



The CMC Book



Carboxymethyl Cellulose (CMC) /
Cellulose Gum

Nouryon

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Leading global CMC production and innovation

CMC – A versatile bio-based hydrocolloid

The sodium salt of carboxymethyl cellulose, CMC/cellulose gum, is a bio-based and bio-degradable, water-soluble polymer, based on renewable cellulosic raw materials. CMC is multifunctional and it is easy to tailor ability combined with cost efficient performance makes it an attractive choice for many industrial and consumer applications.

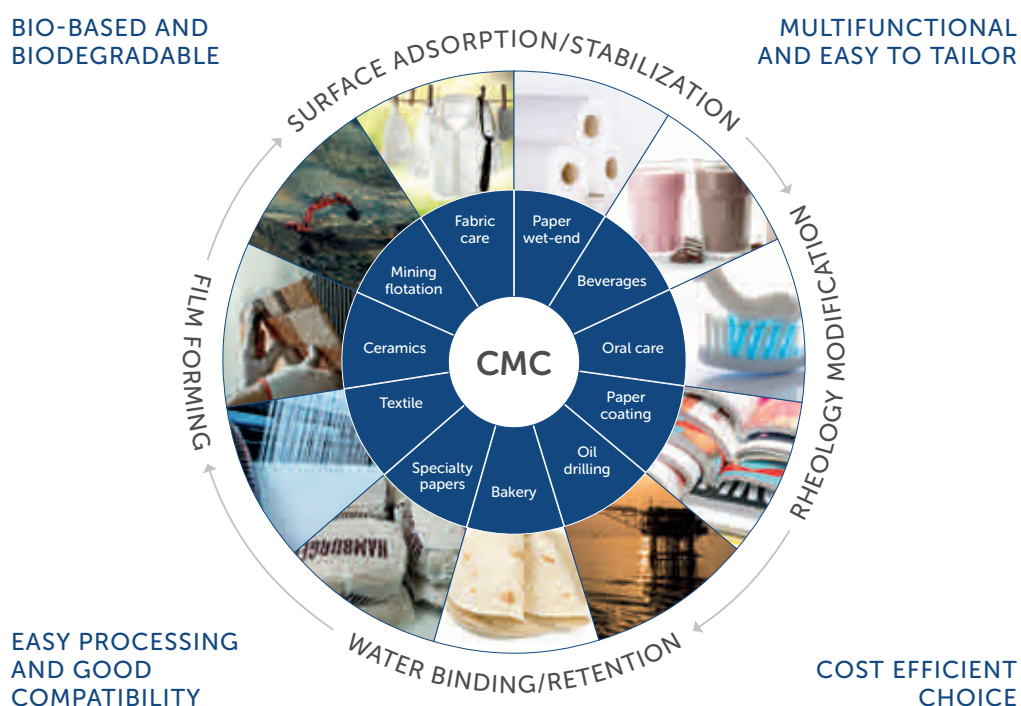
Your reliable partner in CMC innovations

We have been producing CMC since the early 1940 and have extensive knowledge to tailor CMC's functionality for different applications. We aspire to meet our customers' expectations by ensuring all our CMC is optimized for performance, quality and the required application

functionality. Our portfolio includes AKUCCELL® Cellulose gum, CEKOL® Cellulose gum and FINNFIX® CMC standard grades, and application specific grades such as BERMOCCELL® Cellulose ether, CALEXIS® CMC, SELECT® CMC, PERIDUR® CMC, STAFLO® PAC and GABROIL™ CMC.

CMC – Aiming for the highest standards

Our CMC is manufactured in compliance with multiple different internationally recognized standards and Good Manufacturing Principles (GMP). We are committed to the highest standards when it comes to sustainability, quality and safety. Through our excellence in process capabilities and wide inventory stock availability, we ensure security of supply and reliable deliveries.



Tailored CMC performance for different applications

Sodium Carboxymethylcellulose (CMC), also known as Cellulose Gum, E466 and Poly-Anionic Cellulose (PAC), was first prepared in early 1900's, and has been made on an industrial scale ever since. The first applications were as industrial binders and in fabric care. Nouryon's Äänekoski plant in Finland started its operations in 1944 focusing first on wallpaper adhesives, and then on paper industry grade CMC. Later, in 1962 Nouryon's Arnhem plant in the Netherlands started its production on purified specialty grades for the regulated industry. Today, our CMC grades cover a wide range of applications from food and pharmaceuticals to oil, paper, mining and fabric care. Nouryon's Äänekoski plant is the largest CMC factory in the world.

Nowadays, when sustainability and green values are the key drivers in product innovations, CMC is a preferred choice as a bio-based hydrocolloid. The raw material selection and adjustment of the production process steps makes it possible to tailor specific CMC product functionality to different applications.

Sustainability

CMC is a non-toxic, bio-based polymer based on renewable cellulosic raw materials. Nouryon ensures that all wood cellulose used in our CMC production processes come from forests that are certified by the Program for the Endorsement of Forest Certification, or that meet the requirements of certification. Selected wood-based Nouryon CMC grades also fulfill international ECOCERT (for organic and natural cosmetics) and COSMOS standard requirements, including GMO-free status.



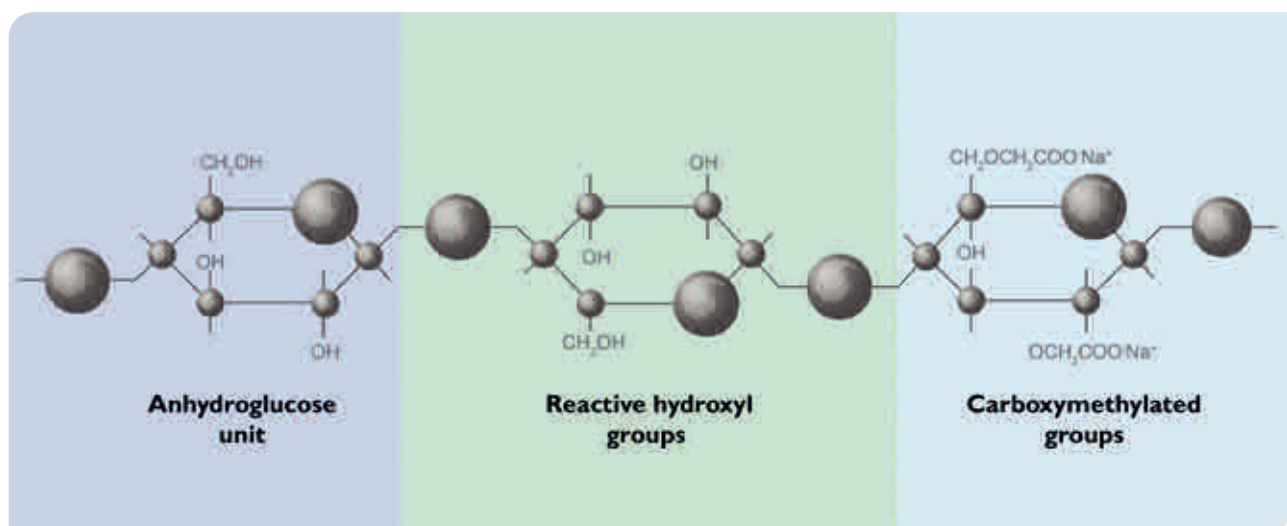
Our team strives for sustainability through the whole CMC value chain - from raw material supply and manufacturing to new product innovation.



CMC molecular structure

CMC refers to the sodium salt of carboxymethyl ether of cellulose, the molecular structure for which is illustrated below. The general chemical formula is $[C_6H_7O_2(OH)_x(OCH_2COONa)_y]_n$ ($x+y=3$). The core building blocks of the CMC molecule are β - D - glucose units. Each glucose unit includes three free hydroxyl groups (-OH), which are partially substituted by carboxymethyl groups (-CH₂ COOH) during the etherification reaction. The side units are irreversibly linked to the cellulose backbone with ether bridges, and thus, CMC belongs

to the group of substances called cellulose ethers. Sodium salt is the most common salt of CMC, which arises in the manufacturing process as a result of the reaction between monochloroacetic acid and sodium hydroxide. The hydroxyl and carboxymethyl groups play an important role in the properties of CMC. The hydroxyl groups enable hydrogen bonding, whereas the carboxymethyl groups carry a negative charge (-CH₂COO⁻ Na⁺) meaning that CMC is an anionic polyelectrolyte. Due to its ionic nature, CMC is capable of exhibiting electrostatic interactions.



CMC manufacturing

CMC is produced from cellulose, monochloroacetic acid (MCA or ClCH_2COOH) and sodium hydroxide (NaOH). Even if the cellulose molecule is highly hydrophilic due to the hydroxyl groups, the strong inter- and intramolecular hydrogen bonding renders cellulose insoluble in water. The molecule is made water-soluble by a chemical reaction, where hydroxyl groups are partially substituted by carboxymethyl groups. The main chemical reactions are illustrated below.

- 1) $\text{Cellulose-OH} + \text{NaOH} \rightarrow \text{Cellulose-ONa} + \text{H}_2\text{O}$
- 2) $\text{Cl-CH}_2\text{-COOH} + \text{NaOH} \rightarrow \text{Cl-CH}_2\text{-COONa} + \text{H}_2\text{O}$
- 3) $\text{Cellulose-ONa} + \text{Cl-CH}_2\text{-COONa} \rightarrow \text{Cellulose-O-CH}_2\text{-COONa} + \text{NaCl}$



Our CMC plant in Äänekoski, Finland



The cellulose raw material is carefully selected and ground to meet the very strict quality requirements of the end product. The ground cellulose is treated with sodium hydroxide in a step known as mercerization. Once all of the cellulose has been converted to alkali cellulose the next step is etherification, in which the cellulose alkali is reacted with monochloroacetic acid.

After completion of the different reaction steps, technical CMC grades can be directly dried, whereas high purity CMC grades are neutralized with an acid to pH 5.5-8. The by-products, sodium chloride and sodium glycolate, are removed by washing with solvents resulting in CMC grades of up to 99.5% purity. The dried product is further ground and sieved to match with the preferred particle size distribution.

CMC is manufactured in compliance with multiple different internationally recognized standards (e.g., ISO 14 001 and ISO 9001).

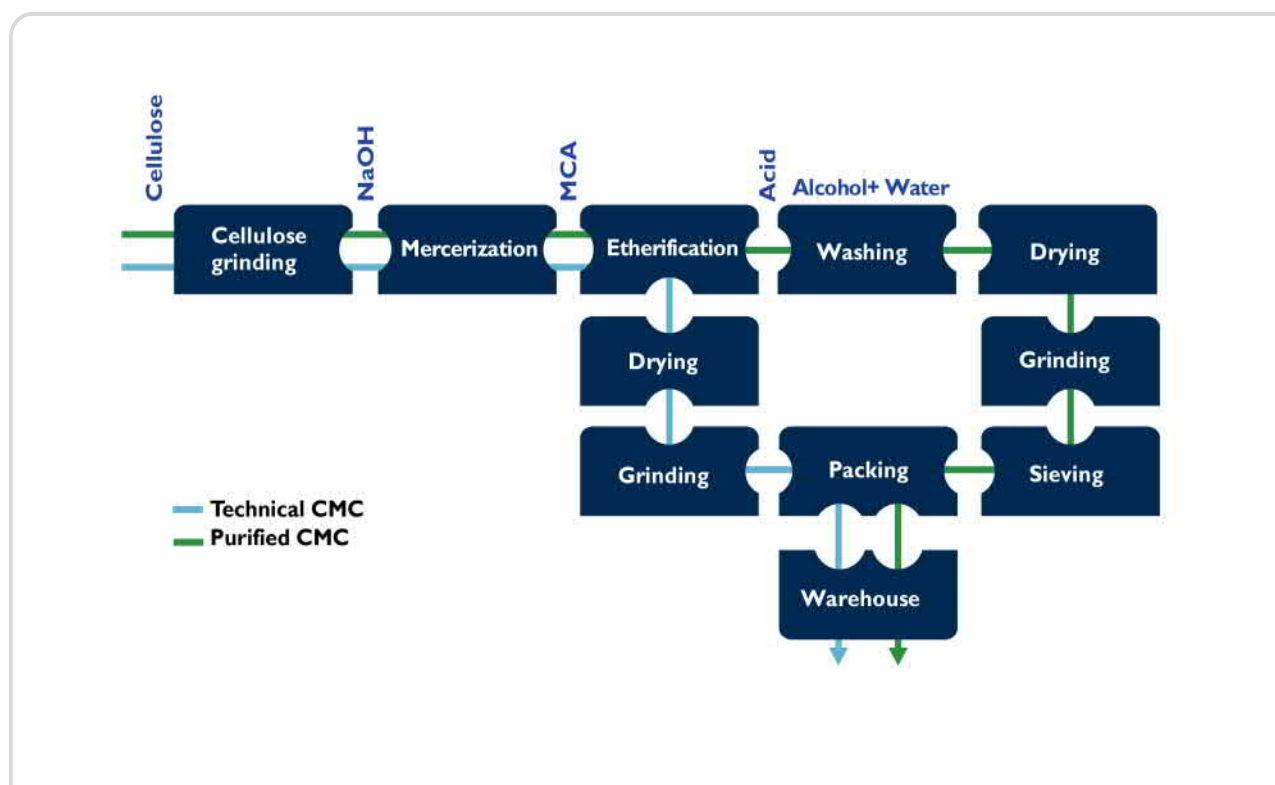
Grades for applications requiring very high purity (e.g., food, personal care and pharmaceutical applications) are manufactured according to recognized principles of good manufacturing practices.

Optimizing CMCs performance

CMC has many interesting functional properties when dissolved in aqueous solutions but these depend on the CMC grade and the solution conditions. CMC's performance is typically influenced by raw materials selection, controlling the molecular weight, degree of substitution, and substitution uniformity of the CMC molecule. Controlling the particle size distribution and the surface chemistry of the final product particle also has an influence on functionality.

Raw material selection

The primary cellulose sources for CMC are wood and cotton fibers, the typical structures of which are illustrated in Figure 1.



The different manufacturing steps for CMC are described in the flow sheet above.



The cellulose fibers are located in the cell wall. Alongside the cellulose there are hemicelluloses, lignin and other impurities which make up the fiber structure. The isolated and purified cellulose fibers have a range of purities, molecular weights, and carbohydrate compositions.

Selecting the cellulose grade is one of the most important factors that influence the final molecular weight and rheological functionality. It also has an impact on the cellulose reactivity and the color (from white to cream) of the final product. By choosing a wood based cellulose we ensure that CMC meets the GMO-free requirement of the food and other industries.

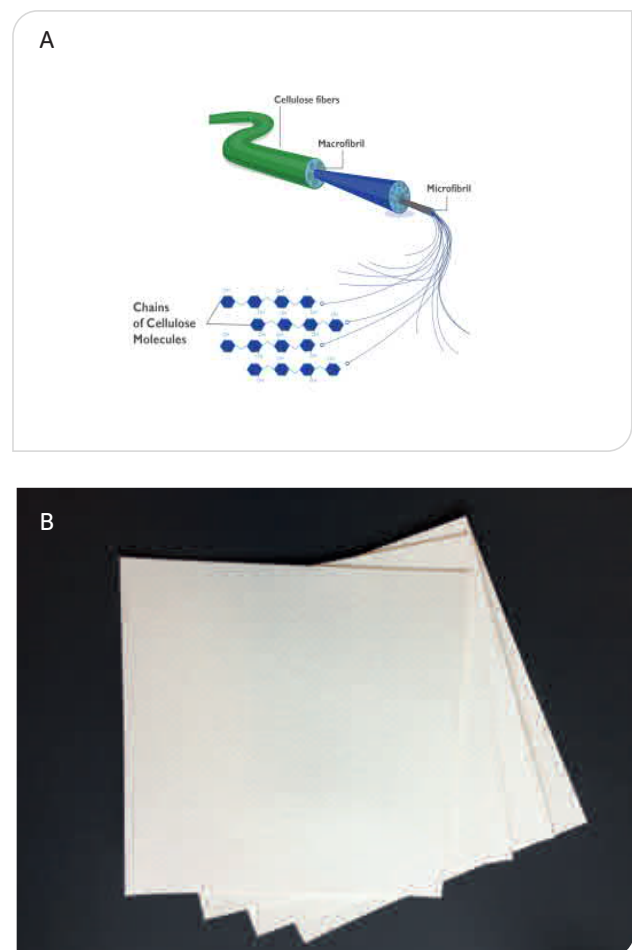


Figure 1: Cellulose is extracted from a plant cell wall. Cotton or wood fibers form the inner building blocks, known as microfibrils, which consists of several parallel cellulose chains (A). The cellulose fibers are extracted in a process that breaks the bonding between lignin, hemicelluloses and cellulose resulting in purified cellulose pulp (B= Cellulose pulp sheets).

Molecular weight (Mw)

The molecular weight of the CMC can be adjusted both by raw material selection and process conditions. The degree of polymerization (DP) and the degree of substitution (DS) determine the molecular weight of the CMC according to the following relationship:

$$Mw = DP \times (162 + 80 \times DS)$$

Table 1. Typical molecular weight averages for some Nouryon CMC grades.

Grade	Degree of polymerization	Molecular weight Mw
FF-30000	3,200	750,000
FF-4000	2,000	450,000
FF-700	1,200	270,000
FF-30	360	80,000



Figure 2. Descriptors function as equalizer and show the influence of the molecular weight on the CMC performance.

Figure 2 illustrates how the molecular weight is linked to rheological behavior, water binding capability and solution stability (this basic rheology terminology can be found in the Appendix). The long molecular chains are able to resist flow and create interactions between polymer chains, thereby increasing viscosity. The long molecular chains also orient along the flow and, therefore, can exhibit shear-thinning (i.e., pseudoplastic) behavior.

Viscosity is related to the average chain length of the CMC molecule, especially in high concentrations as shown in Figure 3 with increasing molecular weight the maximum solution concentration is decreasing.

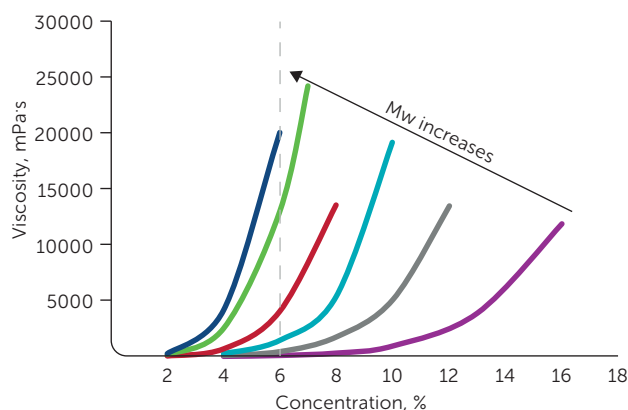


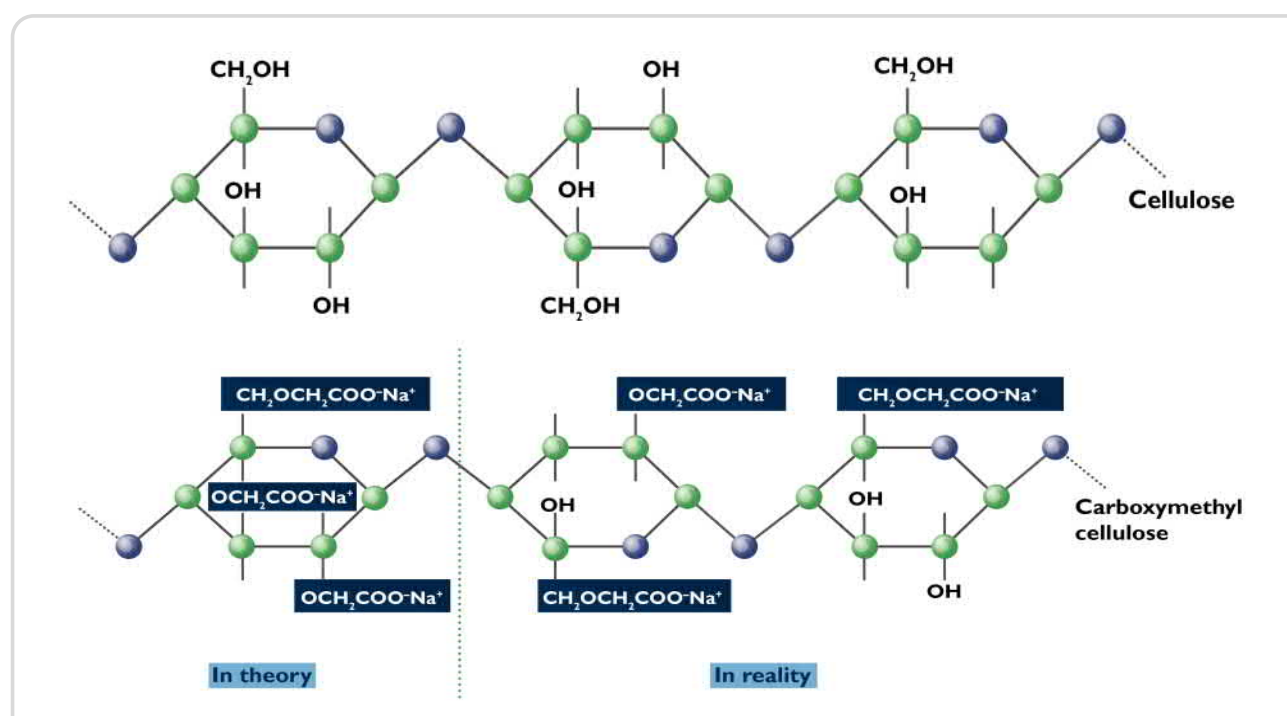
Figure 3: Viscosity of selected products in different concentrations.





Degree of substitution (DS)

The degree of substitution (DS) is the average number of carboxymethyl groups per anhydro-glucose unit. Theoretically, the maximum DS is 3, when all three hydroxyl groups of anhydro-glucose unit are substituted with carboxymethyl groups. This does not happen in practice, and in reality the DS range usually is from 0.4 up to 1.5.



The DS is one of the most important parameters influencing CMC performance (Figure 4). It is used to adjust the proportion of the hydroxyl and carboxymethylated groups and, therefore, impacts on the molecule's capability to create hydrogen bonding and electrostatic interactions in the final application.

High DS improves the solubility of the CMC. If the value is below 0.3, CMC is unlikely to be soluble in water. Low DS provides a higher tendency to have unreacted chain lengths in the polymer resulting as visible fibers in solution. High DS enhances salt tolerance as a higher number of the carboxymethyl groups increases the ability of the added cation to form the soluble salt of the carboxymethyl cellulose. Higher DS values also improve resistance to enzymatic (i.e., cellulases) degradation.

One of CMC's key functionalities is its capability to adsorb onto a particle or fiber surface through its ionic nature. High DS enhances its tendency for electrostatic interactions.



Figure 4: Descriptors function as equalizer and show the influence of the DS on the CMC performance.

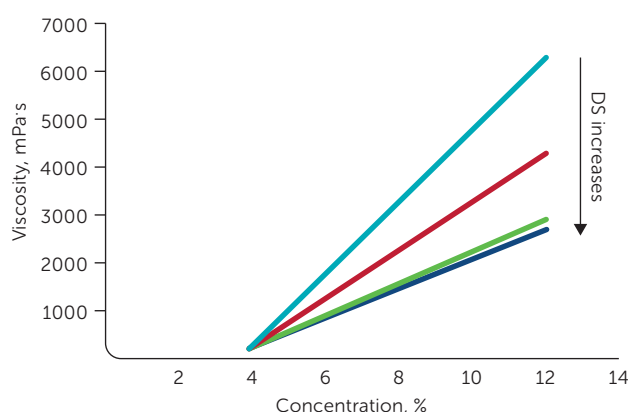


Figure 5: Increasing FF-700 DS reduces the viscosity in higher concentrations due to limited capability to create the intermolecular structures.

■ CMC 1
■ CMC 2
■ CMC 3
■ CMC 4

Substitution uniformity

The distribution of the side units along the chain influences the solution characteristics. Two products having the same molecular weight and DS might still perform very differently due to differences in substitution uniformity as shown in Figure 6. An uneven substitution enhances the polymer's ability for intermolecular interactions via hydrogen bonding. More hydrogen bonds can be formed at places with no or low substituted carboxymethylated regions on the CMC chain. This is seen as a viscosity build-up and thixotropic behavior.

An aqueous solution of an unevenly substituted CMC will also exhibit lower solution stability as shown in Figure 7. The water binding capacity is enhanced by uneven substitution pattern due to two possible mechanisms: 1) The three dimensional network enables the capture of water molecules within the structure, and 2) there is an increased tendency for hydrogen bonding.

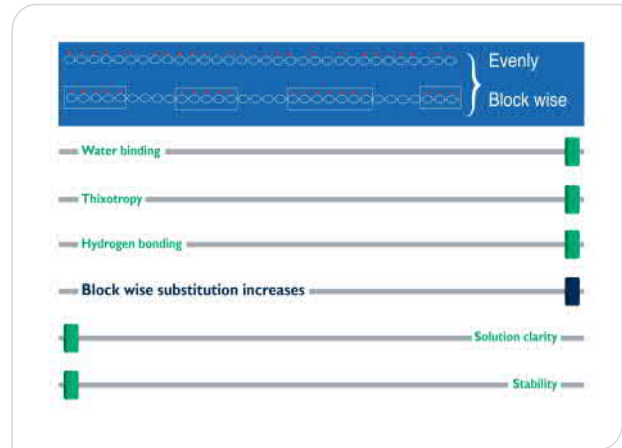


Figure 6: Descriptors function as equalizer and show the influence of substitution uniformity on the CMC performance.

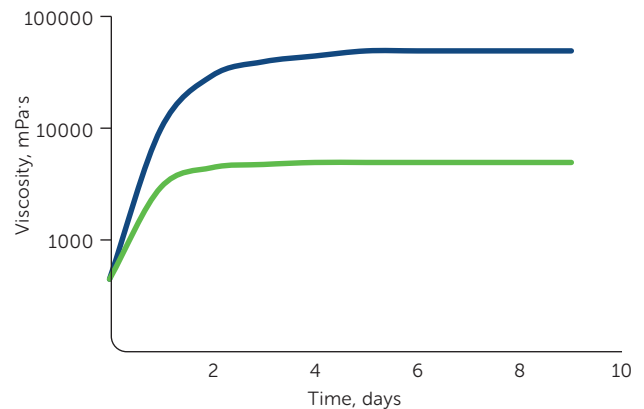


Figure 7: Uneven distribution of the side units along the chain increases the possibility to form hydrogen bonding between the CMC chains creating viscosity build up over time. In the graph above the viscosities of two CMCs in mixed solvent (glycerin/water) are compared. Both CMCs have the same DS (0.7) but are either block wise (grade I) or evenly (grade II) substituted.

■ Block wise substituted (I)
■ Evenly substituted (II)

Particle size distribution

Our CMC grades can be tailored to different particle size distributions. Choosing the correct particle size distribution is important to ensure smooth handling and processing operations. Fine particles are known to hydrate faster as shown in the Figure 8. However, this is only true if the addition of the particles to the aqueous phase is done slowly and there is sufficient mixing. Otherwise, the small particle size increases the tendency to create lumps that dissolve very slowly. The methods for hydrating CMC are discussed in the “Practical guidance for CMC usage” chapter.

Coarser particles are less sensitive to agglomeration and, thus, allow for faster addition speeds into water. The coarse particles also create less dust during handling. For dry-blending it is important to match particle size (and bulk density) with other ingredients to prevent particle separation.

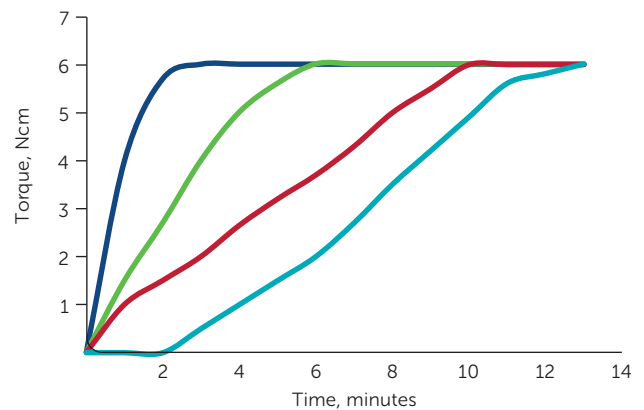


Figure 8: Torque is recorded as a function of time showing hydration profiles for the CMC particles in water. Hydration time is proportional to the particle size when the addition speed is slow enough to allow particles to disperse and hydrate individually.

— 0 - 0.02 mm
— 0 - 0.03 mm
— 0 - 0.05 mm
— 0.2 - 0.05 mm



Figure 9: Example of granular (A) and powder (B) CMC particles

Bulk density

Bulk density mainly influences package and storage space requirements, dry powder flow and blending properties. It is defined as the weight of the particles divided by the packed volume. The moisture content, CMC grade and particle size and shape distribution are key parameters which influence the bulk density of the final product. When bulk density is measured, it is important to take into account how the powder is handled prior to weighing as the particle packing and orientation impact the packed volume.



Functionality of CMC in key applications

CMC is a highly versatile bio-based hydro-colloid, and it adds value through a variety of different functionalities in various applications. The key functionality mechanisms are rheology modification, surface adsorption, water binding/retention and film forming.

Rheology modification

CMC is used as a thickener and rheology modifier in many applications (basic rheology terminology explanations can be found in the Appendix). The CMC molecules' tendency to resist and orient along the direction of flow and its tendency to form intermolecular interactions via hydrogen bonding will define the rheological behavior of the CMC solution.

Influence on viscosity is strongly related to molecular weight. Higher molecular weight molecules are more resistant to flow and increase viscosity compared to lower molecular weight molecules.

Pseudoplasticity, i.e., shear-thinning, can be determined by a molecule's tendency to orient along the direction of flow. Longer molecules show more pseudoplastic behavior, whereas very low molecular weight CMC solutions exhibit Newtonian behavior.

Low DS value and uneven distribution of the side groups increase the tendency to form hydrogen bonds. This can lead to thixotropic behavior, i.e., formation of three-dimensional structures with time. These structures break when sufficient shear rate is applied.

In some applications, pseudoplastic and thixotropic behaviors are important for optimized rheological performance of the final product. For example, pseudoplastic behavior is beneficial when toothpaste is prepared, as the lower viscosity under shear allows using less mixing energy to create a uniform paste and helps with entrapped air removal. Pseudoplastic flow enables the paste to be easily filled in or squeezed out from the tube, as well as staying on top of the brush.




Figure 10: High purity cellulose gum grades are recognized as an excellent binder and rheology agent in toothpaste formulations.

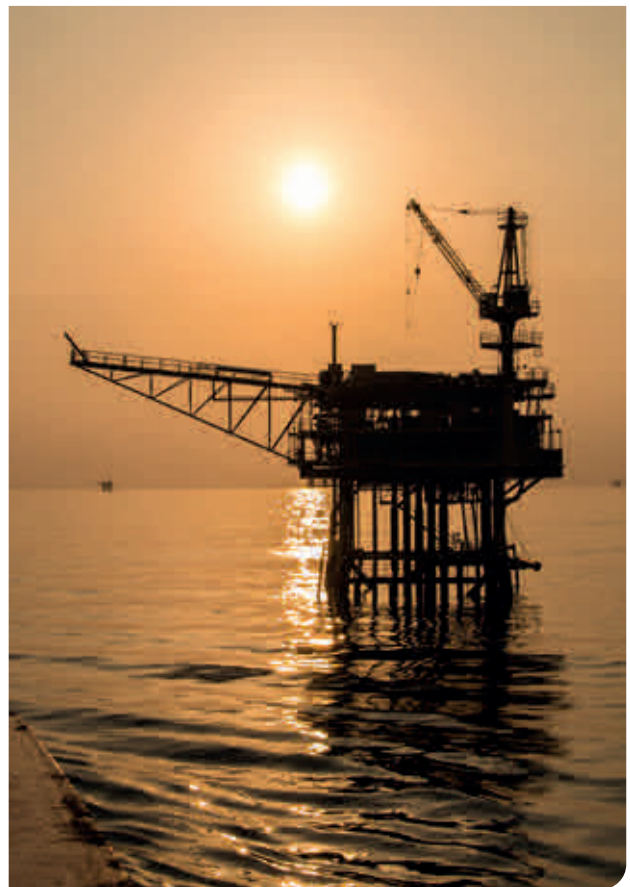
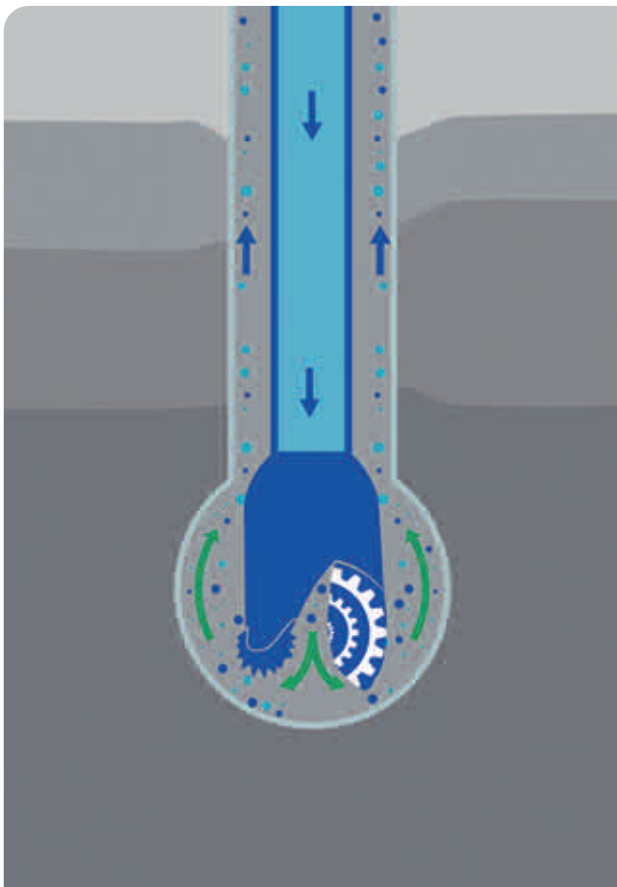


Figure 11: The drilling mud is added to the well borer to facilitate the drilling process. CMC is used as a thickener and fluid loss agent in water-based drilling mud formulations. The PAC grades (Polyanionic Cellulose) also have a great ability to perform under severe conditions, such as in high salt concentration, high temperature and high pressure environment.

Surface adsorption

The ability of CMC molecules to adsorb onto particle and fiber surfaces has an important role in many applications, such as in protein protection of acidified protein drinks (Figure 13), anti-redeposition in fabric care (Figure 12), enhancing wet strength of towel products (Figure 14) and in providing higher recovery efficiency in the mining flotation process. In many cases, the driving forces for the adsorption are related to electrostatic interactions. Adsorption of the CMC molecule on the cellulosic fibers is through hydrogen bonding between the low substituted regions on the CMC backbone and the cellulosic fiber.

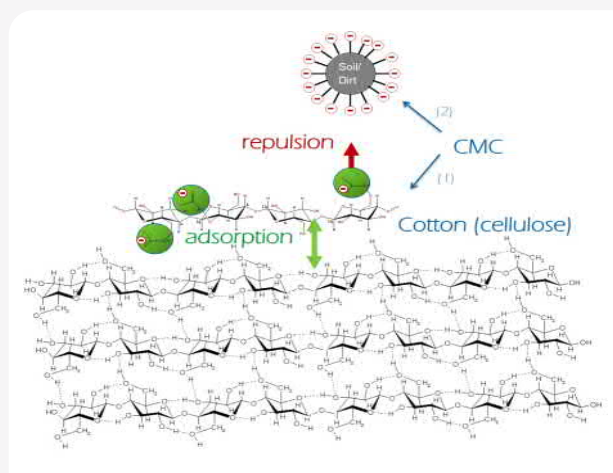


Figure 12: CMC acts as an anti-redeposition agent in the fabric care formulations. It can selectively adsorb onto cotton fibers through hydrogen bonding (1), and also keeps the dirt in the liquid phase by acting as a dispersion agent (2). The created negative charges cause repulsion that prevents the dirt particles being redeposited back on the fabric after the rinsing cycle.

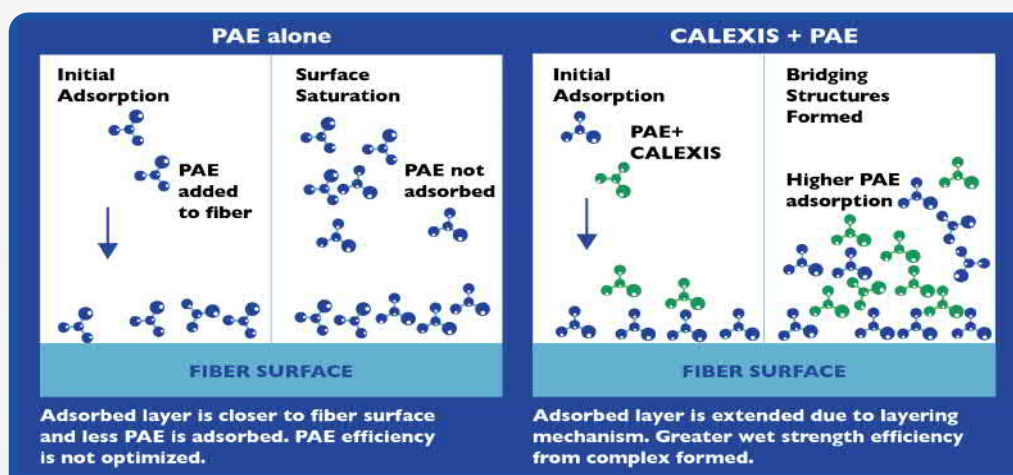


Figure 14: CALEXIS® CMC grades are tailored for paper wet end. CMC is used to improve polyamide epichlorohydrin (PAE) resin to settle on the fiber surface resulting in enhanced wet and dry strength, for example in kitchen towels.



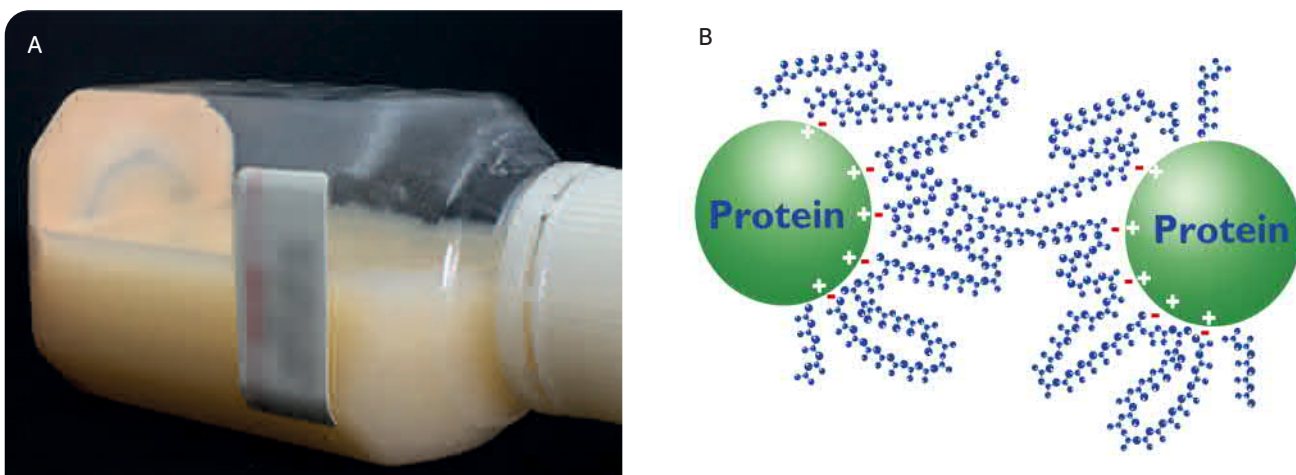


Figure 13: When lowering the pH of milk, as is done during the preparation of acidified protein drinks (APD), the natural stabilization mechanism of milk protein, i.e., casein micelles fails and the protein precipitates out, as shown in the above image (A). Cellulose gum can be used as a stabilizer to avoid the agglomeration of the proteins. Cellulose gum molecules adsorb onto the protein surfaces (B) and also increase the viscosity. Both mechanisms contribute to preventing the proteins from precipitating. The key benefits of the cellulose gum are its ability to stabilize the proteins over a wide range of pH and temperature, and its resistance to molecular degradation during homogenization in production. Tailored acid-stable grades are available to extend the functionality to the low pH range.

Water binding/retention

CMC has excellent water binding capacity, which adds value in many applications. Typical examples include bakery products and paper coating colors (see Figures 15 and 16). Hydrogen bonding and molecular interlocking trap the water molecules inside the molecular network. Note that water binding capability can be reduced by the presence of salt ions; further details are discussed in the “Compatibility with the other substituents” chapter.



Figure 15: Cellulose gums ability to bind water helps to extend the freshness and shelf-life of bakery products. It also gives higher dough strength. Highly purified AKUCCELL and CEKOL grades create clear, color-free and transparent solutions that are essentially odorless and suitable for food applications.

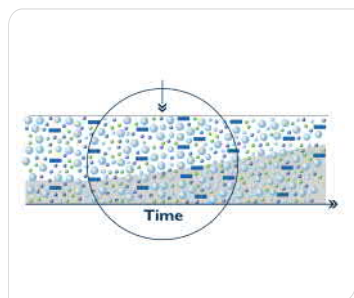


Figure 16: FINNFI grades are widely used in paper coating color formulations. CMC is utilized to control the coating color filter cake formation speed, runnability and coating layer porosity through influencing both the water phase viscosity and dispersion stability. Nouryon's team has extensive experience and laboratory capability to optimize the CMC performance for the industrial coating color process.

Film forming

CMC films are transparent, and exhibit resistance to oils, gases and organic solvents. The film is cold and hot water soluble. Again, CMC performance needs to be optimized to achieve desired barrier and dissolving properties to match different application demands (see Figures 17 and 18). Other ingredients can be used to improve the CMC film properties (e.g., plasticizers to increase film elasticity).



Figure 17: CMC forms an oil and grease resistant film on a substrate, which can be used in food packaging. Bio-based and biodegradable solutions are developed to meet the increasing demand for sustainable packaging.



Figure 18: Sizing of warp yarns with FINNFIX CMC increases the yarn strength providing the opportunity to increase weaving efficiency. CMC creates a strong, abrasion-resistance film that exhibits good adhesion especially to the cotton fiber surface and also reduces dusting.

It is typical that more than one mechanism will determine CMC functionality in different applications. Nouryon's CMC portfolio includes a large number of CMC grades with a variety of specifications and performances. Tables 3 and 4 list the most typical CMC and cellulose gum applications describing what value CMC/cellulose gum brings in each case.

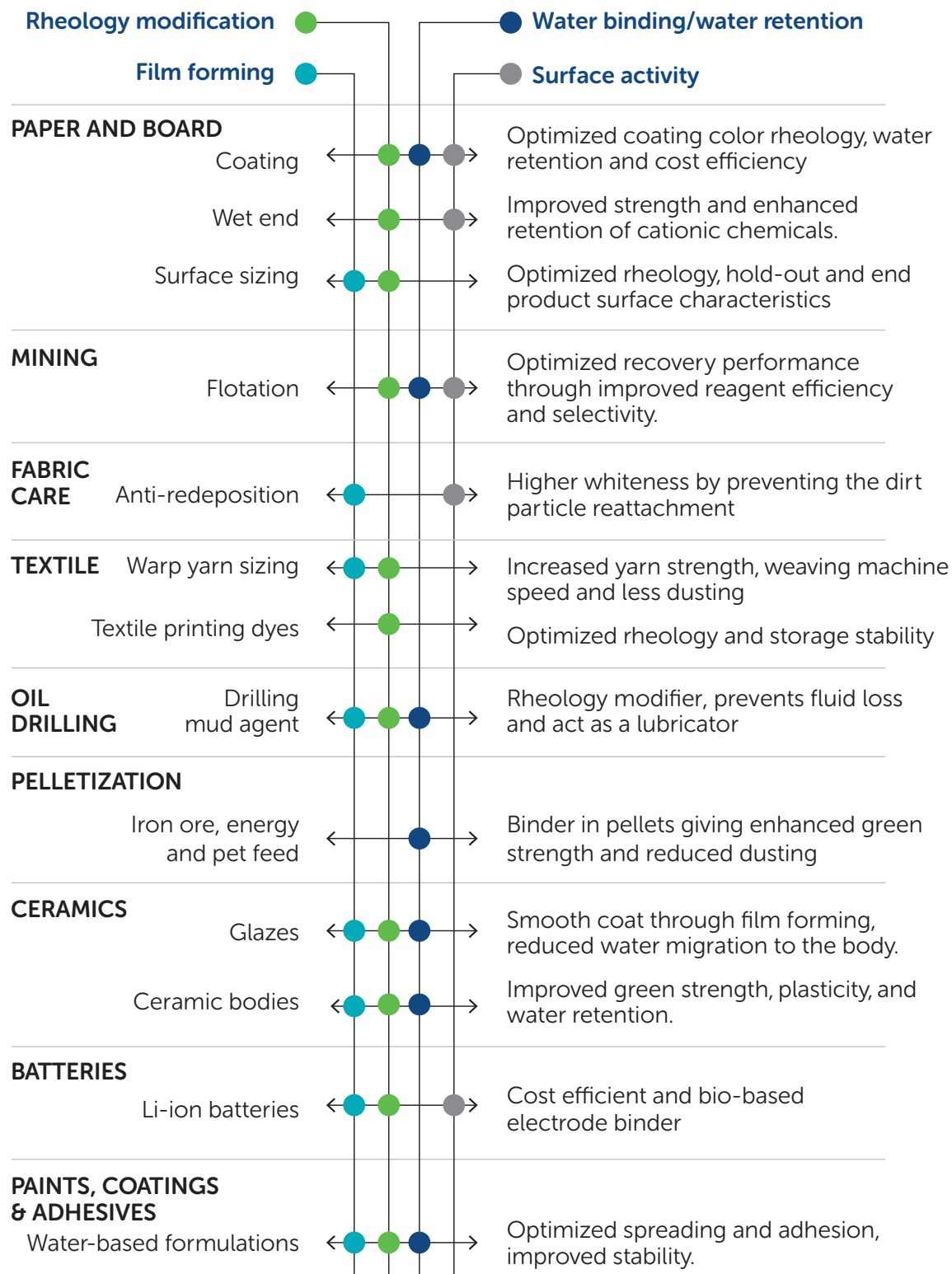


Table 3: Nouryon CMC grades bring value in many applications through different functionalities.

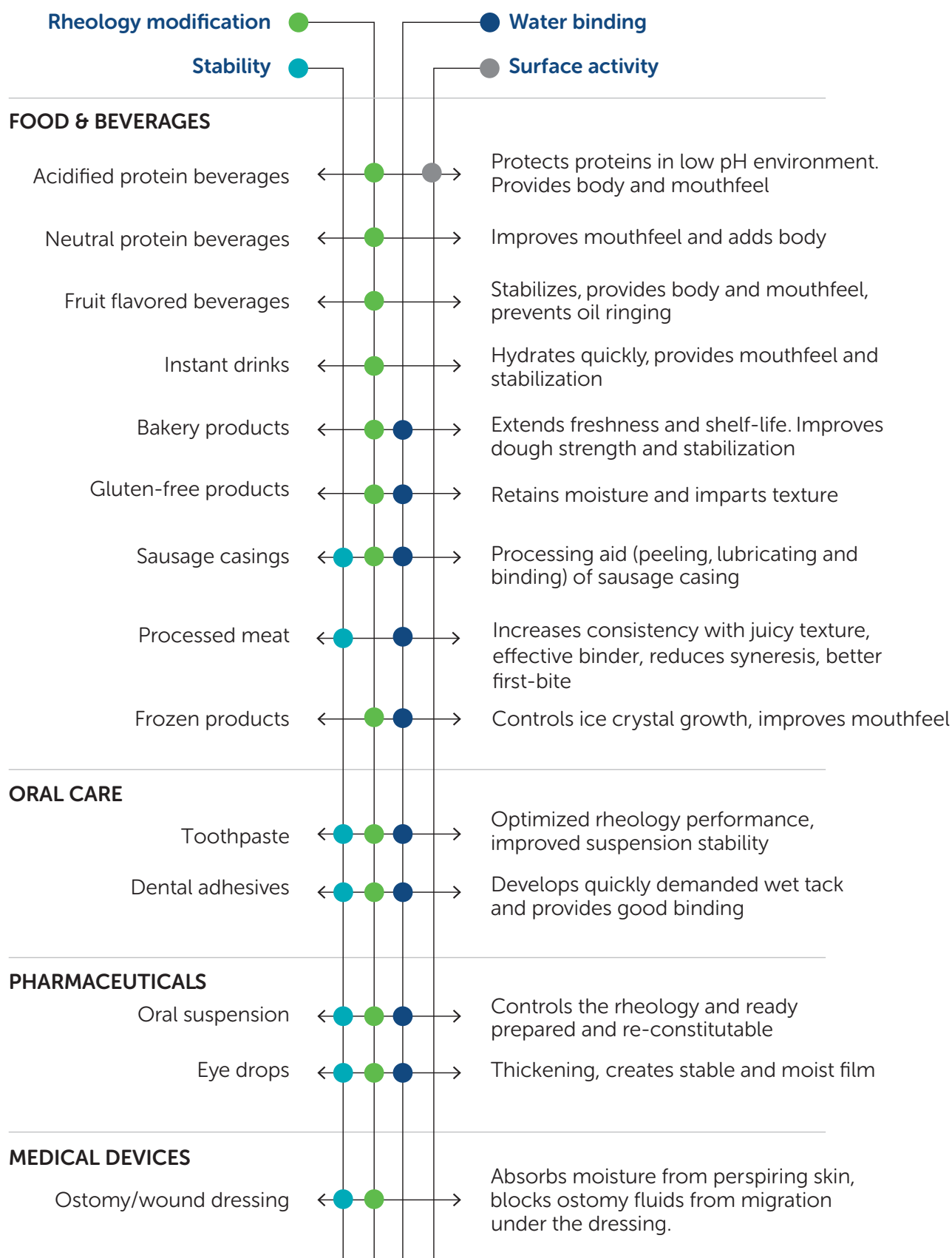


Table 4: Nouryon's cellulose gums bring value in the applications where the highest purity and regulatory compliances are demanded. For more information about Nouryon's CMC and Cellulose gum grades please contact your local Nouryon representative.

Practical guidance on CMC usage

Typically, CMC is delivered as a dry powder and then dissolved in water for the final application. This chapter includes the best practices for CMC handling, including dry addition, dissolving and the key parameters to control the dissolution and the factors to consider while storing CMC. Furthermore, it provides an overview of CMC's compatibility with other components typically found in a variety of applications.

Dry addition

In some applications CMC is added as a dry powder, for example, to maximize the solids content of a paper coating color.

Fine powder CMC grades are not recommended to be used in dry addition, due to their tendency to agglomerate. Order of addition should be also considered, for example, with paper coating colors CMC is added always after the pigments and before the latex to get best dissolving performance. In beverages, the dry CMC particles should be added to the aqueous phase early in the process prior to any salts, sugar or acidic components (e.g., citric acid).

It is critical to use sufficient mixing speed during the dry addition process. The addition point is always at the center of the vortex, and the recommended addition rate is maximum 12 kg/min (granular product). A minimum of 15-30 minutes post-mixing is recommended after addition of all components.





How is CMC hydrated and dissolved?

CMC shows good solubility in both cold and hot water. When dissolving CMC, it is important to emphasize that the rate of CMC addition must be slow and even enough to avoid agglomeration. CMC particles should be dispersed before hydration and viscosity build-up takes place.

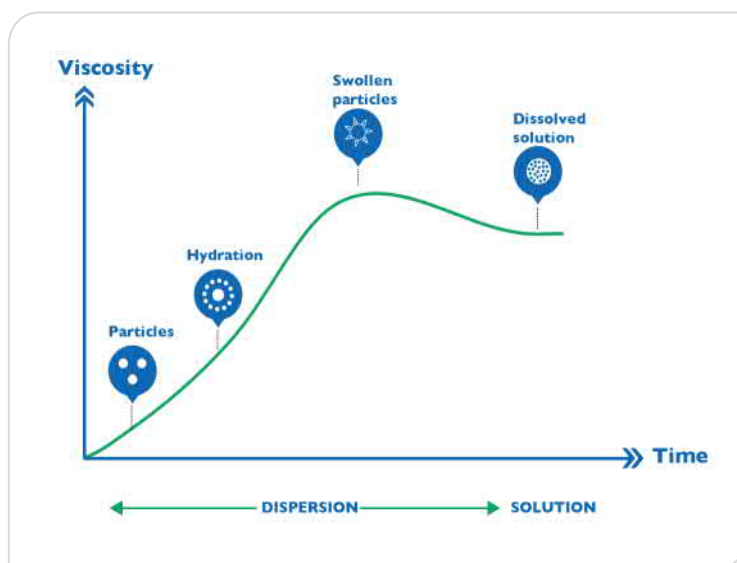


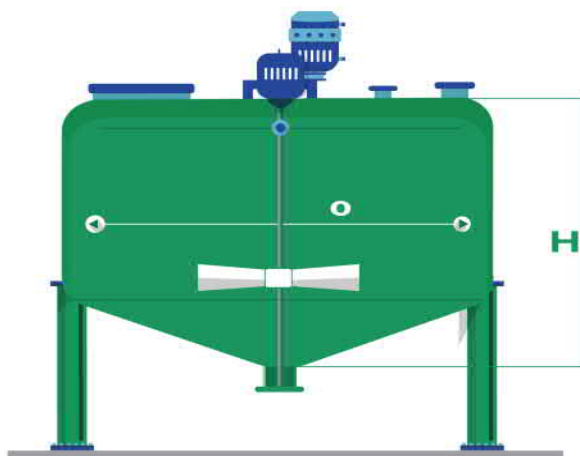
Figure 19: When a CMC particle enters water (A) it will go through a process of hydration by adsorption of water. Particles swell (B) and increase in volume, as shown on the figures above. It is possible to reach even the higher viscosity levels compared to that of the final solution due to higher amount of water bound in this state. It is important to wait until the viscosity is stabilized to reach stable dissolution (C). Dispersion means a uniform distribution of the CMC particles in water. Solution means that the CMC is completely dissolved in water.



A typical way to dissolve CMC is to use a high shear mixer, which is sufficiently vigorous enough to keep the entire liquid in motion and to create a downstream flow and vortex. Too high of shear rates might introduce air bubbles into the system. CMC is added slowly (about 20 kg/min for granular grade) and evenly into the vortex. The principle of dissolving CMC is to wet all the particles as quickly as possible before the viscosity starts to develop.

CMC is by nature hydrophilic ("water-loving"), which means that the CMC particles will instantly start to swell (hydrate) and dissolve when dispersed in water. The mixing device used must be efficient enough to keep the entire liquid in motion to avoid agglomeration or lump formation.

Depending on the mixing conditions and CMC grade, 10 - 60 minutes is adequate to achieve complete dissolution. Below is a more detailed picture of a typical dissolving tank. Because the mixing power requirement is high, the typical size of recommended motors for different sized tanks is included.



	VOLUME	O	H	POWER
①	2 m ³	1350	1650	5.5 KW
②	3 m ³	1540	1840	7.5 KW
③	4 m ³	1680	2080	7.5 KW
④	5 m ³	1800	2250	11KW
⑤	6 m ³	1920	2320	11KW

CMC can also be pre-wetted using an eductor, whereby suction caused by the water stream will take CMC particles separately into contact with water. The only limitation for using an eductor is the fairly low make down solids of the CMC solution. This is especially important in the paper industry where often maximum solids content is required.

Particle size distribution, temperature and/or special surface modification can be used to optimize dissolving performance.

In theory, a fine powder will dissolve faster compared to a coarse material as shown in Figure 8. In practice, the granulated grades give better initial dispersion and reduce any agglomeration tendency and sensitivity to the addition speed.

Dissolving time can be accelerated by using warm water, typically up to 50-60 °C. However, temperatures above 75 °C are not recommended as these can degrade the CMC.

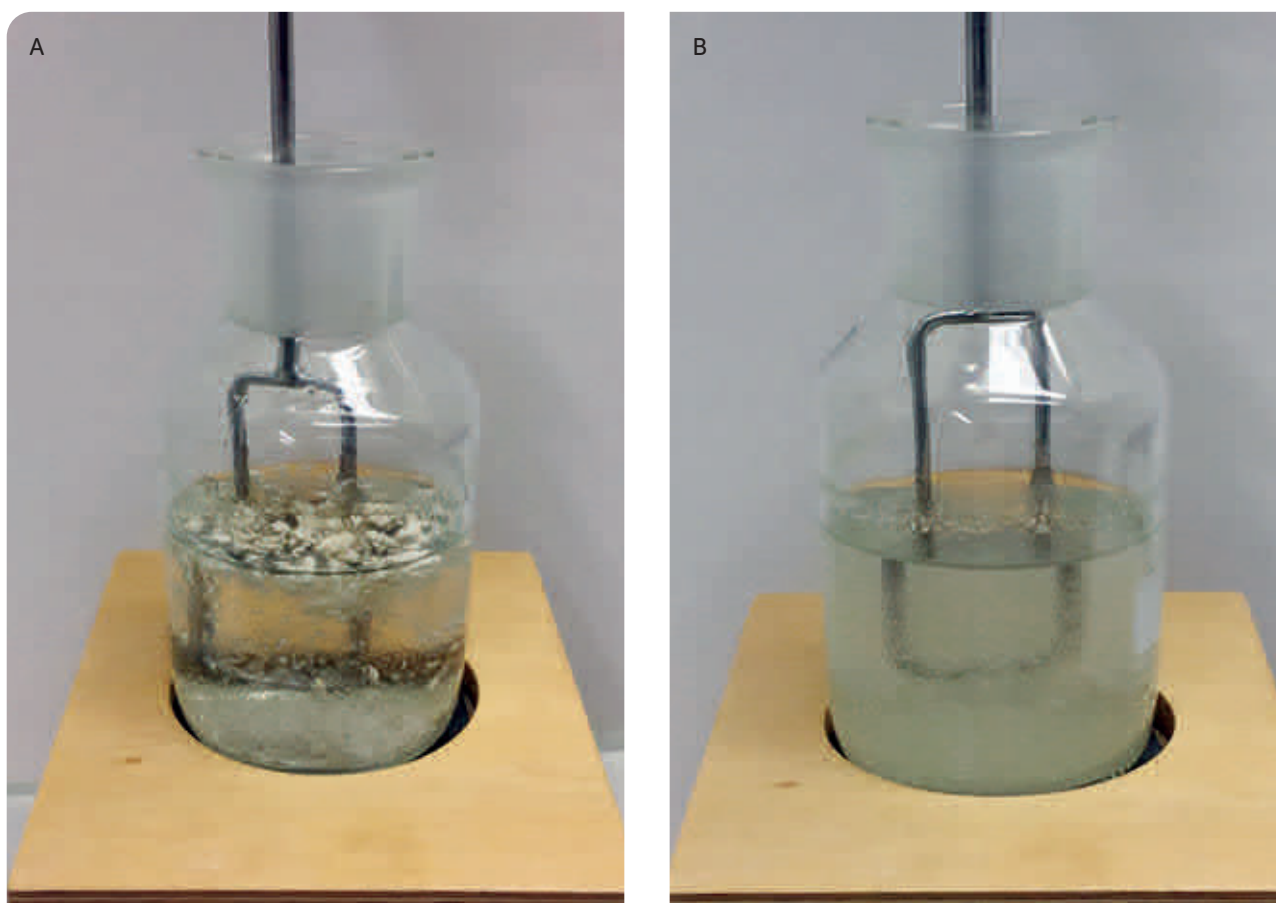


Figure 20: CMC solutions after fast particle addition. See how the fast addition of a fine CMC powder (A) might create lumps in the solution, whereas granular CMC grade (B) is less sensitive to the addition speed and allows particles to disperse. The lumps have entrapped dry particles inside of the hydrated layer. The created lumps will dissolve very slowly and extend the overall dissolving time.

Key process parameters for CMC solution

This chapter includes guidelines to the key processing parameters influencing CMC solution viscosity.

Concentration

The viscosity of a CMC solution increases rapidly with concentration. A fairly good rule of thumb is that viscosity increases eight to ten fold when the concentration is doubled as shown in Figure 21.

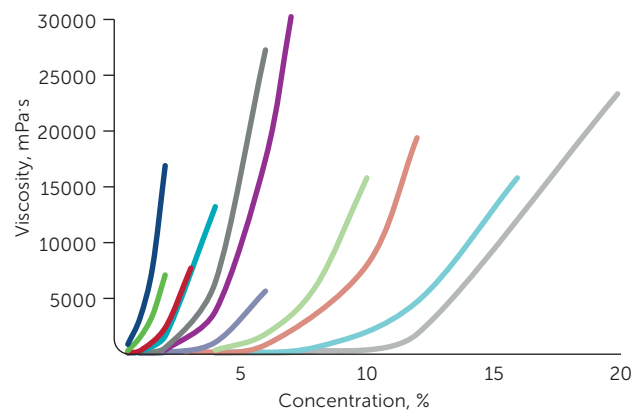
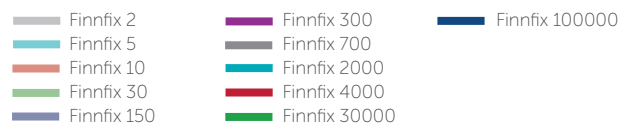


Figure 21: Comparison of viscosity vs. concentration for standard FINNFIX CMC grades. Measured with a Brookfield RV viscometer at 25 °C, 100 rpm.



Temperature

The viscosity of CMC solution reduces with increasing temperature as shown in Figure 22. Temperature dependency is reversible, which means that the viscosity increases again after heating, when the temperature is decreased. As already mentioned, heating for longer periods above 75 °C may cause loss of viscosity due to degradation.

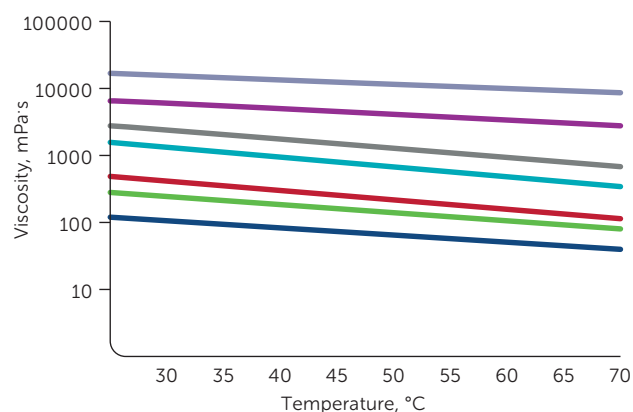


Figure 22: Comparison of viscosity vs. temperature for some Nouryon CMC grades in a 2% CMC solution. Viscosity reduces with increasing temperature; however this behavior is highly dependent on the molecular weight. Low molecule weight grades are less dependent on temperature. Measured with a Brookfield RV viscometer at 100 rpm.



Shear

For non-Newtonian fluids viscosity is dependent on applied shear. For example, with pseudoplastic CMC solutions this is experienced as a decrease in viscosity when a CMC solution is stirred, pumped or sheared in some other way. However, rheological behavior is again greatly influenced by the CMC's properties as demonstrated in Figure 23. High molecular weight CMC is far more "shear-thinning" compared to the low molecular weight CMC. The viscosity of the lowest molecular weight CMC is hardly influenced by the shear rate, meaning that the flow behavior is close to Newtonian.

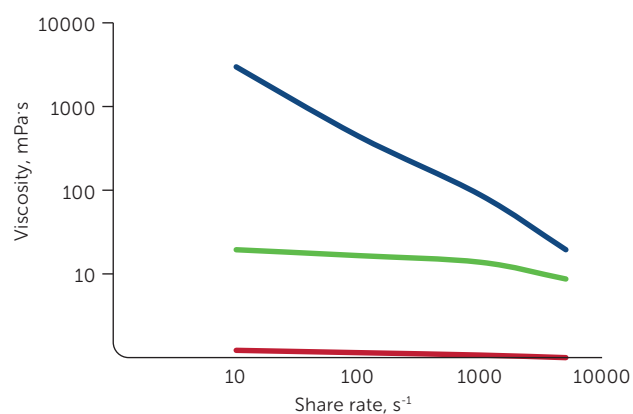


Figure 23: Influence of molecular weight on rheological behavior. High molecular weight, i.e., high viscosity grades are pseudoplastic, whereas low molecular weight, i.e., low viscosity grades, are close to Newtonian. Viscosities are measured for 1% CMC solutions. The viscosity returns to its original value when the shear stops. Typically, this behavior is linear; but, some CMC grades create network structures that result in a time-dependent behavior known as thixotropy. When sufficient shear stress is exerted on a thixotropic solution, the structure can be broken and the apparent viscosity reduced.



pH

The viscosity of a CMC solution is typically stable across a wide pH range, even though CMC grade and solution concentration have an influence on the pH stability. At pH levels of 11-12 and higher, the viscosity can be affected by a high electrolyte concentration and alkaline degradation (hydrolysis) of the CMC molecule that can be seen as decreasing viscosity. At a pH below 3 the acid form of CMC dominates (the Na^+ counter-ion will be replaced by H^+). Electrostatic repulsion is eliminated, and intermolecular interaction starts to increase through hydrogen bonding resulting in precipitation and/or gel formation. However, special acid stable grades will show stable viscosity even under very low pH conditions.

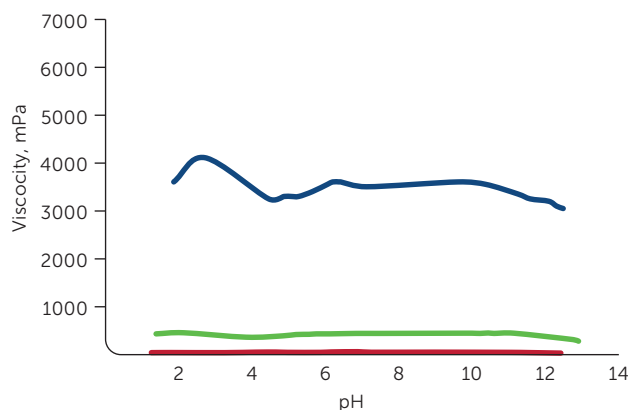


Figure 24: Viscosity (25°C, 100 rpm) as a function of pH shown for some Nouryon CMC grades. NaOH and HCl were used to adjust pH of the CMC solutions (1.5%)

— High Mw
— Medium Mw
— Low Mw



Compatibility with other substituents

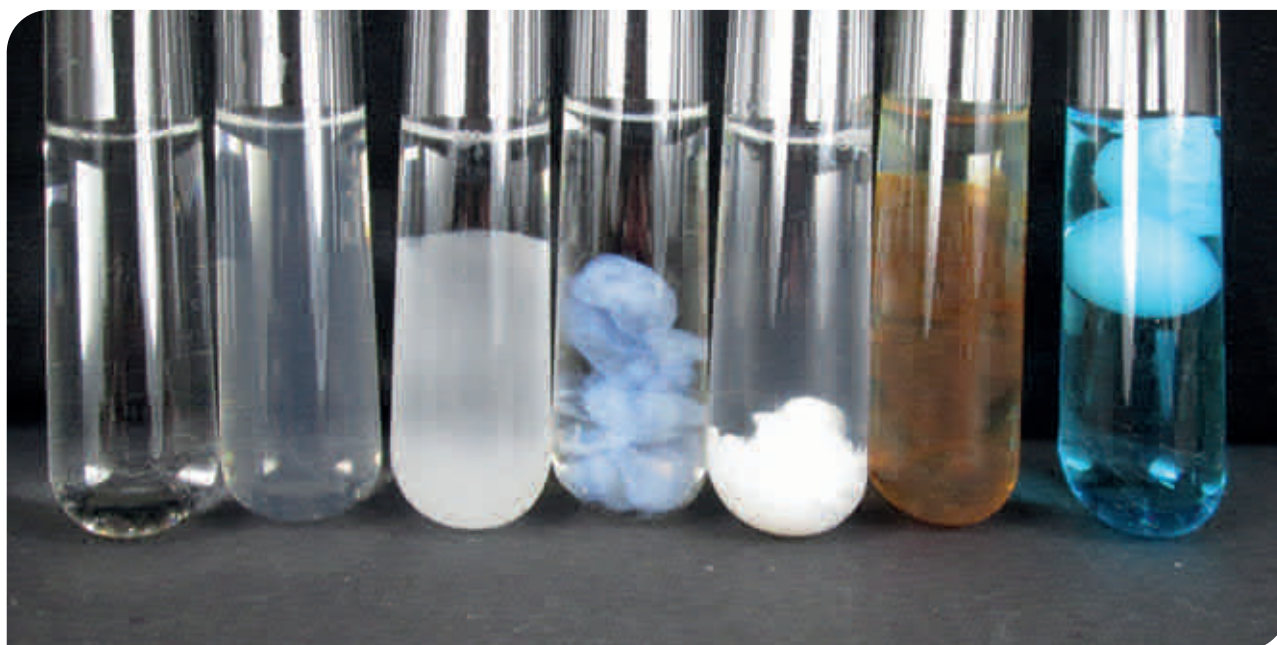
Overall, CMC has good compatibility with other water-soluble polymers and other hydro-colloids. However, some CMC grades have a limited tolerance to salts resulting as decreased viscosity. CMC also has synergic viscosity effects with some non-ionic gums. These special cases are discussed below in more detail. It can be concluded that low-viscosity grades with high DS value and even substitution are typically the most compatible.

Inorganic salts

The CMC molecule will change its conformation (coiling will occur) in solution when exposed to various types of electrolytes (salts, acids, or alkalis) often resulting in a decrease in the viscosity. This behavior is most pro-

nounced in dilute solutions (< 0.5% solution concentration), and high molecular weight CMC grades. At higher concentrations the effect diminishes because the migration of the counter-ions is restricted due to the high local viscosity in the solution. The presence of an electrolyte can also affect the solubility of the CMC molecule.

The effect of inorganic salts on the viscosity of a CMC solution depends mainly on the ability of the cation of the salt to form a soluble salt with CMC. The compatibility also depends on the concentration of the inorganic salt and the CMC properties (degree of substitution, the distribution of the side groups and molecular weight).



Salt	Compatibility	Salt	Compatibility	Salt	Compatibility	Salt	Compatibility
Na ₂ SO ₄	C	K ₂ CO ₃	C	FeSO ₄	P	ZnCl ₂	P
CaSO ₄	C	K ₂ SO ₄	C	NaCl	C	BaCl ₂	P
MgCl ₂	C	NH ₄ Cl	C	CaSO ₄	C	CuSO ₄	P
KCl	C	SrCl ₂	P	Al ₂ (SO ₄) ₃	P		

Figure 25: Compatibility of Nouryon CMC with some inorganic salt solutions (15%). C= compatible and P=Precipitate. Examples of CMC precipitations in strong salt environments are shown above (from left NaCl, SrCl₂, ZnCl₂, Al₂(SO₄)₃, BaCl₂, FeSO₄ and CuSO₄).



Typically, monovalent ions will generally form soluble salts with CMC, while divalent and polyvalent ions form insoluble complexes with CMC. Although calcium CMC is water insoluble, the presence of a small amount of calcium ions in the sodium CMC molecule will not make it water insoluble. Silver is atypical, because it forms an insoluble salt despite being monovalent.

High DS CMC grades have better tolerance with salts. The reason for this is that although some of the sodium ions of the CMC will be replaced, there is still enough Na-CMC to maintain the viscosity.

It should also be noted that order of addition is critical. Viscosity is less affected if the electrolyte is added to a hydrated solution of CMC rather than dissolving the CMC in the aqueous electrolyte solvent. This allows CMC to hydrate and collect the water molecules around it, shielding it from the cations that are added later on.

Polysaccharides

Our CMC products are compatible with most non-ionic and other water-soluble polymers over a wide range of concentrations. However, when working with blends, it is advisable to select reasonably similar viscosity grades unless very special properties of the blend are requested. Blends of CMC and a non-ionic cellulose derivative will, in most cases, show solution viscosities considerably higher than would be expected. Most likely this is due to formation of the hydrogen bonding between the polysaccharide molecule and the hydroxyl groups of the CMC chain. This synergic effect is illustrated in the Figure 26, where the viscosity behavior of blends between CMC and EHEC (ethyl-hydroxy-ethyl cellulose), MC (methyl cellulose), and Guar Gum are depicted.

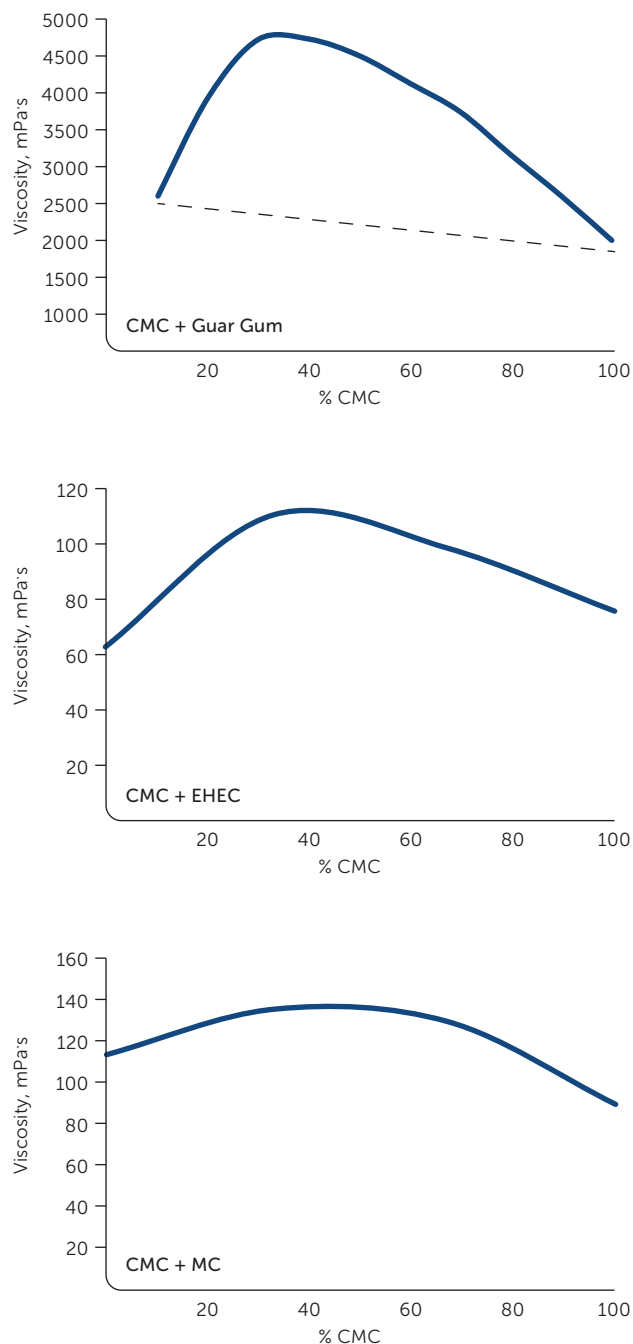


Figure 26: CMC shows synergistic effect in viscosity with some other polymers. Synergy effect is illustrated here with Guar Gum, EHEC (ethyl-hydroxy-ethyl cellulose) and MC (methyl cellulose).





Prevention of chemical and microbial degradation of the CMC solution

Although CMC has good stability towards chemicals, some enzymes (i.e., cellulases) and oxidants degrade the cellulose chain, and thus, might cause serious, irreversible viscosity decreases.

The normal route of enzyme contamination is via micro organisms present in the environment. These contaminate the system where CMC is used and start producing enzymes. It is important to use clean equipment when handling CMC to avoid possible microbial contamination. An efficient way to stop enzymatic attacks is to prevent growth of microorganisms. This can be done by heat treatment or by adding a preservative. Heating a solution for about 30 minutes at 80 °C, or about 1 minute at 100 °C, is normally sufficient to destroy the micro organisms, but not to influence the CMC. Complete inactivation of cellulolytic enzymes may require a somewhat higher temperature and/or longer time.

Some preservatives suitable for CMC solutions are listed below.

- Formaldehyde
- Sodium salt o-phenylphenate
- Hydroxyquinoline
- Phenol

- Thymol
- Sodium pentachlorophenolate
- 2-Biphenylol
- Sodium N-chloro-para-toluenesulfonamide

Suitable preservatives for food, cosmetic and pharmaceutical uses are given below.

- Sodium benzoate
- Methyl parahydroxybenzoate
- Sodium propionate
- Sorbates (Na and K salts)

Further information about type and amount of preservative should be requested from the preservative manufacturer.

Oxidants, e.g., chlorine and hydrogen peroxide, cause degradation of the cellulose chain and lower the viscosity of the CMC solution. Oxidative degradation occurs under alkaline conditions in the presence of oxygen. Metal ions, e.g., Fe^{2+} , accelerate alkaline degradation. To prevent oxidative degradation, CMC solutions should not be exposed to the open air for longer than necessary, especially at elevated temperatures and pH. For prolonged storage, CMC solutions should be preserved as soon as possible after preparation and, if possible, maintained at neutral pH. Oxygen and sunlight should be excluded.

Packaging and shelf-life

Standard package is a 20 Kg paper bag but also big bags and bulk deliveries are available. our CMC package material, size and labeling can be tailored according to customer needs.

All CMC/cellulose gum grades are derived from wood or cotton cellulose, and since they are biodegradable, the shelf-life of these products is limited. The shelf-life for our CMCs/cellulose gums is between 24-36 months depending on the grade.

After this period some minor changes in the chemical properties of the product are unavoidable.

able. This is particularly noticeable for the high viscosity grades. The viscosity and moisture content analyses can be used to confirm the product quality (further details of methods can be found in the Appendix).

CMC is hygroscopic, meaning that it easily absorbs moisture from the environment (Figure 27). The product should be stored in its original, sealed package, in a dry and well-conditioned place. It is important to keep the storage area dry, clean, and dust free. Although no specific temperature levels are set, our recommendation is not to store the products higher than 35 °C over an extended period of time.



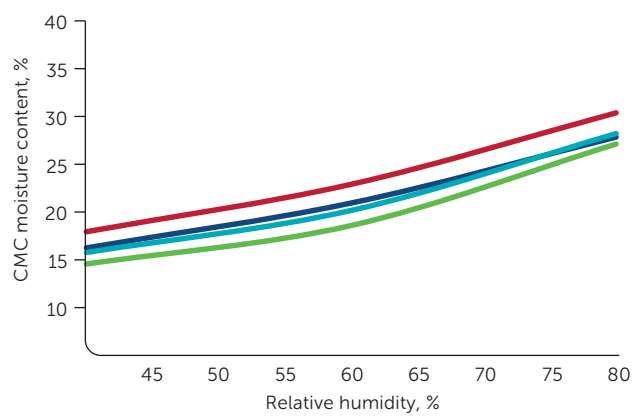


Figure 27: Influence of relative humidity on CMC moisture content at 20 °C and 45 °C. CMC remained in the humidity chamber for 48 hours prior the moisture content measurements. CMC moisture content increases as a function of relative humidity. High molecule weight grades also show more moisture absorption compared to low molecular weight grades. The elevated temperature show here less CMC moisture absorption as the warmer air is capable to hold more moisture.

Low Mw, 20 °C
 Low Mw, 45 °C
 High Mw, 20 °C
 High Mw, 45 °C



Appendix

Key rheological terms for CMC solutions

Rheology is the science of the deformation and flow of matter. Rheological analyses provide important information for many industrial processes and commercial products, where a fluid's processing and flow properties need to be optimized.

When rheological behavior is analyzed, the matter is subjected to deformation by applying a known force, and the response to that deformation is measured.

Shear stress and shear rate

The applied force is typically expressed as a shear stress, that is, the applied force per unit area. Shear rate allows us to take into account a velocity gradient. With shear rate we can quantify the speed of the shear flow resulting from the applied shear stress. This is important as fluids may behave differently with low and high shear rates. And, the application defines the relevant shear rate area. For example, in the paper industry it is well-known that the lower shear rates are relevant to the pumping and mixing of the coating colors, whereas the high shear rates are needed to mimic fluids behavior in the blade coating process.

Viscosity

Viscosity is one of the key rheological parameters used to differentiate CMC grades. It is a fluid's resistance to flow and is typically reported in units of centiPoise (cP) or milliPascal seconds (mPa·s). In shear deformation, viscosity

is the ratio of applied shear stress to the resulting shear rate. Viscosity is also highly dependent on the temperature and, thus, the temperature value should be always reported along the measured values.

$$\text{Viscosity, } \eta = \text{Shear stress, } \tau / \text{Shear rate, } \dot{\gamma}$$

With non-Newtonian fluids the viscosity depends on shear rate and, therefore, it is typically expressed as a function of the shear rate. When reported as one single value for the non-Newtonian fluids, the term apparent viscosity is used to highlight that it is valid only at the certain shear rate.

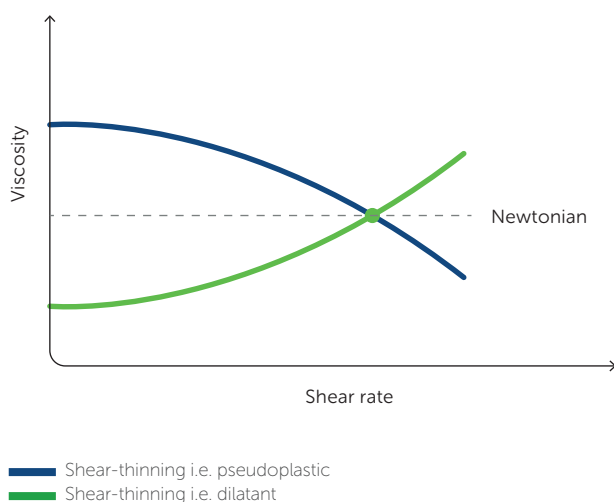
In extensional viscosity, deformation is not caused by shear stress, but by pulling the material in an extensional manner to test the fluid's resistance to stretch. This parameter is typically used to describe flow behavior of polymer solutions. The extensional viscosity plays an important role especially in pressure-driven flows (e.g., in spraying, inkjet printing and high pressure homogenizers in food processing), but also, for example, in stretching of a dough or in a roll coating.

Newtonian and Pseudoplastic behavior

A fluid can be considered to be Newtonian if the viscosity shows no dependency on the shearing rate and time. Most fluids are non-Newtonian, but can still show Newtonian behavior over some shear rate range. CMC

solutions are typically Newtonian or shear-thinning, i.e., pseudoplastic. This shear-thinning behavior is typically due to a polymer's tendency to orient along the flow when the shear rate is increasing.

Many real-life fluids need a critical level of stress to initiate the flow. This is called as a yield stress. This behavior can be seen in ketchup, for example, the bottle needs to be shaken to make the ketchup flow.



Time dependent flows – Thixotropy

For many fluids, viscosity is independent of time, and behavior changes only as a function of shear rate and temperature. However, some fluids can create internal networks as a function of time at constant shear rate, which influences the viscosity. This is called as thixotropy. The viscosity of a thixotropic solution decreases as a function of time with constant shear rate. However, if the shear is removed, the viscosity and the inner structure recover over time.

With fluids that have time-dependant behavior the apparent viscosity values are influenced by their shear history.

Literature references for the key rheology terms chapter Malkin, A.Y. and Isayev A.I., Rheology. Concepts, Methods, and Applications (2006), ISBN 1-895198-33-X Mezger, T., The Rheology Handbook (2014), ISBN 3-86630-842-6

Standard analytical methods for CMC

Product delivered by Nouryon is typically accompanied with the following analytical data as a minimum: moisture content, CMC content and apparent viscosity. The test methods for these are briefly explained here to enable correct interpretation. Viscosity and moisture content can be also measured after longer storage period to ensure sufficient product quality. In the viscosity measurement it is crucial to only compare results that are measured with similar experimental approaches (e.g., shear rate and temperature).

Moisture content

Weigh accurately 5 g sample of CMC in a beaker. Let it dry for 4 hours at 105 ± 3 °C. Cool the beaker in a desiccator for 30 minutes and weigh it again.

$$\text{Moisture, \%} = \frac{(A - B) \times 100}{A}$$

Where:

A = weight of the original sample, g

B = weight of the dried sample, g

CMC content

Technical grades:

Determine the moisture content of CMC.

Wash 1 - 1.5 g CMC free from salts with 80% ethanol. Dry and weigh the residual CMC.

$$\text{CMC content, \%} = \frac{A \times 10000}{\{B \times (100 - C)\}}$$

Where:

A = weight of the dried residue, g

B = weight of the sample, g

C = moisture of the sample, %

Purified grades:

Determine the sodium chloride and sodium glycolate contents of CMC according to the instructions of ASTM D1439.

$$\text{CMC content, \%} = 100 - A - B$$

Where:

A = sodium chloride content, %

B = sodium glycolate content, %

Apparent viscosity

Our quality control viscosity measurement protocol is optimized for each grade to see potential variances in the product quality.

Depending on the CMC grade, the viscosity is determined either in 4%, 2% or 1% aqueous solutions. Viscosity is typically measured with a Brookfield LV viscometer .

It is important to note that viscosity is dependent on the shear rate, and it can be time-dependent. Therefore, one point viscosity value is typically called apparent viscosity and is comparable only when similar sample preparation is followed and, when the values are measured with same shear rates.



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