Use of Plasticisers/Strength Enhancers in Ceramic Bodies

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In recent years, the ceramic industry has seen a growing need for bodies with higher levels of green plasticity/strength. In the tiles industry, the latest product developments include large panels and slabs with thicknesses ranging 3–20 mm with widths of more than 1,6 m and lengths of more than 3 m. These slabs are currently shaped using bodies that, in many cases, diverge considerably from the classic ceramic compositions.
The industrial technologies for shaping these ceramic products, by pressing or compaction, display some similar characteristics. During shaping, the ceramic body contains the water quantity (5–6 %) necessary to ensure the success of the operation, but, anyway, the green piece has a certain fragility. This is sometimes incompatible with the dimensions and complexity of the product or with the subsequent handling operations. The drying stage strengthens the piece, increasing its modulus of rupture (MOR) by up to 3 or 4 times with respect to the green MOR value and modifying the surface porosity according to the needs of the subsequent glazing and decoration stages.

The possibility of increasing the dried MOR by introducing temporary film-forming organic polymer-based binders is not a new idea. It is perfectly possible to increase the modulus of rupture by up to 100 % of the initial value or more. The real limitations in industrial applications are economic and, above all, the difficulty of achieving complete combustion of organic substances. The incompatibility between the firing cycle rate and the decomposition rate of organic substances (which include substances already present in the raw materials and those supplied by the additives) leads to the well-known phenomenon of the black core defect.

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There are various reasons why it is useful, if not essential, to have a higher dried MOR to make easier the possibility of:

- producing larger or more complex shaped pieces
- producing thinner pieces
- producing high-thickness slabs with a low specific pressure
- using raw materials that are less valuable, less expensive (with lower plasticity), geographically closer to the manufacturer and by that susceptible to fewer problems in terms of supply and logistics
- producing slabs with limited clay content to get a whitest, vitrified, and translucent body.

Nonetheless, the problem of product green strength remains.

Increasing green strength

For these reasons, the Lamberti researchers asked themselves how they could increase the green mechanical strength of unfired ceramic articles by using binding additives, and, more specifically, plasticizers/binders. The traditional binders act only when water is evaporated while the Lamberti's plasticizers begin to act in the presence of water, exploiting the binding effects of temporarily inhibited organically-modified smectites.
Alongside plasticisers/binders, other products that are being developed and evaluated include special high molecular weight polymers synthesized in an emulsion, which also act in the presence of water, and exploit the binding mechanisms (adsorption, coalescence, and diffusion on the granules surface).

But why is it necessary to increase the product green strength?

Generally speaking, higher product green strength is needed for the same reasons, technical and economical, as higher dried strength is required. This aspect has become particularly important following the development of fully digitalized lines and shaping of large tiles and panels.
From a strictly technical point of view, it is questionable whether it still makes sense to position the dryer immediately after the press. Moving the drying device of the plant to a pre-kiln position would have the advantage of being able to glaze and decorate green products at low temperature, without the need to cool the pieces prior to digital applications.
On the other hand, the chemical and physical conditions of the surface would be considerably modified, especially in terms of green porosity and absorption. In any case, a change of plant layout is feasible, in fact large-extruded or pressed slabs are currently produced according to this model. A higher green strength would certainly help to achieve the expected results.

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Tab. 1 Case history: standard body vs. body with Tenagreen

	Original Standard Body	Body Modified with Tenagreen
Plastic clay [%]	24	8
Other clays [%]	16	31
Total clays [%]	40	39
Fluxes + aggregates [%]	60	61
Tenagreen [%]	0	0,6
Density [g/l]	1750	1810
Percentage water difference	0	–3,5
Green MOR [kg/cm²]	8,2	9,1
Dried MOR [kg/cm²]	35–37	36–39
Saving in total costs of the body formula (including Tenagreen): EUR 2/t		
Saving regarding natural gas consumption: 10–15 %, corresponding to –3,5 % evaporated water		
Production increase: approx 3 %		

Tab. 2 Standard body vs. modified body with semisynthetic Tenagreen

	Standard Formula	Modified Formula with Tenagreen
Tenagreen [%]	0	0,6
Green MOR [kg/cm²]	7,9	9,0
Dried MOR [kg/cm²]	34	40

The Tenagreen system

Lamberti focused on products capable to have a positive effect on both green and dried MOR. The aim was to reproduce the overall effect of adding highly plastic clay systems while using:

- very low dosages without undesirable effects
- a product in a physical form (stable pumpable liquid), that can be easily dosed at any time and at suitably chosen positions within the plant, i.e. in the plunger, in the service tanks of the spray dryer, injected in the feeding pipeline of the spray dryer
- raw materials of natural origin with low environmental impact, and low organic content.

The result was the new developed Tenagreen system for which a patent was applied for.

One particularly interesting case history is that of an Italian ceramic company which has used the new system for more than a year for its entire output. The company produces yearly around 3 Mm² of porcelain tiles, most of which are glazed (along with a small amount of full-body porcelain). The tiles were produced in the formats 30 cm × 60 cm, 60 cm × 60 cm, 45 cm × 90 cm and 60 cm × 120 cm with a thickness of 9–10 mm, while firing cycles ranged from 46 min at a maximum firing temperature of 1215 °C to 54 min at 1220 °C.

The company's goal was to reduce production costs by reformulating the body. This involved reduction of the plastic clay percentage by achieving the previous conditions of green MOR and dried MOR by adding Tenagreen plasticiser/binder. Tab. 1 shows a comparison between the composition and characteristics of the original body vs. those of the modified body.

In the present case, the body reformulation does not include modifications to either the type or percentage of deflocculant used, so the relevant costs have remained unchanged while achieving greater plant efficiency and lower gas consumption.

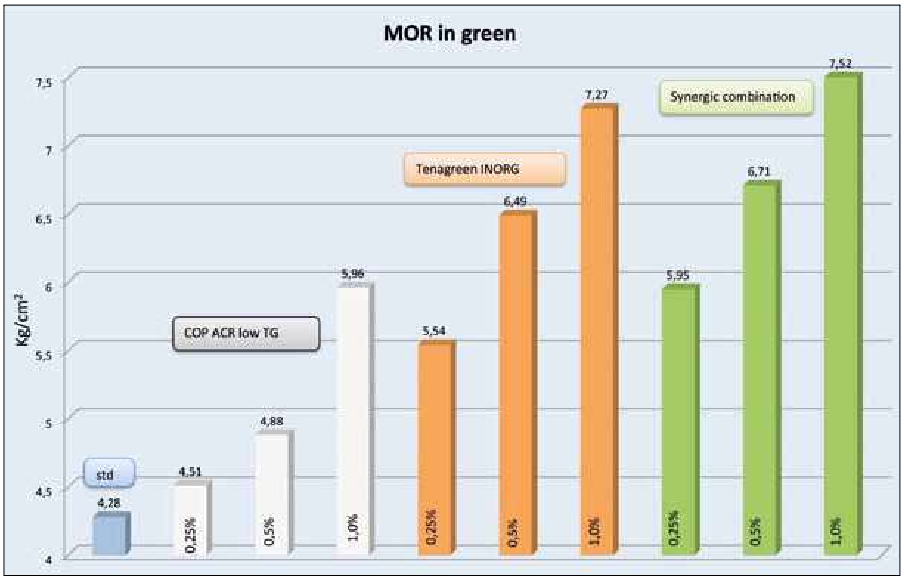

Fig. 1 Tenagreeen inorganic and superplasticiser: experimental results for green MOR

New developments

Lamberti laboratory researchers are currently engaged in improving the Tenagreen rang with the following targets:

- Tenagreen inorganic, which has a total organic content <4 % compared to 40–50 % in a conventional binder and 10–15 % in Tenagreen
- Tenagreen semisynthetic, which contains a portion of synthetic polymers with specific plasticising properties and a wider range of action
- Tenagreen superplasticisers, containing emulsion polymers that display an interesting synergy with the inorganic fraction and decompose much more easier during fast firing cycles.

For the Tenagreen semisynthetic family, the authors can already present results of an industrial case history. In this case, the aim was to keep the ceramic body unchanged while achieving higher green and dried strengths for the production of extremely large glazed porcelain tiles using unconventional pressing. Tab. 2 shows the results after few months of operation while over 500 000 m² have been produced.

As for the Tenagreen inorganic and Tenagreen superplasticiser range, the authors can provide some experimental laboratory results obtained with real standard bodies, but with a low degree of plasticity to further accentuate the differences.

As can be seen in Figs. 1–2, the results are interesting and justify further study both in the laboratory and in industrial applications.

A further area of research of the Lamberti R&D laboratories is that of applying the specific properties of Tenagreen in other sectors. Tests were performed:

- on red bodies, in order to reduce the percentage of higher-plasticity clays which give rise to fluidisation difficulties in wet grinding and black core defect
- on sanitaryware, manufactured by casting, especially at high pressure, in order to increase casting rate (wall thickness formation) and green mechanical strength (to avoid cracking)
- on tableware.

Although only laboratory results are currently available, they are encouraging.

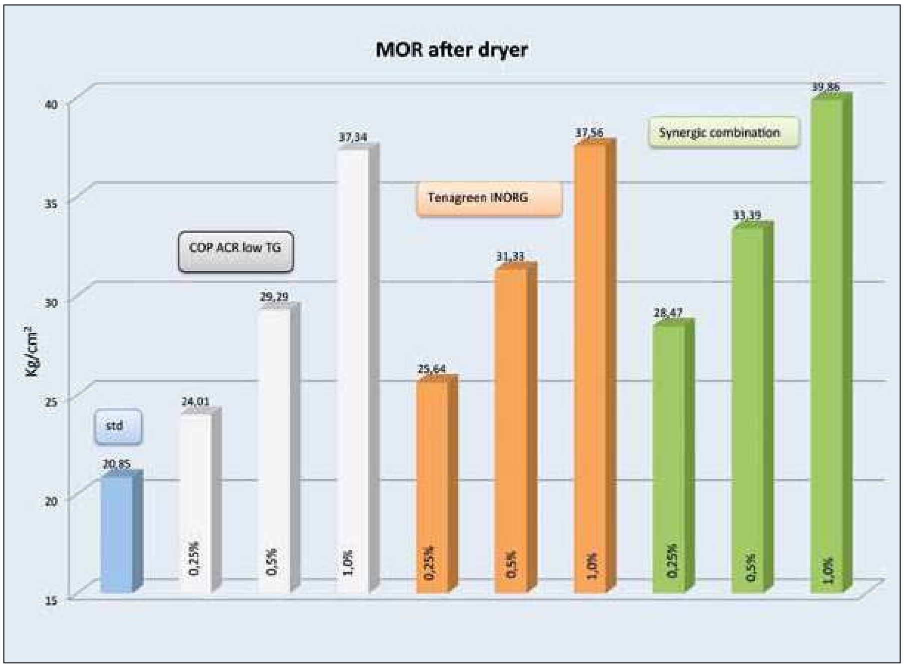

Fig. 2 Tenagreeen inorganic and superplasticiser: experimental results for dried MOR