

NANOSIZED CELLULOSE FIBRILS– A NEW GENERATION STABILIZER FOR CONCRETE AND GROUTS

**JAN-ERIK TEIRFOLK, ANTTI LAUKKANEN, MARKKU LEIVO,
HANNELE KUOSA, TAPIO VEHMAS**

Abstract

Cellulose is the most abundant biopolymer in nature. It gives plants and trees their defined shapes and structures. The basic structural element of a wood fiber is called an elementary fibril. The length of a fibril is several micrometres, while the diameter varies from 4 nm to 200 nm. In UPM Biofibrils products, these nanosized cellulose fibrils and fibril bundles, have been separated and purified from wood pulp by proprietary process. After the fibrils have been fully separated, the product forms highly viscous dispersions in water. UPM Biofibrils hydrogels are shear thinning and viscoplastic materials which have remarkably high zero shear viscosity and yield stress. Thus, the product can be utilised as an efficient stabiliser for various heterogeneous systems. UPM Biofibrils works as an efficient stabiliser in concrete and grouts where low viscosity and a thixotropic rheology in combination with controlled yield stress are required.

Biofibrils has shown excellent properties in stabilizing self-compacting concrete (SCC) mixtures. UPM Biofibrils as an admixture in SCC reduces aggregate settlement and water bleeding. Addition of a small amount (in order of 0.05% dry on dry cement) of UPM Biofibrils gives the mixes a high yield stress and a considerably low viscosity with thixotropic nature. This gives a new possibility to increase the robustness of SCC while enabling less use of cement and additional fine material.

In addition to SCC application, UPM Biofibrils can be utilized also in rock injection grout formulations, where good penetrability, stability and low water bleeding are the main requirements. By adding UPM Biofibrils to grouts water bleeding is essentially lowered and stability of grouts is increased. This allows the use of higher w/c-ratio compared to reference. Penetrability will also be adequate due to the shear thinning behavior of fibrils. Low viscosity under shear allows better penetrability in pressure injections; while still a high enough yield stress gives high stability and low leakage after the injection.

Keywords

Biofibrils, workability, stability, segregation, self-compacting concrete, rock injection

Biographical notes

Jan-Erik Teirfolk, Lic.Sc. (Tech), Senior Advisor at UPM Corporation

Antti Laukkanen, PhD (Chem), Development Manager at UPM Corporation

Markku Leivo, D.Sc. (Tech) Principal Scientist at Technical Research Institute of Finland

Hannele Kuosa, M.Sc. (Tech) Research Scientist Technical Research Institute of Finland

Tapio Vehmas, M.Sc. (Tech) Research Scientist Technical Research Institute of Finland

Introduction

Cellulose is the most abundant biopolymer in nature. It gives plants and trees their defined shapes and structures. The most common form of commercial cellulose is wood fibers used for the manufacturing of e.g. paper and board. The basic structural element of a wood fiber is called an elementary fibril and its size is in the nano range. The length of a fibril is several micrometers while the diameter varies from 4 to 200 nm. In UPM Biofibrils products, these nanosized cellulose fibrils and fibril bundles have been separated and purified from wood pulp by a proprietary process. After the fibrils have been fully separated, they form highly viscous dispersions in water due to their extremely high surface area and hydrogen bonding capability. About 20% of the atoms in a fibril are located on the surface, where they are available for forming hydrogen bond interaction with the surrounding water molecules. This leads to a unique functionality as a suspension aid and rheology control agent. UPM Biofibrils are produced from renewable raw material, namely wood from sustainably-managed forests.

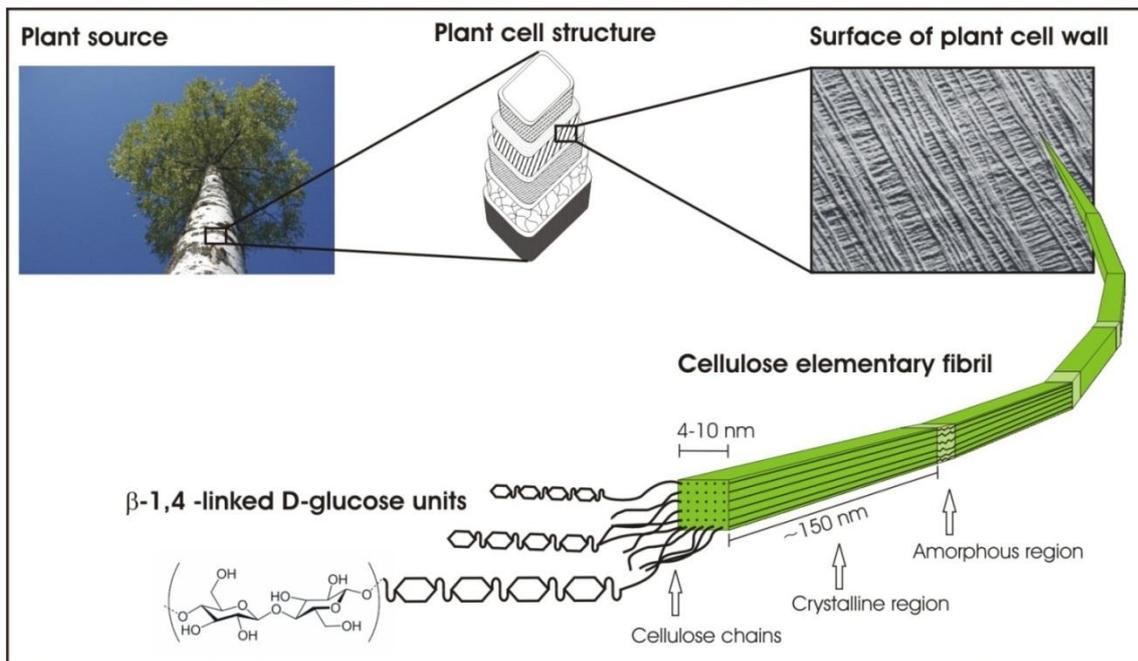


Figure 1. A plant cell wall is partially composed of well organized cellulose fibrils. These nano-sized fibers are composed of aligned β -D-glucopyranose polysaccharide chains, which form cellulose I crystals where parallel chains are intermolecularly hydrogen bonded.

UPM Biofibrils can be described as a collection of isolated cellulose fibrils, or fibril bundles. The length of a fibril is several micrometers while the diameter varies from 4 to 200 nm. Figure 2 shows an electron microscope picture of the fibrils.

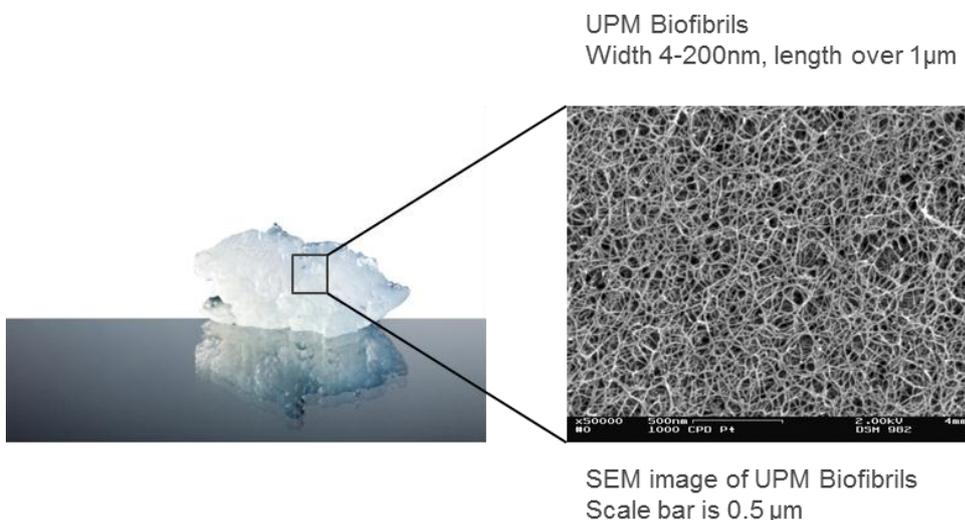


Figure 2. Biofibrils gel structure.

Rheological properties

Biofibrils is a very efficient rheology modifying agent for aqueous systems. It forms a strong hydrogel already at low concentrations, typically starting at 0.1 wt-%. Biofibrils hydrogels are shear thinning and viscoplastic materials. The hydrogels also have a remarkable high zero shear viscosity and yield stress. Thus, the fibrils can be utilized as an efficient stabilizer of various heterogeneous systems. Biofibrils hydrogels are relatively inert to ionic strength and pH changes.

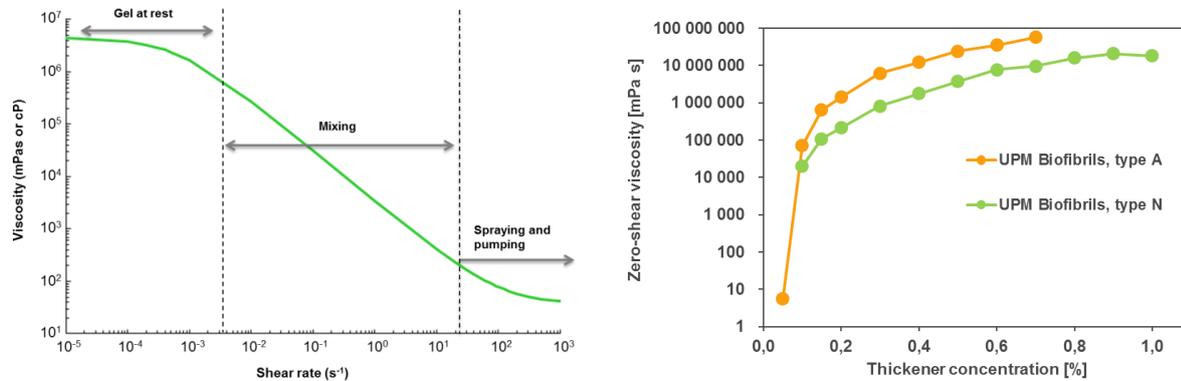


Figure 3. Typical flow curve for a 0.5% Biofibrils dispersion and zero-shear viscosity as a function of concentration.

UPM Biofibrils in self-compacting concrete

Self-compacting concretes (SCC) have shown great promise in their usability in various casting processes. The most important property of self-compacting concrete is the ability to fill all parts of the form work and the reinforcing constructions without applied vibration. Thus the concrete needs to have a suitable low viscosity for flowability and preferentially a thixotropic rheology. If this is achieved by increasing the water to cement ratio, severe problems with water bleeding and aggregate settling will occur leading to a construction with inferior properties.

Adding a small amount of Biofibrils to SCC mixes results a high yield stress and a considerably low viscosity with thixotropic nature. This effect enables a new way to stabilize SCC by modifying only the mixes' yield stress value without affecting the plastic viscosity as described in Figure 4 for a Biofibril stabilized mortar. Plastic viscosity of Biofibrils mortars was lowered with water addition and yield stress was restored with Biofibrils, resulting a total lower plastic viscosity and higher yield stress. Biofibrils stabilized mortars were more flowable in shear speeds over 60 1/s and more stable in shear speeds under 60 1/s. This gives a new possibility to increase the robustness of SCC and enables less use of cement and additional fine material.

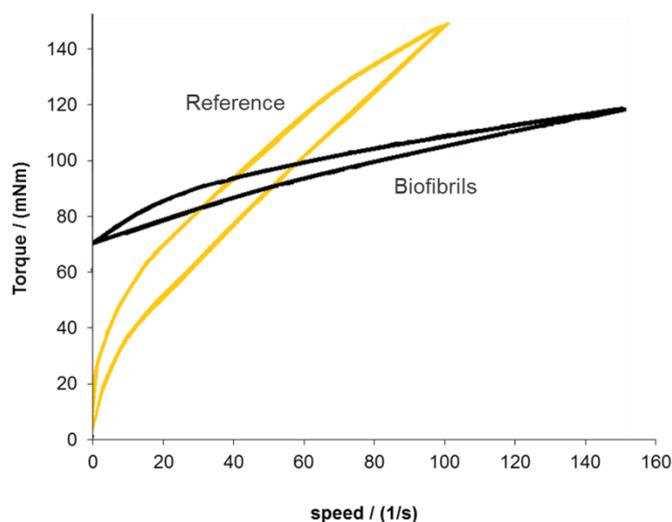


Figure 4. Rheology of reference and Biofibrils stabilized mortars. Mortars had identical Haegermann flow value.

Adding Biofibrils for the purpose of increasing the yield value for a SCC mixture greatly diminishes the segregation of aggregate particles as well as water bleeding (Figure 5.)



Figure 5. Segregation and water bleeding test with SCC using UPM Biofibrils

Another way to demonstrate the segregation control is by way of optical thin section studies on hardened concrete or mortar. In Figure 6, optical thin sections are presented for hardened concrete samples for reference and for a sample with UPM Biofibrils.

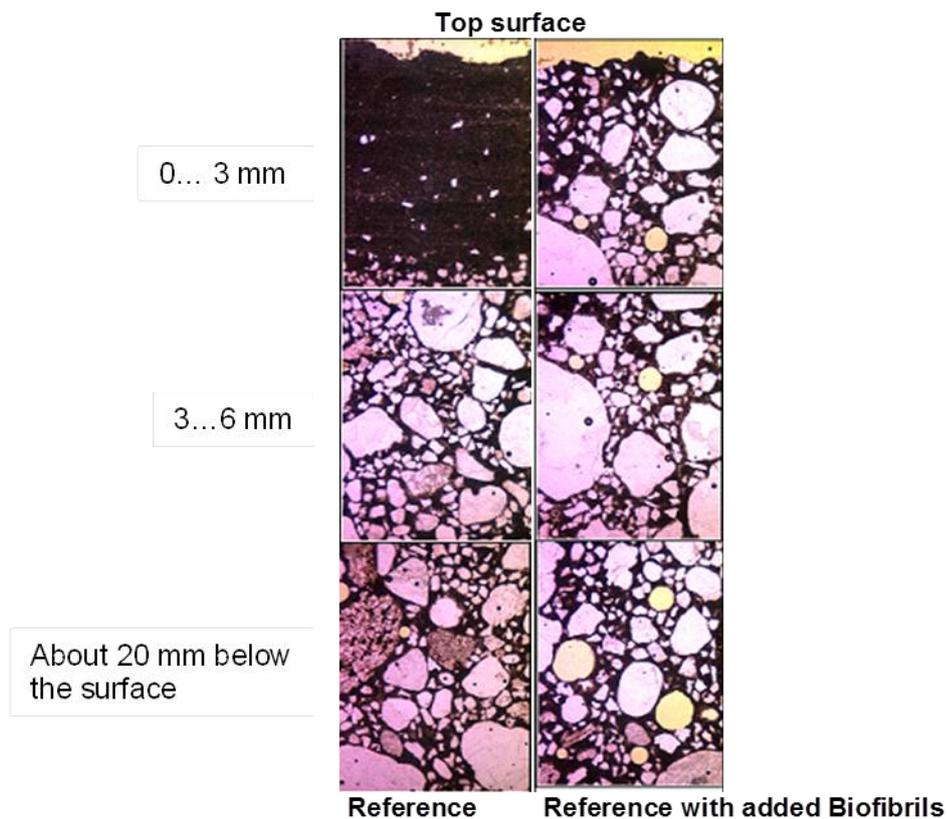


Figure 6. Optical thin sections of hardened concrete.

In the mix design, the robustness of SCC has to be evaluated properly. This means that there must exist test results on the effect of water content variation (for instance $\pm 5\%$) on workability and segregation. These common SCC testing methods can be used for robustness evaluation and based on chosen limits, the operational window for water content variation, i.e. the robustness can be determined. In Figure 7 the robustness evaluation of a SCC mix containing Biofibrils is presented using slump flow (550 mm) and bleeding (1.5 %) values as criterions.

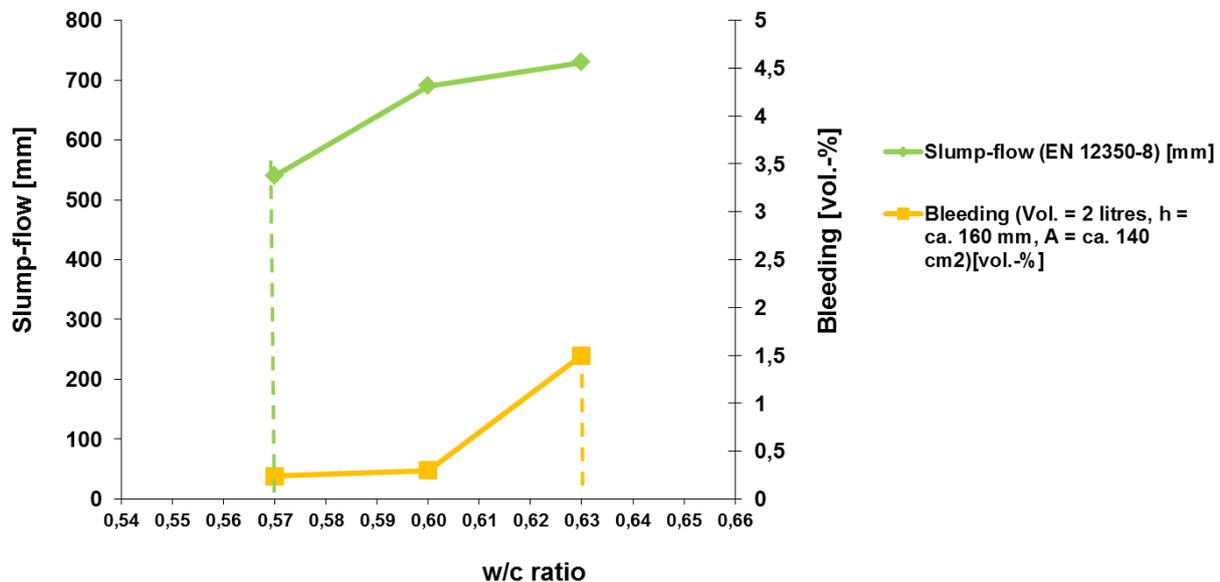


Figure 7. Robustness of SCC containing Biofibrils.

It was found that adding Biofibrils is an efficient way to enhance the robustness of SCC. The needed level of dosage is remarkably low, typically 0.05 – 0.01% dry on dry cement.

UPM Biofibrils in rock injection formulations

Good penetrability, stability and low water bleeding are the main requirements for rock injection grouts. These demands are due to the fact that good penetration and stability are the most affecting properties for rock water tightness. Penetrability is influenced by grout and cement grain size distribution and also by grout rheology, i.e. yield value and viscosity. Good stability is also needed for good penetrability and low bleeding is needed to maintain the grout volume after injection. It is also necessary to have a grout that will not leak easily out of rock fissures and injection holes after injection. A high enough grout yield value will control leaking. The main mix design variables affecting grout properties are cement type and especially the cement grain size distribution, water/cement-ratio (w/c), additives and admixtures such as superplasticizer and setting accelerator. Efficient high-shear type mixing is needed to achieve good grout properties.

By adding Biofibrils, water bleeding is considerably lowered and viscosity, as measured by Flow cone (EN 14117), is higher. This means that the grout water content and thus the w/c-ratio can be higher and still good quality and stable grout can be obtained. This also means, that less cement (kg/m^3) is needed. Higher w/c and low viscosity means potentially better penetrability during pressure injection. Still a high enough grout yield value, induced by Biofibrils, gives high stability and low leakage after the injection.

Biofibrils can be used with various kinds of cements. With normal graded cements ($d_{95} < 128 \mu\text{m}$) w/c can be e.g. 1.00 instead of 0.75. This means, that ca. $180 \text{ kg}/\text{m}^3$ less cement is needed. In Figure 8, bleeding and Marsh cone viscosity are presented for grouts containing different amounts of Biofibrils and w/c 1.00. Reference grouts are presented with w/c ranging from 0.50 to 1.00.

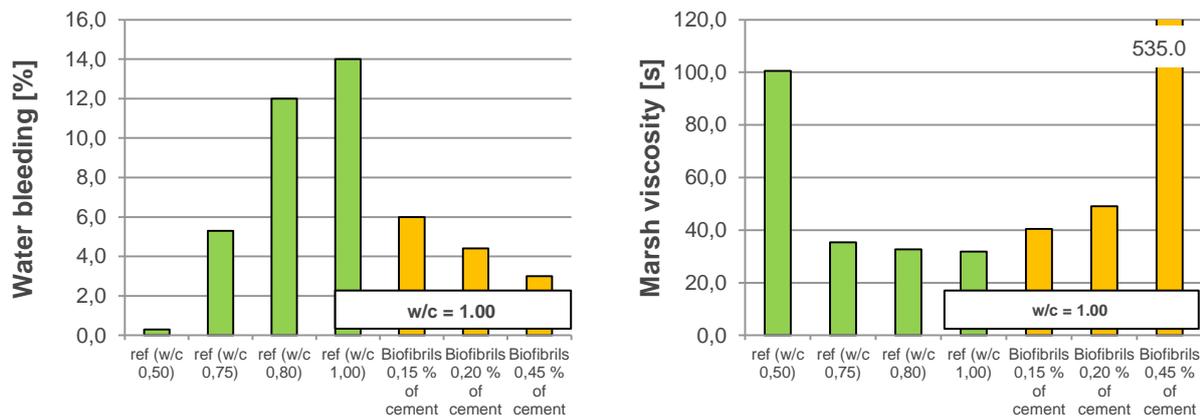


Figure 8. Water bleeding (2 h) and Marsh cone viscosity for normal graded cement based grouts.

Filtration stability as measured according to EN 14497 is presented in Figure 9. For normal graded cements there are no large differences between the grouts when the w/c is over 0.80 and when filtration stability is measured with mesh sizes 200 μm , 300 μm and 400 μm .

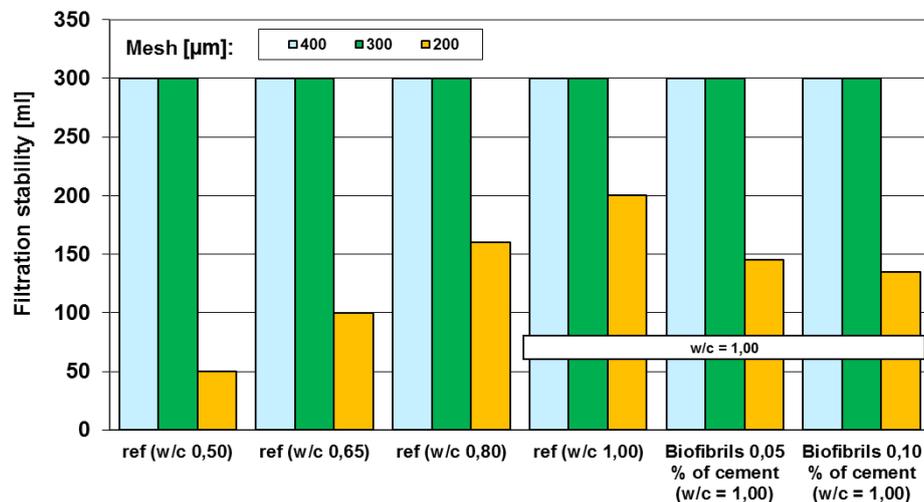


Figure 9. Filtration stability as measured according to EN 14497.

Also with microcements ($d_{95} < 20 \mu\text{m}$), comparable reference grouts needed more cement, i.e. lower w/c, when low bleeding and comparable viscosity are the criteria. A reference grout with w/c 1.00 can be replaced with a grout having a w/c 1.50 when Biofibrils is added. Figure 10. This means, that ca. 210 kg/m^3 less cement ($d_{95} < 20 \mu\text{m}$) is needed.

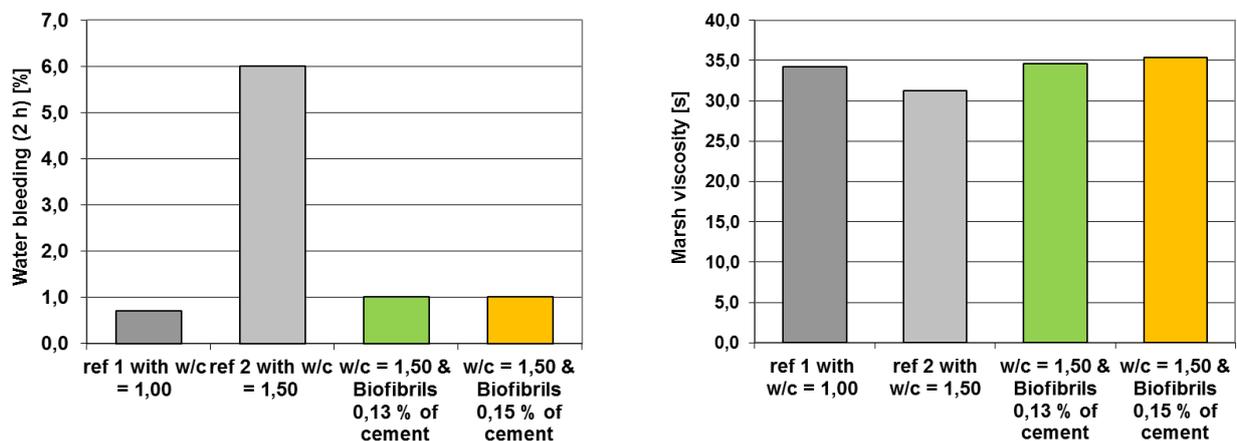


Figure 10. Water bleeding (2 h) and Marsh cone viscosity for CEM 650-grouts.

Summary and conclusions

Nanosized cellulose fibrils are novel bio-based materials that show exceptional properties in various aqueous formulations. When dispersed in water, the fibrils form a strong hydrogel, which has a remarkable high yield stress and zero shear viscosity. The properties can be utilized in concrete and mortar formulations to improve stability and to prevent segregation of water and aggregates.

In SCC formulations, addition of a small amount (in order of 0.05% dry on dry cement) of UPM Biofibrils, gives the mixes a high yield stress and a considerably low viscosity with thixotropic nature. This gives a new possibility to increase the robustness of SCC while enabling less use of cement and additional fine material.

In injection grout formulations, UPM Biofibrils reduce water bleeding and stability of grouts is increased. This allows the use of higher w/c-ratio compared to conventional mixes. Penetrability will also be adequate due to the shear thinning behavior of fibrils. Low viscosity under shear allows better penetrability in pressure injections; while still a high enough yield stress gives high stability and low leakage after the injection.

References

- Klemm D. et al. *Angewandte Chemie*, **2011**, *50*. 5438–5466. Nanocelluloses: A New Family of Nature-Based Materials.
- EN 14497 + AC. 2005. Products and systems for the protection and repair of concrete structures. Test methods. Determination of the filtration stability. 12 p.
- EN 14117. 2005. Products and systems for the protection and repair of concrete structures - Test methods - Determination of time of efflux of cementitious injection products. 7 p.
- EN 12350-8. Testing fresh concrete. Self-compacting concrete. Slump-flow test. 14 p.
- Kuosa, H. 2011. High water-cement ratio SCC robustness with novel cellulose based admixture. Proceedings of XXI Nordic Concrete Research Symposium, Hämeenlinna, Finland, 2011, p. 69 – 72.
- Vehmas, T. & Leivo, M. 2011. A novel cellulose based stabilizing admixture for self-compacting concrete. Proceedings of XXI Nordic Concrete Research Symposium, Hämeenlinna, Finland, 2011, p. 281 – 285.