Fibers for Life.

JRS CHEMISTRY

Plant-based Additives for Waterborne Adhesives

Technical Properties and Case Studies.

Bio-Adhesives – What does it mean?

Background solvent based vs waterborne adhesives

Adhesive materials are as diverse as their areas of application. Attempting to group them, one could name pressure sensitive adhesives (PSA), water- or solvent-borne solutions/dispersion adhesives, one component (1K) -as well as two components (2K) ones, and lastly, hotmelts. Within this list, we focus mainly on one component waterborne systems, which account for an increasing proportion of globally produced adhesives.

In recent years, the focus has shifted gradually from solvent based to water based systems, driven by the megatrend for solutions with a lower environmental footprint. Nonetheless, it is clear that solvent based adhesives are still most common in sectors, where fast and strong bonding as well as short drying times are very important. They are also favored in areas where their resistance against low temperature is crucial. However, considering all facts, waterborne systems are superior in almost all environmental aspects, security, pollution and handling. More and more, modern waterborne formulations can match solventborne adhesives even in high performance applications.

Renewable materials pathways in adhesives

In many sectors, waterborne systems are already well established and in others on the rise, but how is it with biobased materials?

Still, almost all waterborne formulations are dispersions of fossil based acrylates, polyurethanes, rubbers and polyvinyl acetates. Meanwhile, some sources claim a CAGR of 10 % or more for adhesives based on renewable polymers like bioplastics, polysaccharides and proteins. Especially consumer awareness in the packaging industry is a driver for more sustainable solutions.

There are three main opportunities for adhesive formulators to fully or partly replace their fossil-based ingredients with bio-based and renewable ones. From these opportunities two aim to replace the main binder in the adhesive and one aims at the various additives. The most straightforward one is to wait for the chemical industry to offer 1:1 replacements of common binder polymers which are synthesized with a bio-based feedstock. However, it is unlikely that all polymers can be synthesized in such a way, while staying economically attractive. The second pathway to quickly get a large bio-based percentage in the adhesive is to replace the binder with new bio-based polymers or even natural ones. Nonetheless, especially at early stages of development it is a challenge to compete with established solutions. This is also the reason, why many formulators are more reluctant to touch the additives, which have a relatively low mass percentage. But, it is essential to tackle this challenge at some point to get a fully bio-based and sustainable product.

For the additive class of rheology modifiers, JRS took the challenge and developed a unique set of plant-based additives for waterborne formulations, which also bring the needed performance into the formulation. On the following pages we are going to highlight key properties of two of our most innovative product classes: Microcrystalline Cellulose Gels and natural alginates.

Your Sustainable Alternatives

Alginates & cellulose gels

First of all, the main function of a rheology additive is to thicken the solution to the desired viscosity. Of the two products we are looking at, alginates and Microcrystalline Cellulose Gels (MCG), both do this well over a wide pH range.

Furthermore, MCG shows excellent stabilizing properties even at low viscosity and quantity. Alginate on the other hand does only stabilize dispersions after their gelling reaction with multivalent cations such as Calcium cations. This gelling reaction with Calcium happens exponentially, meaning that low concentrations of Calcium cations under 0.033 % do normally not induce gelation. Therefore, average quantities and fluctuations of calcium in tap water do not hinder the production process and various pre-gels can be formed.

While alginate gel-networks are irreversibly destroyed by high shear energy and then form lumps, non-gelated alginates are shear thinning. Here, grades with lower viscosity show a more intensive behavior (Figure 2).

Regarding the impact of shear stress, MCGs show intriguing properties. Due to a strong thixotropic character of MCG containing solutions (as seen in Figure 3), they are ideal candidates for e.g. spraying applications and defined destabilization of static dispersions during application.

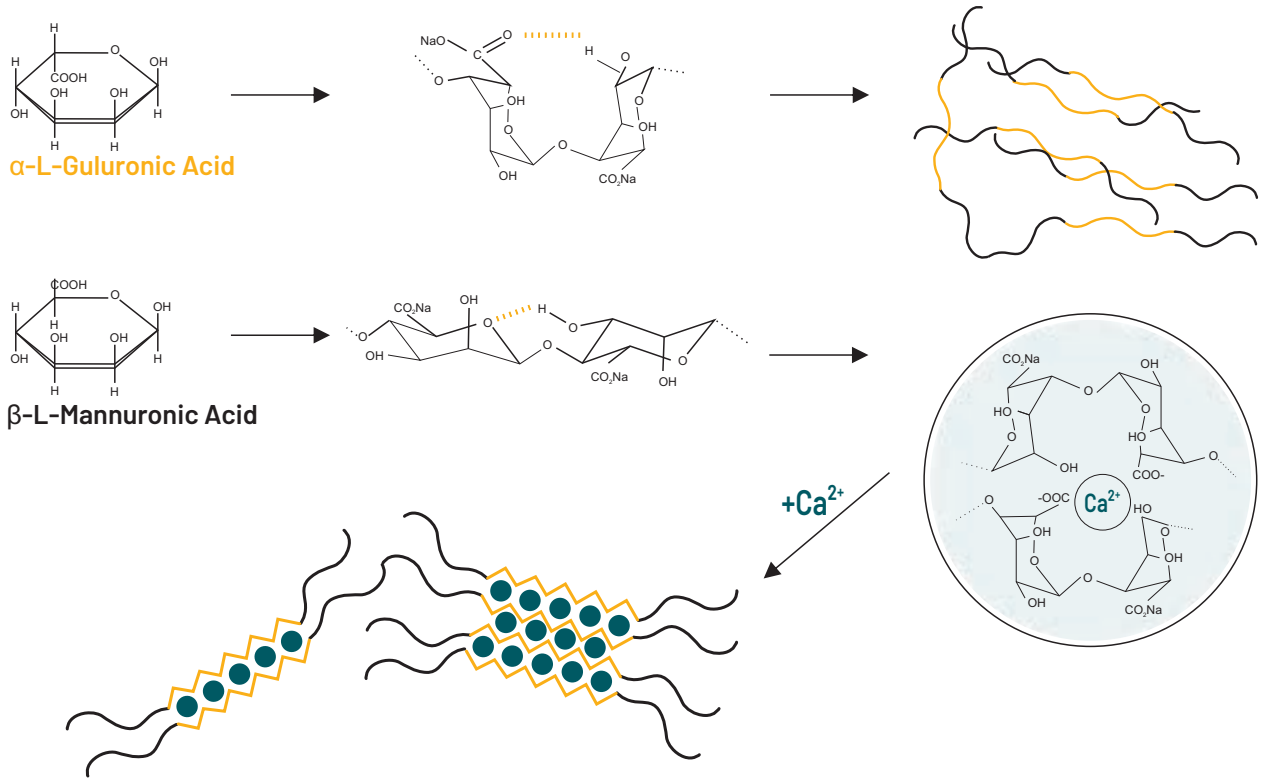

Figure 1: Sodium alginate gelation mechanism according to the 'egg-box' model.

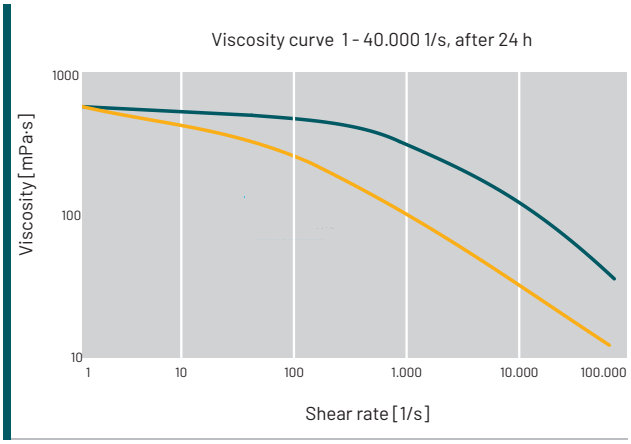

Figure 2: Shear dependent viscosity of low viscous (orange) and higher viscous (blue) alginate grades with the same initial viscosity.

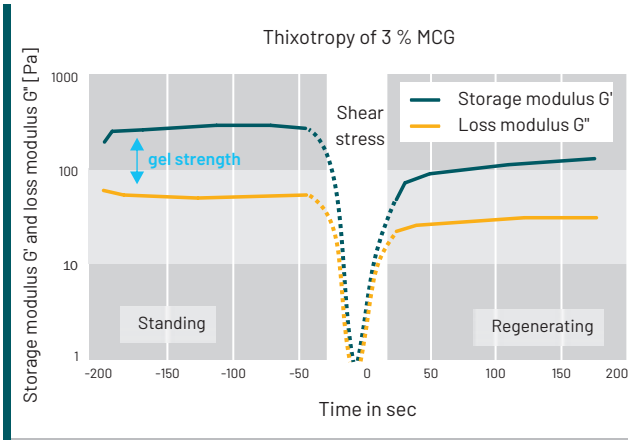

Figure 3: Gel strength and viscosity of MCG under shear stress.

As displayed in Figure 4, MCG gels and alginate (which was gelled with Calcium) maintains the gel character even at higher temperatures. However, in contrast to MCGs, non gelled alginates will undergo a degradation process at elevated temperatures in a short time-frame (as seen in Figure 5). This has to be considered during formulation design. The chemically unmodified nature of alginates and their tunability through ion content make them excellent components of bio-based and renewable adhesive as well as coating systems. Furthermore, the unique synergies with other hydrocolloids such as pectins offer countless opportunities for tailoring your unique formulation.

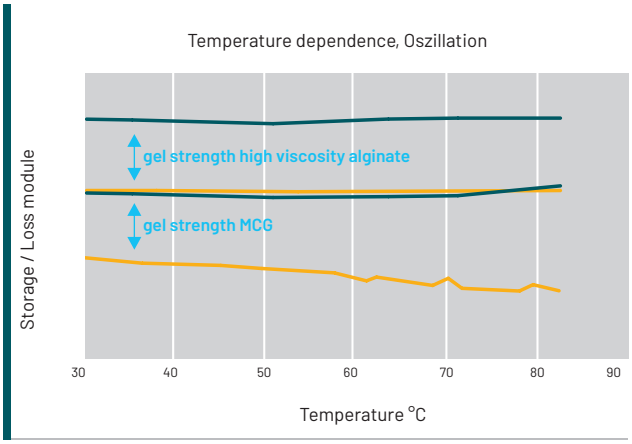

Figure 4: Temperature stability of MCG and crosslinked alginate gels.

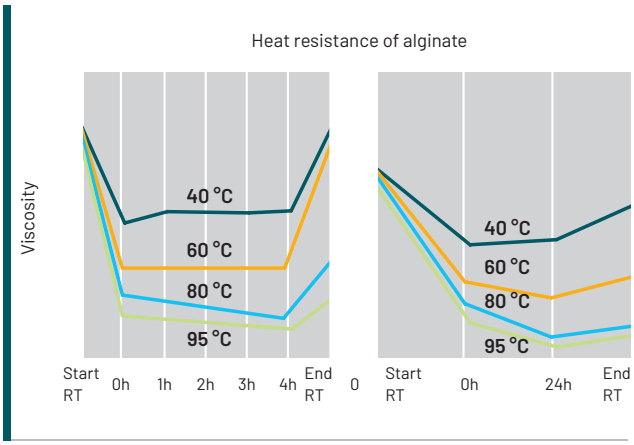

Figure 5: Heat resistance and degradation of alginates in solution (RT = room temperature).

Proof of concept in PSA

To find out how plant based hydrocolloids fare against acrylate thickeners, we commissioned trials at the Fraunhofer Institute IFAM to test a formulation of pressure sensitive adhesives. In the trials, a commercially available waterborne system was used, consisting of 98 % (w/w) binder (with 50 % water), 1 % defoamer and 1 % rheology additive. As a proof of concept, two other formulations were created with the commercial acrylate rheology additive being substituted with JRS hydrocolloids. The goal was, to define the impact of hydrocolloids on adhesion performance in PSA.

The formulations (F0 (Standard), F1 and F2) were applied on PET foils (25 mm width and 25 µm strong) with a wet film thickness of 150 µm via doctor blade, then dried at 110 °C for 10 minutes.

With the produced tapes, three different basic adhesion tests were conducted:

1. Peel adhesion test (after Afera 5001), determining the permanent adhesion and the initial tack of an adhesive tape.
2. Shear adhesion failure temperature (SAFT) (after Afera 5013), evaluating the resistance of a PSA to a static load with continuous temperature increase (0.5 K/min).
3. Static shear adhesion test (after Afera 5012), exploring the resistance of an adhesive as a measure of time to withstand a static load.

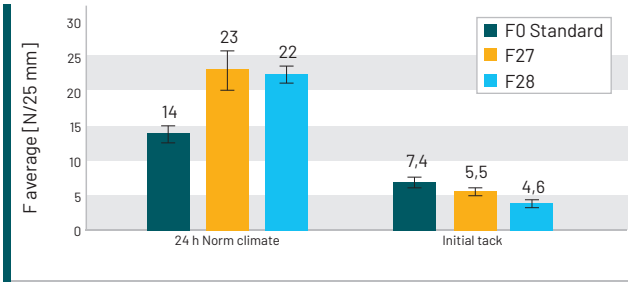

Figure 6: Adhesive strength corresponding to Peel adhesion test after 24h (left) at norm climate and after 1 minute (initial tack) (right).

PSA formula	SAFT [°C]	Shear resistance [h]
F0	224 ± 2	> 675
F1	115 ± 4	> 675
F2	114 ± 3	> 675
Binder only	93 ± 4	~ 92

Table 1: SAFT temperature and static shear test results (weight of 1000 g used).

Summarizing the testing data, the proof of concept has been given that hydrocolloids can easily substitute the fossil based additive in the tested formula. The PSA shows even better adhesion strength after 24 h, whereas it becomes more sensitive to higher temperatures. Remarkably, we could substitute 1 % (w/w) of rheology additive with only 0.3 % of JRS hydrocolloids to achieve the desired rheological profile.

It is clear, that such a formula needs optimization and that only a small proportion of the PSA has been changed to plant based ingredients, but it shows the feasibility and is a simple step for an increased biobased content.

Product Portfolio Selection

Product	Description	Viscosity [mPa·s]	pH Stability	Preparation	Gelation Conditions
ARBOCEL® MCG MF 40	Microcrystalline cellulose gel, white powder	8-200 in 2.6 % dispersion	4 - 12	High shear mixing necessary: dissolver, 10 min, 2000 rpm	Shearing in distilled water for at least 2 min
VIVAPUR® MCG 30 F		1600-4000 in 2.6 % dispersion	3 - 12		
ARBOCEL® P 4000 SE		7000-11000 in 2 % dispersion	3 - 12		
ARBOCEL® CE 2910 HE 50 LV	Hydroxypropoyl-methylcellulose, whitish powder	40-60 in 2 % solution	3 - 11	4 wing stirrer, 15 min, 400 rpm	Reversible gelation: heating above gelation temperature
VIVAPUR® HPMC E4M		3000-5600 in 2 % solution	3 - 11		
VIVAPUR® Alginate FD 170		20-50 in 1 % solution	4 - 8		
VIVAPUR® Alginate FD 155	Sodium alginate, creamy-white powder	350-550 in 1 % solution	4 - 8	4 wing stirrer, 10 min, 2000 rpm	Gelation after addition of higher valent ions, e.g. Ca^{2+}
VIVAPUR® Alginate FD 127		750-950 in 1 % solution	4 - 8		
VIVAPUR® Pectin LA-S10P	LMA pectin, beige powder	150-300 in 2 % solution	2.5 -5.5	4 wing stirrer, 10 min, 2000 rpm	Gelation after addition of higher valent ions, e.g. Ca

J. RETTENMAIER & SÖHNE GMBH + CO KG

Holzmühle 1, 73494 Rosenberg (Germany)
T. +49 7967 152-906
chemistry@jrs.de