Abstract

Methyl Cellulose and its derivatives are water-soluble polymers used since decades in modern drymix mortars to retain water and to control rheology. The type and level of substitution as well as the molecular weight of these polymers have a strong impact on the application properties as well as the final strength of the mortar. This article will give a perspective on the structure of cellulose ether molecules and how they can be designed to meet the requirements of the specific mortar application.

Introduction

Drymix mortars are still gaining worldwide acceptance in the construction market due to their specific performance profiles, ease of preparation, high quality and limited waste generation. Cellulose ethers are water soluble polymers which are a key enabler for drymix mortars as they provide water retention, rheology control and ensure high strength of the mortars after cure. The numerous applications for drymix mortars require that the additives in the formulation are selected based on the specific performance profile. Different sub segments and performance classes of i.e. cement based tile adhesive further contribute to the large number of different products in the market. Cement, Sand and other fillers are mainly from local sources. These are the reasons why many drymix mortar products need tailored additive packages in order to be competitive and meet the respective norms. Achieving the high performance requirements for drymix mortars is only possible with a profound understanding of the structure property relationships of cellulose ethers and their interaction with other formulation ingredients. This paper will give an overview of the structural elements of cellulose ethers and their impact on the rheology of aqueous solutions, the rheology of the fresh mortars and the interaction with cement.
Cellulose Ether Properties

Cellulose is the most abundant natural polymer. It forms the backbone of a class of water soluble polymers called cellulose ethers. Cellulose, due to its strong intramolecular bonds is water insoluble. Only after activation with caustic soda and methyl- and hydroxyalkyl substitution the internal crystallinity is broken up and the polymer chains become water soluble. Hydroxyethyl- and hydroxypropyl methyl cellulose are the preferred cellulose ethers in drymix mortars.

The anhydroglucose unit of cellulose polymer has three free OH-groups which can react with substituents. The degree of substitution (DS) of methyl groups is typically in the range of 1.4 – 1.9 whereas hydroxyethyl-(HEO) or hydroxypropyl (HPO) substituents are present in much lower amounts. Their molecular substitution level (MS) varies normally between 0.1 and 0.4. A HEO MS of 0.2 indicates that only every fifth anhydroglucose unit carries this substituent on an average.

This possibility to modify the cellulose polymer results in a number of cellulose ether products defined by their substitution pattern. The substitution level has a strong impact on rheology, interfacial activity and thermogellation properties.

The molecular weight of the cellulose ether is mainly controlled by the molecular weight of the raw material being used in the process. Wood pulp or cotton linters, in the case of very high viscous products are typically being used. The molecular weight is normally not determined. Instead, the viscosity of a 2 % aqueous solution is used as a quality control measure, assuming that the molecular weight is directly correlated to it.

Aqueous Solution Properties

We studied the viscosity enhancing effect of cellulose ethers in aqueous solutions and its evolution around the so-called overlapping concentration[^1]. With increasing dosage the viscosity of an aqueous solution of a cellulose ether increases strongly. From a certain concentration onwards the increase becomes even more pronounced as can be seen in Figure 2. Concentration-dependent measurements of the hydrodynamic diameter of CE showed that large associates were formed above a critical overlapping concentration[^2].

Figure 3 illustrates the measured viscosity of a HEMC solution, plotted as a function of the shear rate for various dosages. HEMC strongly increases the viscosity of distilled water with increasing dosage. The solution viscosity mostly remains Newtonian below the critical concentration \(c^*\). We observe the appearance of a slightly shear thinning behavior above \(c^*\) (0.6 % of polymer in water).

[^1]: Overlapping concentration
[^2]: Critical concentration
When applying increasing shear force on a CE solution viscosity drops as a result of shear thinning behavior. The Cross model can be applied to quantify the shear thinning behavior and to identify the zero shear viscosity. We investigated a number of different cellulose ethers at a dosage of 1.5\%, clearly in the region beyond the critical concentration (Figure 4)\(^3\).

The shear dependent viscosity can be expressed by the following equation, described in literature as the Cross model\(^4\).

\[
\eta(\dot{\gamma}) = \frac{\eta_0}{1 + (\dot{\gamma}/\dot{\gamma}_r)^{1-n}}
\]

The highest solution viscosity after extrapolation to zero shear force in called zero shear viscosity \(\eta_0\). The relaxation time \(\tau\) indicates the beginning of the shear thinning at \(\dot{\gamma} = \dot{\gamma}_r\). And the power law exponent \(1-n\) is equivalent to the slope of the shear thinning curve. When plotting the molecular weight of the cellulose ethers against zero shear viscosity \(\eta_0\) and the power law exponent \(1-n\) the strong impact of polymer chain length on viscosity and shear thinning behavior becomes obvious (Figure 5).

Zero shear viscosity is a measure for the viscosity of the aqueous solution in the non-sheared state as it is present as the interstitial fluid in cementitious mortars. The stronger shear thinning of higher molecular weight polymer solutions is in line with the expectations.

Hydroxyalkyl methylcellulose products are polymers with hydrophilic (i.e. OH-Groups) and hydrophobic (i.e. Methyl-groups) substituents. As a consequence solutions of these polymers in water are surface active; their surface tension is lower as compared to pure water. When plotting the surface tension of 0.01\% solutions against the methyl DS and hydroxyalkyl MS it became obvious that interfacial activity depends on both substituents. With increasing substitution levels (DS and MS) the surface activity of the cellulose ether solution increases (Figure 6).
Excellent water retention properties are a prerequisite for the mortar to develop strength during curing. This is particularly important on strong absorbing substrate. The cellulose ether in the drymix formulation quickly solubilizes when water is added. It strongly thickens the mobile aqueous phase and ensures that the water remains in the mortar layer for some hours and is available for the hydrolytic curing process of the inorganic binders such as cement or gypsum.

With increasing molecular weight of CE the viscosity of the interstitial aqueous phase increases and water retention as a consequence improves. In order to achieve the same water retention CE with high molecular weight can be used at lower dosage, thus saving formulation cost (Figure 7).

![Figure 7: Cellulose ether dosage as a function of molecular weight in a cement mortar at a fixed water retention of 95%](image)

We have adjusted the cellulose ether dosage to obtain the desired water retention of 95 ± 1%. Depending on the viscosity of the cellulose ether the addition levels ranged from 0.095% to 0.230%.

Effective dosage in the interstitial solution could be lower than expected, because the polymer is partially adsorbed on the surface of cement grains. The lower the adsorption rate of the CE the more CE will be present, and increase water retention. Highly substituted cellulose ether show better water retention in mortars at a given molecular weight. Only in cement based tile adhesives we are reaching the critical overlapping concentration. In mortars and renders the CE dosage is in most cases below the overlapping concentration. Below overlapping concentration, water retention can be seen as a biphasic filtration process and rheological properties of the interstitial solution dictate the ability of water to resist migration under a pressure gradient. Above the overlapping concentration, the CE aggregates start to dominate water retention as they plug the pores in the mortar and prevent the free mobility of the aqueous phase.

Besides providing water retention the cellulose ethers in mortars also have an impact on air entrainment and fresh mortar density as they are surface active. The surface activities of cellulose ether correlate well with methyl DS and hydroxyalkyl MS. Higher substitution increases the surface activity as the intramolecular polarity of the polymer increases. This effect results in reduced fresh mortar density. We found increased air entrainment with high viscous CE and high level of hydroxyalkyl substitution (Figure 8). There must also be a rheological component to stabilize air entrainment as the dependency on molecular weight suggests.

![Figure 8: Fresh mortar density as a function of CE molecular weight and substitution level](image)

Measuring the rheology of a complex slurry such as a cement mortar can be done with various equipment. The flow table is commonly used and is considered a robust method which is easy to use. But the amount of scientific information is limited. The rotating T-Spindel – Helipath of a Brookfield rheometer provides a simple tool and allows information about shear profile as the shear rate can be adjusted. Oscillation Rheology is a sophisticated method to understand complex multi-phase systems like cement renders. The rather expensive equipment also requires complicated sample preparation. The information on mortar rheology based on this test method allows complete structure/property understanding.

Workability of mortars can only be a subjective measure. Ratings on ease of spread, stickiness and standing strength have to be considered with the necessary skepticism.

Cellulose Ethers are retarding the cement setting as they adsorb on the clinker phases. The hydration of the C3S phase is delayed in the presence of cellulose ethers. We could also demonstrate that with increasing substitution the cement setting retardation becomes less pronounced (Figure 9).
The peak temperature of the cement setting reaction is achieved after about 12 hours. The time to reach the peak temperature correlates well with the methyl degree of substitution (DS). Higher substitution results in less retardation. High substitution also reduces the number of unsubstituted anhydroglucose units (AGU) along the cellulose ether backbone. When we plot the time to reach maximum temperature against the AGU percentage of the cellulose ethers we can achieve even better correlation.

The cement setting rate competes with the loss of water in the mortar by adsorption to the substrate or by evaporation. Strongly retarded formulations will dry out before cement can completely set resulting in reduced strength. Therefore the level of methyl substitution has a strong correlation with bond strength after standard ageing conditions.

The reason why molecular weight of the cellulose ether reduces the standard bond strength can only be explained by the higher consistency of the mortar which has a negative impact on the wetting of the backside of the tile. All formulations have been formulated with the same amount of water. The methyl degree of substitution increases bond strength as its impact on the setting retardation of cement is less pronounced.

The macroscopic properties of cellulose ethers also play an important role in drymix mortar application. The particle size of the powder controls its dissolution rate. In spray plaster application the cellulose ether only has 10 – 20 sec time to dissolve before the plaster is projected to the wall. At this moment the cellulose ether has to be completely hydrolyzed to that it can unfold its full water retention capacity. The finer the cellulose ether powder is the faster it will dissolve. Spray plaster application therefore requires very fine powder quality. Coarse particles simply do not dissolve fast enough to be able to contribute to water retention.

However, there are also some limitations to the fineness of the CE powder. Mainly in gypsum based spray plaster the CE often dissolves too quickly and prevents the complete wetting of the gypsum powder. As a result the gypsum mortar on the wall contains high amounts of dry gypsum lumps, which cause unpleasant surface defects on the gypsum surface after the first leveling step. Designed particle morphology has helped us to resolve this problem by optimizing the CE particle shape and adjust the rate of dissolution\[7\]. The CE powder is more spherical and has a lower specific surface. The optimized dissolution profile now gives the water sufficient time to fully wet the gypsum powder and still completely dissolve in the hose of the spray machine to provide maximum water retention.
Summary

Methyl cellulose and derivatives are widely used in construction applications. Their substitution levels and molecular weight can be controlled over a wide range. Understanding structure/property relationships allow to predict performance in a given application. Applying our knowledge of structure/property relationships is prerequisite to develop new products and help the market with tailored solutions. The performance of cellulose ethers in construction applications is a consequence of their molecular structure and particle morphology.

References


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