Plant based chemical admixtures – potentials and effects on the performance of cementitious materials

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Abstract
While today, engineers can choose from a wide range of rheology modifying admixtures, in some parts of the world, these are difficult to access, due to their complex processing. However, alternatives can be bio-based polymers such as polysaccharides from various sources. These are easily accessible all over the world, do not demand for complicated processing, and typically they are more sustainable than many established materials, which are crude oil-based.

The paper presents the effects of acacia gum, cassava starch and the gum of triumpfeta pendrata A. Rich on the rheological performance of cementitious systems. It is shown that acacia gum can be as efficient as polycarboxylate based superplasticisers, cassava starch can reduce the yield stress slightly with little effect on the plastic viscosity, and the gum of triumpfeta pendrata A. Rich increases the thixotropy of cement pastes with plasticizing polymers significantly.

Keywords: Polysaccharides; Rheology; Cement; Chemical admixtures; Bio-based concrete

1 Introduction
In spite of its often rather negative societal perception, there is no better alternative to concrete, due to its relatively low carbon footprint and its global and local availability. But the global consumption of concrete is extremely high, and the demand is increasing [1], which has dramatic consequences for the global climate. Particularly the typically used Portland cement binders produce high amounts of carbon emissions, even under most modern production conditions. Therefore, more innovative, sustainable concrete types need to be developed in the future, which require lower amounts of Portland cement at identical or even enhanced performances.

In order to minimise the carbon emissions from concrete production, parts of the Portland cement binder can be reduced by replacement with more sustainable supplementary cementitious materials (SCMs). Furthermore, the binder in concrete should be used as efficiently as possible. This means, construction components or buildings should ideally contain exactly the amount of binder, which is required to assure the structural integrity and durability, but not more. The incorporation of high-performance chemical admixtures seems to be inevitable to achieve such optimisation. Chemical admixtures can compensate for the changes in workability induced by SCMs, and in parallel they can help to minimise the total water volume, in order to obtain maximum performance of the binder.

Today, superplasticisers have emerged as the most important group of admixtures for concrete. They reduce the water demand and help to use cement most efficiently. Another important group are stabilising agents, which can improve the robustness of the casting process. Flowability and robustness are key specifications for the construction technological challenges of the near future, such as pumping over long distances, casting at extremal climate conditions, or additive manufacturing in highly industrialised processes.

To date, the most crucial developments in the field of cement and concrete technologies took largely place in the industrialised countries of the northern hemisphere, which were also the first countries that applied these materials in construction [2]. Therefore, most globally established

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concrete technologies are based on the raw materials that are available in the industrialised countries. However, in a global dimension, it is often neglected that many regions of the Southern hemisphere do not have these raw materials readily available, for example due to lack of iron ore processing or a chemical industry. The usage of some established materials would thus be economically and ecologically not feasible [3]. Nevertheless, due to the growing demand for infrastructure and housing the construction with concrete is inevitable. Therefore, it becomes necessary to look at local alternatives for established constituents, that can help to protect the climate, produce at low cost, and create new value chains in the respective region. One promising technology for sustainable construction with concrete, which is of highest global relevance, is the usage of calcined clays that can occur in certain regions in abundance [4, 5]. Further binder technologies have been recently presented and discussed in a UNEP report on low carbon cement-based industries [1]. In this context the use of chemical admixtures for sustainable construction is also discussed.

Besides the aforementioned approaches, further strategies for sustainable construction exist, which may have a less relevant global impact but have a tremendous impact in certain regions. 60% of the global unused arable land areas are located in Africa, 30% in South America, while the entire rest of the world shares the complementary 10% [6]. Hence, agriculture is an immanently important economic driver in South America and Africa with large growth potential. It is therefore reasonable to take a closer look on possible uses of bio-based waste products as construction constituents in countries with large agricultural sector:

- Polysaccharides can be excellent precursors for performance enhancing chemical admixtures, that can help reducing the cement in concrete and using cement more efficiently [7-11].
- Various ashes of agricultural waste products exhibit pozzolanic or hydraulic properties, provided they are processed adequately. They can, thus, replace Portland cement clinker [12-16].
- Eventually, plant-based components can be used as aggregates or fibres to enhance the physical properties or the ductile behaviour of concrete components [17-19].

Future oriented, sustainable binder systems and the implementation of concrete technological high-performance applications inevitably demands for construction chemicals. Due to their scarcity in most regions of the global South without complex and expensive supply chains, it is necessary to find local solutions. Some of these possible local alternatives and their potentials for high-performance applications are discussed in the present paper.

2 Experimental programme

Experiments with varied dosages of the gums were conducted in order to observe stiffening and liquefying effects. The reference mixture only contained 600 g of ordinary Portland cement (CEM I 42.5 R) and 282 g of water. The acacia gums were obtained from South Africa and Sudan. The gums were brownish, blurred and with vegetable enclosures, and yellowish, transparent and pure, respectively. They were firstly dissolved in tap water at room temperatures, secondly coarse impurities were filtered off, and at last, the liquid was dried and ground. The gum of the triumfetta pendrata A. Rich was firstly dissolved from the bark in tap water, and then treated like the acacia gums. The cassava starch was dissolved at 70 °C in tap water. The residual coarse particles were then sieved off, and eventually the pulp was dried and ground to obtain the admixture.

Rheological properties were determined with a Couette type rheometer (Schleibinger Viskomat NT). In order to observe the effect of varied polysaccharide dosages, a stirrer for cement paste was used that can ensure that no segregation takes place during the shearing. The measurement profile can be seen in Fig. 1. During the two velocity steps of 240 and 120 rpm in the first 8 minutes, no admixture was in the system. After 8 minutes, every 4 minutes the dosage of admixture was increased. The rotational velocity of 240 rpm guarantees a rapid homogenization. The measurement at constant shear velocity cannot provide information on the yield stress and the plastic viscosity, but the two velocity profiles between 0 and 8, and 32 and 40 minutes provide information on changed yield stress and plastic viscosity without and in the presence of the highest added admixture dosage, respectively, under the assumption that the material follows largely a Bingham function. In total, the measurement profile lasts for 40 minutes. In preliminary experiments, it was shown that the measured torque remains largely constant over the course of this time.

Without addition of admixtures, the torques measured for the reference mixtures were approximately 75 Nmm, so that within the measurement range from 0 to 300 Nmm, both, stiffening and liquefying effects could be effectively indicated by increasing or reduced torque values.

For further measurement, a double-gap grid cell was used. In total three consecutive ramp profiles over a time of 70 minutes were adjusted as shown in Fig. 2.

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3 Results and Discussion

3.1 Acacia gum as stabilising agent and plasticiser

Research of Mbugua et al. showed that acacia gum from the karroo semi-desert exhibits liquefying properties [20-22]. This could be confirmed for the two types of acacia gum compared to a lignosulfonate and two commercial polycarboxylic (PCE) superplasticisers, as shown in Fig. 3. Both gums initially cause a stiffening effect initially, then, at further addition a plastifying effect can be observed. This liquefying effect is significantly stronger for the gum from Sudan, while the stiffening effect is more prominent for the karroo gum. At higher dosages, the effect of the gum from Sudan compares to the effect of the pre-cast PCE, while the effect of the karroo gum compares to lignosulfonate and ready-mix PCE.

The different stiffening and plastifying effects of the acacia gums are assumably based on their different chemical compositions. Gums from Sudan contain higher fractions of glucuronic acid than gums from the karroo, thus the gums from Sudan contain more anionic charges, causing a more effective adsorption on cementitious surfaces and hydration phases.

3.2 Cassava starch as stabilising agent or plasticiser

Cassava is an agricultural crop of the Southern hemisphere. Various researchers have shown that cassava peel ashes (CPA) qualify as SCM [7, 12, 13]. The starch of cassava contains about 80% amyllopectin and 20% amylose, which is very similar to potato starch, which has already been used as concrete admixture [23-25] with plastifying and stiffening effect [8, 26-28].

Applying the profile presented in Fig. 1, it could be found that with increasing dosage, hydroxypropylated potato starch causes an increasing torque value, while cassava starch rather caused a slight torque reduction with increasing dosage. Fig. 4 shows the respective yield torques and the slopes of cement pastes without and in the presence of the two starch types. It can be observed that the potato starch does not significantly affect the yield torque, but strongly the slope of the torque curve, indicating that potato starch rather affects plastic viscosity without significant effect on yield stress. The influence of the cassava starch is different. Here, the similar slope indicates no strong effect on plastic viscosity, but the curve’s parallel shift indicates an effect on the yield stress, which explains the plastifying effect of the cassava starch.

However, it is important to note that the effect of starch in cementitious systems is complex and depends upon the modification of the starch as well [8, 29-31]. Due to the high versatility of potato starch, thus, the potentials of cassava starch for the chemical industry is also very promising.

3.3 Gum of triumfetta pendrata A. Rich as thixotropy agent

The gum of the triumfetta pendrata A. Rich is typically used as food ingredient for a dish called nkui, which exhibits an extremely cohesive consistency. It can also be used to enhance the thixotropic properties of fresh concrete. In conjunction with additive manufacturing processes, the issue of thixotropy gains increasingly importance. Former studies have shown that cementitious systems could be effectively stabilised with this gum [32, 33]. The addition of supplementary plasticising polymers could furthermore generate excellent flow properties, which at rest, are

Figure 2. Experimental setup for the investigations with the double gap basket cell.

Figure 3. Torque evolution depending on admixture dosage.

Figure 4. Bingham approximations for the two-step measurements.
followed by a rapid structural build-up, which is largely fully thixotropic, thus reversible. Fig. 5 shows the hysteresis loops of the ramps shown in Fig. 2 for cement pastes at a w/c of 0.3, gum dosage of 0.08% and a dosage of 0.35% of a plasticizing polymer, both dosages related to the weight of cement.

The hysteresis is most prominent for the first ramp. Although the hysteresis is less strong for the second and the third ramp, it remains significant, indicating that the thixotropic effect is reduced with repeated shear load or time, but can be maintained.

Since in industrial processes repeated shear loads are typically not necessary after casting, the gum of triumfetta pendrata A. Rich can be an interesting chemical admixture. However, its effect needs better understanding, and further research is required.

Figure 5. Hysteresis loops of cement paste in the presence of plasticiser and the gum of triumfetta pendrata A. Rich.

4 Summary and Conclusion

It was shown that a variety of bio-based polysaccharides can potentially be used as environmentally friendly chemical admixtures in regions where the accessibility of established construction chemical admixtures is limited.

- Acacia gum can act as plasticiser.
- Cassava starch can be stabilising agent and plastifying agent.
- The gum of triumfetta pendrata A. Rich can incorporate strong thixotropic effects into cementitious systems.

The investigated polysaccharides are easily available in many regions of the Southern hemisphere at low cost. Although the chemicals are partly used as food consistency modifiers, they are not major source of carbohydrates, thus, causing no conflict with global nutrition demand. While the gums of acacia and triumfetta pendrata A. Rich need to be harvested directly, cassava starch can even be obtained from the unused waste residues of food processing.

Eventually, polysaccharides can be excellent concrete technological admixtures, which are very versatile. Ongoing research has to focus more on their effects in cementitious systems as well as in synergy with additional polymers.

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