems, a release agent (oil or grease) is required to reduce concrete adhesion to the formwork.

To better understand the interfacial phenomena, research should be conducted to build a model for predicting facing quality and to develop oil formulations.

The present study deals with the triphasic concrete-oil-formwork system. Each interface first underwent separate concrete-oil and oil-formwork studies, then the respective data obtained were correlated to characterize the previous triphasic system.

2. Release agents

Approximately 10000 tons and 80000 tons of release oils are consumed a year in France and Europe respectively [1]. The market is currently dominated by oils of petrochemical origin. These are entrained into the ground by formwork cleaning and rainwater leaching. This causes water and soil contamination by highly undegradeable and toxic compounds. In addition, operators' exposure to mineral oils through skin contact or inhalation of vaporized droplets generates occupational diseases observed by public health agencies.

At a technical level, the polarity of vegetable esters has advantages for demoulding applications. The use of vegetable oils would make it possible to reduce considerably the impact of these products on the surrounding natural environment. From a sanitary point of view, the use of vegetable formulations would be likely to improve working conditions.

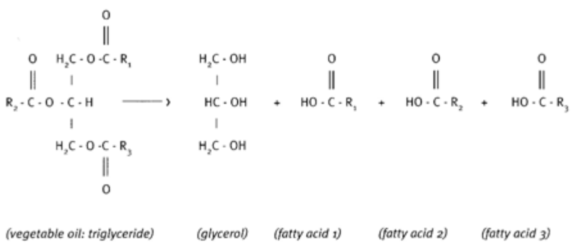


Fig. 1- Modification of pure vegetable oil

Vegetable formulations are divided into three categories [2]: neat oils of vegetable origin, semi-vegetable oils containing a fraction of solvent, and emulsions based on vegetable oil in water.

The vegetable oils used are triglycerides (three fatty acids combined with a glycerol molecule). Additives can be added to correct the raw materials: these are generally fatty acids, surface-active agents or anti-corrosion agents.

The effectiveness of the release agent strongly depends on its physicochemical characteristics, so these must be fully understood. A list of analytical techniques has been compiled [3].

3. Interaction between formwork and release agents

The formwork is a significant parameter of the demoulding operation. It governs the surface quality and is the "negative" facing. The nature of the formwork determines the choice of demoulding product. There are three types of formwork: metal, wood and composite. The qualitative parameter of the formwork is its roughness, which is the micrographic and macrographic irregularities of a surface. The lower the roughness index, the higher the quality of the facing.

Knowledge and analysis of the roughness parameters (Ra is the arithmetic mean of the profile variations compared to the average line and Rv is the depth of the deepest hollow over a length of evaluation) allow prediction of the behaviour of the oil on the wall.

3.1. Roughness

A roughness comparison was carried out between a new surface and an active surface. Surfaces are nominally plane and smooth and may display an undulation. Roughness can vary from fine to coarse according to the finishing process used.

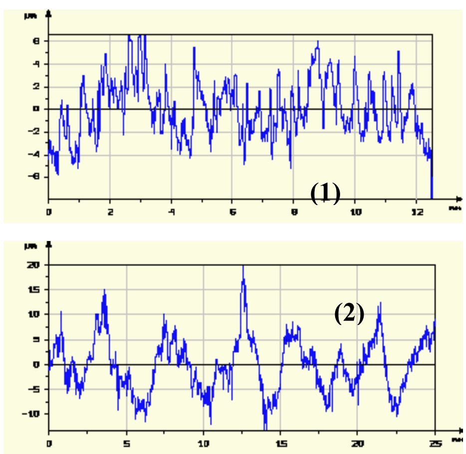


Fig. 2 Example of roughness profile : (1) new wall, (2) worn wall

Roughness measurements were carried out using a Surtronic 3+ roughometer. It is a standalone portable instrument for measuring surface quality.

Roughness was measured by moving a feeler along a line in a direction parallel to the average test surface. The parameter defining roughness was Ra.

Measurements were taken on 30x30x10 cm active moulds at various horizontal and vertical points. We separated the moulds into two measuring areas: one where the concrete was in contact with the mould, and another where it was not (this was deemed a "new" wall). We could thus observe the static effect of the concrete on the mould. The part in contact with the concrete measured a roughness Ra of 0.77µm. On the "new" part, roughness was measured at 1.2µm. (Fig.2).

The metal surface was thus subjected to polishing by abrasion under the action of the many passes of the concrete.

The aggregates in the concrete levelled off the peak of the asperities.

Because the oil film was thin and roughness hollows were up to 15 µm deep, the oil could not fully perform its lubricating function. It was thus useful to determine the maximum tolerable depth of a hollow.

Measurements were also performed on formwork walls. Roughness Ra is 0.3 µm for a new surface but can reach 1.6 µm for a worn surface. In such cases, the wall exhibits wear. The aggregates both widened and deepened the asperities. The concrete-steel dynamic behaviour was studied using a tribometer [4].

The release agent must be evenly applied to clean formwork surfaces, to create a continuous and uniform film. Spraying is the method most commonly used on building sites.

After characterizing the surfaces, we surveyed the behaviour of the release agents on the metal walls.

3.2. Dynamic viscosity

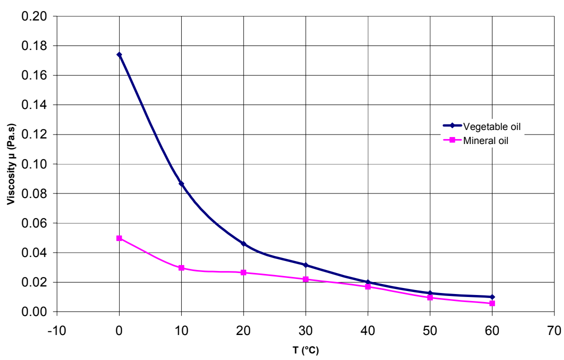


Fig. 3 Evolution of viscosity according to temperature

The behaviour of the oils in contact with a metal plate was studied using a controlled stress rheometer with parallel geometry cone according to temperature [0°-60°C] (Fig. 3).
At high temperature (40-60°C), the viscosity of the vegetable and mineral formulations evolved similarly. These temperatures can be reached during concrete setting or when the sun heats oiled moulds.
At low temperature, the vegetable base tends to solidify more quickly.
At constant temperature, vegetable and mineral oils display Newtonian behaviour, i.e. stress is proportional to the shear rate:

$$\tau = \mu \times \overset{\circ}{\varepsilon}$$

where $\overset{\circ}{\varepsilon}$ is the shear rate and µ the dynamic viscosity. The characteristics of the oils are given in Table 1.

Table 1: Characteristics of oils

	viscosity at 20°C	density	color	flash point
mineral oil	27.55 mPa.s	0.85	yellow	>100°C
vegetable oil	46.1 mPa.s	0.93	yellow straw	>85°C

3.3 Wettability

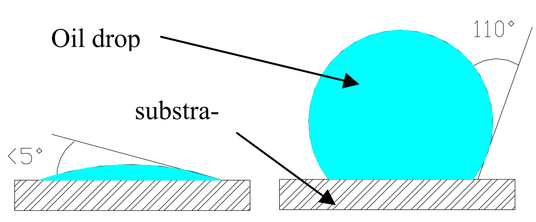


Fig.4 Measurement of contact angle

Samples of formwork walls (5x3 cm) were made by a formwork manufacturer in northern France (Outinord).The affinity of oil to the substrate was assessed by its wetting ability according to surface type and ambient temperature. The value of the contact angle formed by the oil drop on a substrate was determined using DIGIDROP equipment [4]. It consists of a camera, a source of light, a display screen, a plate and a motorized piston. The drop formed by the syringe is deposited on the rising substrate. Following contact between drop and substrate, a photograph is taken. The contact angle is then measured automatically between the drop tangent and the substrate surface. (Fig. 4) A low angle of drop indicates high dampening capacity.

Table 2 Contact angles for mineral and vegetable formulations

Mineral REF	002	004	Vegetal REF	003	005
13.2°	11.3°	9.6°	14.9°	23.6°	16.5°

3.4. Optical microscopy

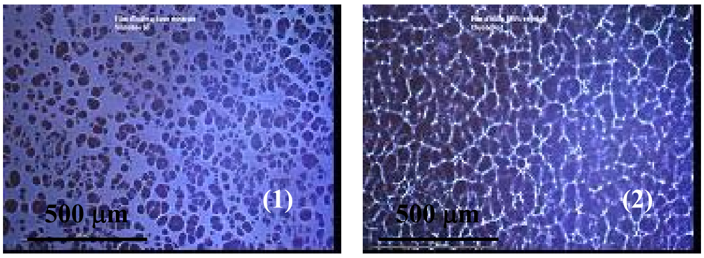


Fig. 5 Film micrographies on steel foil with mineral oil (1) and vegetable oil (2)

To characterize the uniformity of the oil film deposited on the formwork, optical micrographies were carried out. We compared a vegetable oil to a mineral oil (Fig. 5). The structure of the vegetable oil film is more homogeneous, with the mineral film appearing in the form of disjointed droplets. This shows that the substrate covering rate is higher in the case of vegetable ester.

4. Interaction between concrete, release agents and formwork

Wetting agents are generally made of a hydrocarbon chain and a polar or ionic head. The chain has no affinity to the surrounding water molecules. However, the head is solvated and thus hydrophile. This difference confers on surfactants the property of reducing interfacial tension.

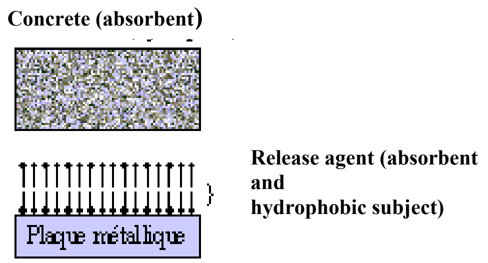


Fig. 6 Schematic representation of a formwork-release agent-concrete interface

Two hypotheses define the organization of the ester molecules at the interface. The typical arrangement is a double layer with orientation of the molecules perpendicular to the formwork and to the concrete (Fig. 6).

But we cannot exclude a more complex organization with long-chain molecules which inter-attract according to the model (Fig. 7). This is the case of structured micro-emulsion.

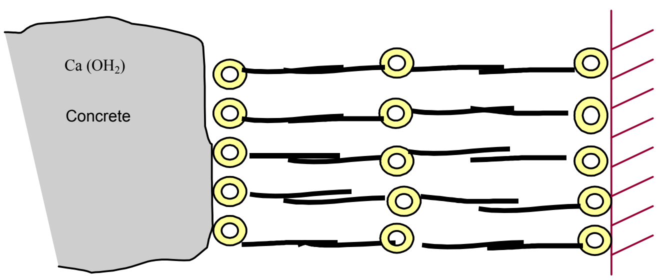


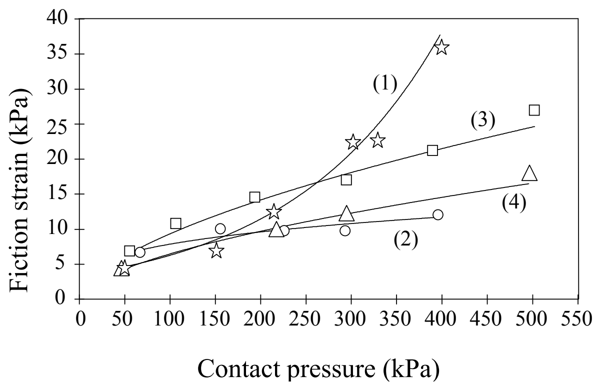
Fig. 7 Schematic representation of a multi-layer arrangement of molecules at the concrete-formwork interface

Three types of vegetable-based formulations (oil from rapeseed and soya) were used in this study: [5] a vegetable oil (V), a semi-vegetable oil blended with a solvent (S), and a water-oil emulsion (E). Most additives are fatty acids, but for the emulsion, anti-corrosion and emulator agents were added (Table 2).

Table 3: Physico-chemical characteristics regarding the formulations

Formulations	S	E	V
Content of surface-active (%)	2.5	2 to 2.2	0
Presence of fatty acid (%)	1	0	0
Active matter concentration (%)	35	1	95
Viscosity to 20°C	4.5	5	22
Flash point (°C)	80	-	185

The behaviour of the three release agents was characterized using a tribometer [6]. Evolution of the dynamic friction stress versus pressure was given for a slip speed of 2.5 mm/s and a roughness Ra of 0.3µm (Fig. 8). The case of the concrete was also studied in order to compare the use and non-use of release agents.



The shape of the curves made it possible to highlight the dominant role of two parameters:

- The presence of surface-active agents is essential for the concrete to be hydrophobic, by emulsifying water on the concrete surface. In the case of a type E emulsion, all of the ester is emulsified, a less favourable outcome than in the case of formulation S.

Figure 8 Evolution of the dynamic friction stress according to the contact pressure (v = 2.5 mm/s, Ra = 0.3 µm):(1) concrete-plate; concrete-oil S-plate;(3) concrete-oil E-plate; (4) concrete-oil V-plate.

- The quantity of deposited active matter is a significant parameter. In contact with calcium oxides, the esters are converted into insoluble carboxylates (soap), which form a hydrophobic film that prevents the concrete from adhering. Conversely, excess active matter disorganizes the orientation of the molecules on the surface and increases viscosity at the interface, which does not promote stress reduction.

Formulation S appeared to generate the lowest friction stress. The "solvent" matrix helps to deposit an uniform quantity of active material adapted to hydrophobation of the concrete. The presence of surface-active agents supplements this process. Formulation V also exhibited low friction stresses, thus giving it a good performance rating.

5. Conclusion

Control and knowledge of the physicochemical properties of release agents are essential to properly understand the phenomena occurring at the formwork-concrete interface. Problems of airholes, chalking and facing colour variations must be explained and controlled. The thickness of the oil film deposited on the formwork will be one of the parameters of our future work.

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