Sustainable Cellulose-derived Rheology Modifiers for Personal Care Applications

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Abstract (Maximum of 250 words)

Rheology modifiers (RMs) are key ingredients in the Personal Care formulations that affect product function, stability, and perception. While synthetic acrylate based RMs are the most common RMS in the market currently, they are being phased out due to lack of biodegradability. In this article we introduce a more sustainable alternative based on cellulose chemistry, a hydroxyethyl methylcellulose (HEMC) polymer with INCI name Methyl Hydroxyethyl Cellulose. This HEMC polymer was evaluated in various rinse-off and leave-in formulations, and its performance as a RM was assessed with standard rheological methods. It showed excellent thickening and suspension benefits when compared to a hydroxyethyl cellulose benchmark. Additionally, it showed superior pH and electrolyte tolerance when compared to acrylate based RMs. To boost its suspension performance in shampoo chassis, blends with natural gums were explored. Combinations of HEMC with low levels of xanthan gum showed good suspension without compromising viscosity or texture. Overall, the new cellulose based HEMC polymer is a suitable RM for a wide range of hair and skin care formats, and it provides a sustainable alternative to carbomers and other acrylate based RMs.

Keywords: rheology modifier; cellulose derivatives; sustainable; biodegradable.

Introduction. Rheology modifiers (RMs) play a key role in Personal Care products as they affect formulation stability, product performance and customer perception. The rheology modifier market has grown at ~3% every year during the 2015-2020 period [1]. More than 60% of the market is captured by synthetic RMs, around 25% by semi-synthetic molecules and only 13% of the market is captured by natural RMs. Within this category, three polymers stand out: xanthan gum, guar gum and carrageenan [2].

On the synthetic category, RMs based on acrylate free-radical chemistry are the most common class of RMs in the market due to their low cost and multiple advantages. The most common RMs based on INCI names are Carbomer and Acrylates Copolymer. Their basic structure is shown in Figure 1 (left panel) although it is important to note that there is structural variation between different grades and suppliers within the same INCI name. Key performance advantages of Carbomer include efficient viscosity building, emulsion stabilization and particle suspension, yet the powder form of many Carbomer products makes them difficult to handle. Acrylates Copolymers have similar performance benefits than Carbomer and are easy to handle as most products are low viscosity water dispersions. Synthetic RMs, however, show negligible biodegradability. [3]

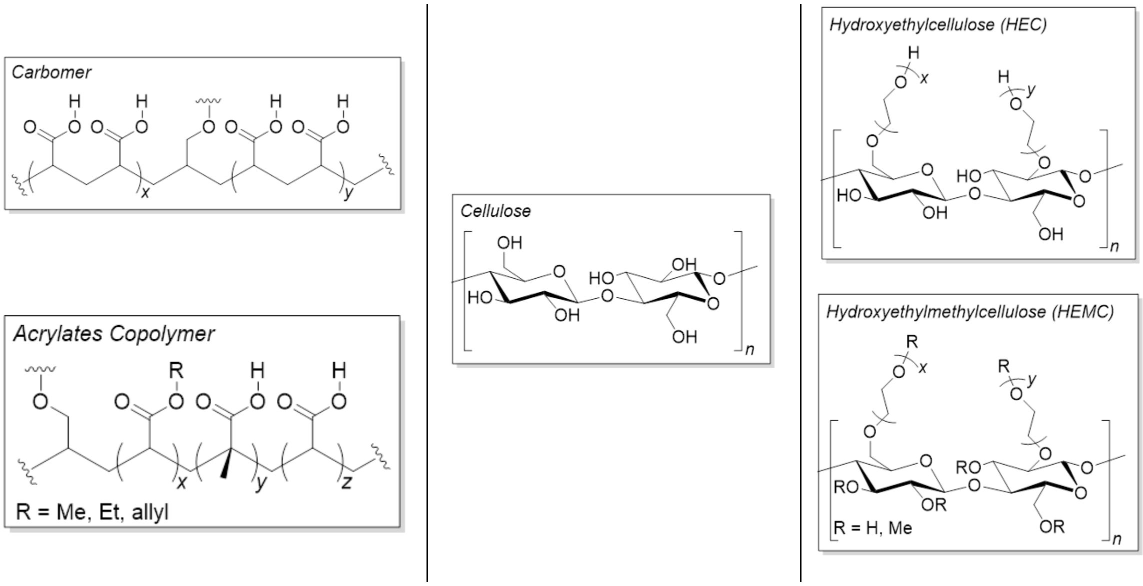


Figure 1: Chemical structure of synthetic (left) and sustainable (middle, right) rheology modifiers

The personal care market has seen a rising demand for ingredients with a better sustainability profile. Due to new regulations and changing expectations from brand owners and end consumers, the market has been looking for versatile, efficient, and cost-effective innovations with high biobased content and biodegradability to substitute acrylate based RMs.
Semisynthetic polymers such as cellulose ethers are a potential solution. Cellulose (Figure 1 middle panel) is the most abundant biopolymer on Earth, but it is not water soluble and doesn't perform as a RM [4]. Polymers derived from cellulose such as hydroxyethyl cellulose (HEC, top right of Figure 1) show efficient thickening behavior, primary biodegradability, and a large fraction of bio-based material (~50-70 wt.%). However, they have limitations due to their semi synthetic origin and the fact that they contain ethylene glycol and/or propylene glycol moieties.

Natural polymers like guar gum, starch, xanthan gum or carrageenan are potential solutions as well. They are biodegradable, mostly bioderived, and show good suspension properties in formulation. However, they tend to be expensive, don't perform well as thickeners, and cause undesired textures such as stringiness, sliminess, or jelly-like consistencies when not used at low concentrations. Some natural gums are incompatible with surfactant formulations and/or lead to hazy formulations. Additionally, there are significant variation between suppliers and sources since these materials are bio sourced.

In this article we introduce a new cellulose-derived RM polymer (HEMC) with INCI: Methyl Hydroxyethyl Cellulose and the structure shown in Figure 1 (bottom right panel). It is supplied as a 100% active powder without glyoxal surface treatment, is readily soluble in cold or warm water, and is stable at pH values in the 3-10 range. It contains ~80 wt.% of bio-based material (from cellulose) and shows inherent ultimate biodegradation under OECD 302 testing. We characterized its performance in a wide variety of personal care formats (shampoos, conditioners, skin lotions and creams) and compared it against synthetic and semisynthetic RM benchmarks. Further studies were conducted in a shampoo format to optimize suspension benefits, and here we present results obtained using blends of the HEMC product with a commercial xanthan gum.

Materials and Methods. All formulations were made with standard lab equipment and overhead mixer, and commercial materials as indicated in each subsection.

Shampoo: Water, EDTA and the RMs were added to a clean beaker and mixed at 400rpm. Amino methyl propanol was added to neutralize the RM as needed. Sodium laureth sulfate was added and the solution was heated to 60 °C. Cocamide MEA and Cocamidopropyl betaine were added while mixing until homogeneous. Then the solution was cooled down to 40 °C and the preservative and make-up water (due to evaporation) were added. After 24h of equilibration, the pH was adjusted to ~6 with Citric acid.

Ingredient	**Supplier**	**Wt. %**
Aqua (Water)		~87-88
Rheology Modifiers	Dow, various	0.45-0.9
Sodium Laureth Sulfate	Pilot Chemical	9.0
Tetrasodium EDTA	Dow	0.2
Cocamide MEA	Croda	1.0
Cocamidopropyl Betaine	Croda	1.8
Phenoxyethanol	DuPont	0.5
Citric Acid	SigmaAldrich	q.s.
Amino methyl Propanol	SigmaAldrich	q.s.

Conditioner: Water, EDTA and RM were added in a clean beaker and heated with mixing at 400rpm. Cetearyl alcohol and Glyceryl Stearate (and) PEG-100 Stearate were added once the solution reached 70 °C and mixed at high speed (750 rpm) for 10 min. The formulation was cooled to 40 °C, the preservative and make-up water were added, and mixed for 5 min more at 400rpm. After 24h of equilibration, the pH was adjusted to ~6 with Citric acid.

Ingredient	**Supplier**	**Wt. %**
Aqua (Water)	DI	~94
Rheology Modifier	Dow	0.5-1.5
Cetearyl Alcohol	Croda	1.5
Tetrasodium EDTA	Dow	0.2
Glyceryl Stearate (and) PEG-100 Stearate	Making Cosmetics	1.5
Phenoxyethanol	DuPont	0.5
Citric Acid	SigmaAldrich	q.s.

Emulsion formulations: Water and HEMC were added to a clean beaker and mixed at 400rpm until homogeneous. The oil phase (Coconut + Argan oils) was mixed separately and added to the water phase in small increments under fast mixing (800 rpm). Once all the oil phase was added, the mixture was homogenized at 10,000 rpm for 1.5 min (IKA Ultra Turrax). The preservative was then added under gentle mixing. The formulation was equilibrated for at least 12 hours prior to testing.

Ingredient	**Supplier**	**Wt. %**
Aqua (Water)		~93.5
HEMC	Dow	0.4-1
Cocos Nucifera Oil (Coconut Oil)	MakingCosmetics	3.0
Argania Spinosa Kernel Oil (Argan Oil)	MakingCosmetics	3.0
Phenoxyethanol	DuPont	0.5

Skin Cream formulations: The water phase (Water, RM and Butylene glycol) was added to a clean beaker, mixed until homogeneous at 400rpm and heated to 70 °C. The Caprylic/capric triglyceride was added to a separate beaker, mixed with the emulsifiers (PEG-100 stearate, Glyceryl stearate, Cetearyl alcohol and Ceteareth-20) and heated until molten. The oil phase was added to the water phase under fast mixing (800 rpm) in small amounts. The mixture was stirred for 5 min and cooled down to 40 °C. Make-up water and preservative were added, and the formulation was allowed to equilibrate 24h. The pH was adjusted to ~7 with Citric acid. For select formulations, salt and Lactic acid were added to and mixed until uniform.

Ingredient	**Source**	**Wt. %**
Aqua (Water)	DI	~68-73
Rheology Modifiers	Dow, Various	0.4-0.8
Butylene glycol	Across Organics	2.0
PEG-100 Stearate	Croda	1.0
Glyceryl Stearate	MakingCosmetics	3.0
Cetearyl Alcohol	Croda	1.0
Ceteareth-20	Croda	1.0
Caprylic/Capric Triglyceride	Croda	20.0
Phenoxyethanol	DuPont	0.5

Amino methyl Propanol	SigmaAldrich	q.s.
Citric acid	SigmaAldrich	q.s.
Sodium Chloride	SigmaAldrich	4.0
Lactic Acid	LotionCrafter	4.0

Rheology: The rheology of the formulation was characterized using a TA Instruments DHR-3 rheometer with parallel plate (60mm, cross-hatched, gap 1mm) and cone and plate (60mm, 0.5 degrees, gap 17 um) geometries at 25 °C. The formulations were pre-sheared for 30s at 0.5 s^{-1} and then equilibrated for 3 min prior to starting. Typical tests included oscillatory amplitude sweeps (0.02 to 200% at 1 rad/s), oscillatory stress sweeps (0.2-200 Pa at 0.5 Hz), frequency sweep tests (0.01-100 rad/s at 2% strain) and shear rate sweeps (0.01 to 750 s^{-1}).

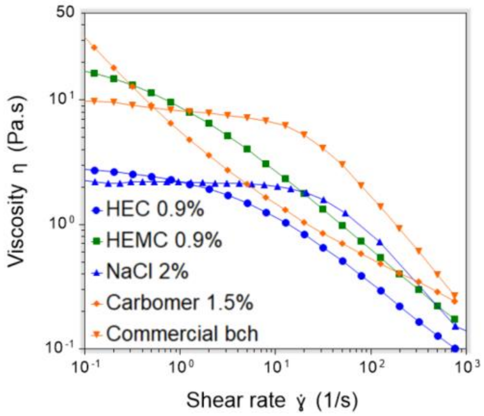
The G' and tan δ values were obtained from the amplitude sweep in the linear region (< 5% strain). Yield strain was obtained from the crossover of G' and G" curves. The viscosity values were obtained from the shear rate sweep. The shear rate index and zero-shear viscosity values were determined by fitting a Cross-Williamson model to the shear rate data if a plateau was observed at low shear rates, $\eta = \frac{\eta_0}{1+(K*\dot{\gamma})^n}$, where η_0 is the zero-shear viscosity and n is the shear rate index. If no plateau was observed, the data was fitted to a power law, $\eta = C(\dot{\gamma})^m$, where m is the shear rate index.

Suspension: A basic suspension test was carried out in which a small amount of fuchsia glitter was mixed into a 3mL aliquot of the formulation and placed in a small glass vial for several days at room temperature. Images were taken at various time points and the relative concentration and height of the glitter were used to rate the suspension abilities of the formulation.

Results. The stability for all formulations made was assessed at room temperature and 40 °C for two weeks. All formulations were stable, and the rheology was then tested. For each format, representative shear rate sweeps curves were plotted, and the extracted rheological parameters were tabulated. Curves for the amplitude sweep, frequency sweep and other tests done were not included in this article for clarity.

The results for the shampoo formulations are shown in Figure 2. As compared to traditional thickeners (HEC and NaCl), the new HEMC showed similar or higher viscosity values across the shear rate range. The zero-shear viscosity of the HEMC formulation was noticeably higher, which indicates potential suspension benefits vs. the traditional thickeners. The carbomer benchmark (30% solids) had higher zero-shear viscosity, however the thickening performance is inferior, the use level is higher, and the texture is too solid-like for a shampoo, as evidenced by tan delta << 1.

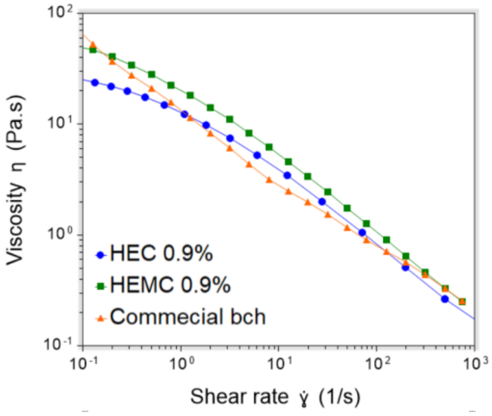
When compared to the commercial benchmark (containing sodium chloride and cocamide MEA), the HEMC formulation showed similar viscosities in the low and mid shear rate range and lower viscosities at high shear rates. This was caused by an earlier onset in shear thinning and not by an increased shear rate index. It is possible to tune this by adjusting the use level and blending with other RMs, yet it is important to mention that not all commercial shampoos have the exact rheology profile shown here.



RM	wt. %	Shear rate index	Zero-shear viscosity (Pa-s)	Viscosity at 1 s^{-1} (Pa-s)	Tan delta
HEC	0.9	0.67	2.97	2.25	2.81
HEMC	0.9	0.69	23.46	9.19	1.45
NaCl	2.0	1.08	2.22	2.19	-
Carbomer	1.5	NA	NA	6.16	0.27
Commercial bch.		1.038	8.827	8.19	6.01

Figure 2: Shear rate sweep curves for shampoo samples (left) and rheology parameters (right)

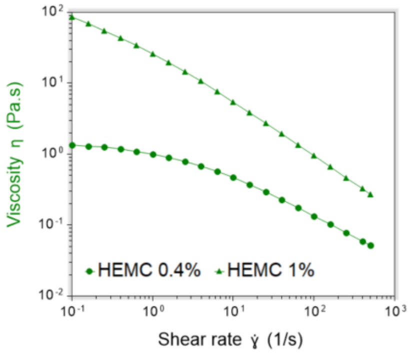
The results for the low-solid conditioner formulations can be seen in Figure 3, below. Here only HEC was tested as a competitive benchmark since NaCl and acryate RMs are seldom used in this format. HEMC showed higher efficiency as evidenced by the higher viscosities across the shear rate range. When compared to a commercial conditioner, the viscosity and shear rate index values were comparable. However the texture was different, with the commercial conditioner being solid-like (tan delta ~ 0.45) while the HEMC formulation was a viscous liquid with tan delta above unity. The difference stemmed from the commerical conditioner having higher solids content and relying on surfactant lamellae networks to provide rheology. HEMC and HEC can be good alternatives for low-solid formulations and for those in which the surfactant combinations does not result in lamellar morphologies.



RM	wt. %	Shear rate index	Zero-shear viscosity (Pa-s)	Viscosity at 1 s^{-1} (Pa-s)	Tan delta
HEC	0.9	0.711	31.14	12.39	1.725
HEMC	0.9	0.722	68.23	18.97	1.165
Commercial bch.		0.606	NA	12.19	0.447

Figure 3: Shear rate sweep curves for conditioner samples (left) and rheology parameters (right)

In addition to the rinse-off formats described in the previous paragraphs, we evaluated the HEMC polymer in emulsion formats. Given the more hydrophobic nature of its backbone (as compared to HEC and carbomer), we expected performance benefits as a polymeric emulsifier. Oil-in-water emulsions with varying HEMC concentrations were formulated and they showed good stability at room temperature for at least a month. The emulsion with 1.0% HEMC also showed good stability at 50 °C while the emulsion with 0.4% HEMC showed some phase separation – additional stabilizing agents or emulsifiers would be required to achieve stable formulations. The shear rate sweep curves and rheology parameters for the emulsions are shown in Figure 4.

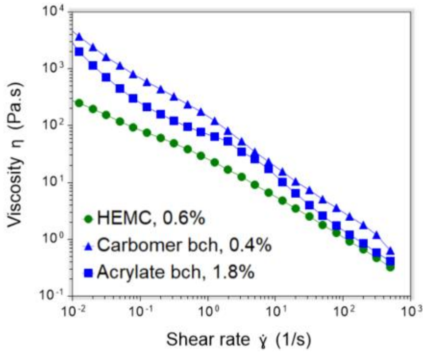


RM	wt. %	Shear rate index	Viscosity at 1 s^{-1} (Pa-s)	G' (Pa)	Tan delta	Yield strain (%)
HEMC	0.4	-0.512	1.01	0.347	2.4	NA
HEMC	1.0	-0.725	26.07	19.54	0.92	30

Figure 4: Shear rate sweep curves for simple emulsion samples (left) and rheology parameters (right)

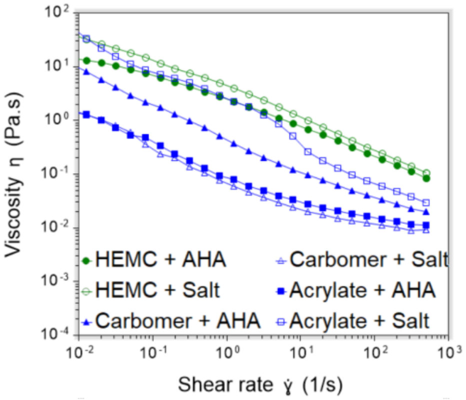
The viscosity values for the 0.4% emulsion were lower than those for the 1.0% emulsion, as expected. The tan delta for the 0.4% emulsion was much higher than for the 1% emulsion and its shear rate index was lower than for typical skin creams, indicating low HEMC concentrations are suitable for lotions and other formats with liquid consistency. Higher HEMC concentrations are suitable for creams and other formats with solid-like consistency.

The performance of HEMC was also assessed in more complete formulations featuring common emulsifiers. First, three skin creams were formulated with HEMC, a carbomer benchmark and an acrylate benchmark (30% solids). These creams were stable at room temperature and at 50 °C for a week. The shear rate sweeps and rheology parameters are shown on the top row of Figure 5. The creams formulated with the synthetic RMs showed the highest viscosity and storage modulus, as well as the lowest tan delta values. While the texture of the HEMC cream was similar to that of the benchmarks, it would be necessary to increase the use level slightly to match the viscosities achieved by the other RMs.



Standard Creams

RM	wt. %	Shear rate index	Viscosity at 1 s^{-1} (Pa-s)	G' (Pa)	Tan delta	Yield strain (%)
HEMC	0.6	-0.626	22.4	68.4	0.664	25
Carbomer	0.4	-0.797	122.3	1485.6	0.225	25
Acrylate	1.8	-0.767	64.9	2047.6	0.202	10



AHA Creams

	wt. %	Shear rate index	Viscosity at 1 s^{-1} (Pa-s)	G' (Pa)	Tan delta	Yield strain (%)
HEMC	0.38	-0.495	2.26	4.26	0.98	5
Carbomer	0.3	-0.578	0.37	1.65	0.521	15
Acrylate	0.95	-0.464	0.08	0.13	0.862	2

Salt creams

	wt. %	Shear rate index	Viscosity at 1 s^{-1} (Pa-s)	G' (Pa)	Tan delta	Yield strain (%)
HEMC	0.38	-0.547	3.97	14.8	0.64	10
Carbomer	0.3	-0.489	0.06	0.09	4.41	NA
Acrylate	0.95	-0.683	2.25	42.6	0.196	15

Figure 5: Shear rate sweep curves for skin cream samples (left) and rheology parameters (right). Top row are standard creams, bottom row are creams with added AHA and salt

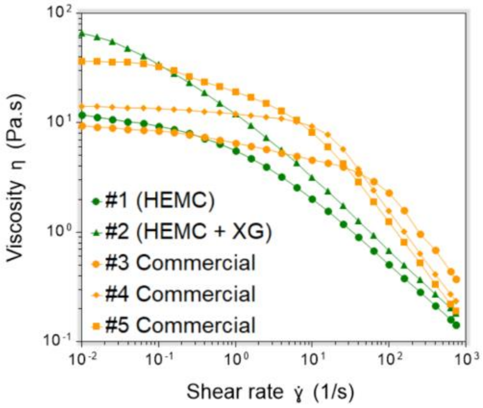
Subsequently, two different sets of skin creams were made with lower RM concentrations. One set contained a model alpha hydroxy acid (lactic acid) and the other set contained a model electrolyte (NaCl). These sets were made to study the effect of the addition of active ingredients on the rheology of such creams. The rheology curves and parameters are shown in the bottom row of Figure 5.

The viscosity of the carbomer and acrylate creams was noticeably lower than that of the HEMC cream, a reversal of the trend observed in the base formulation discussed above. The reason for this observation is that HEMC is a nonionic polymer that is unaffected by moderate changes in pH and ionic strength of the formulation. In the presence of the AHA, the viscosity of the synthetic RM creams was 1-2 orders of magnitude lower than than of the HEMC cream. The carbomer cream showed some phase separation after one week at room temperature. In the presence of salt, the viscosity of the acrylate cream was lower (but similar) than that of the HEMC cream, while the viscosity of the carbomer cream was much lower. The carbomer cream lost all structure, as evidenced by the high tan delta value, and showed phase separation a few days after being formulated. It is evident that nonionic polymers such as HEMC are better RMs for formulations with water-soluble acids and salts.

As discussed earlier, the HEMC material showed excellent thickening performance and potential suspension benefits in surfactant-containing rinse-off formats. While these benefits were enough to suspend emulsified natural oil and silicone droplets, it was found that they were not sufficient for denser or larger particles. We explored two strategies to boost suspension performance, increasing the use level and blending with a natural suspending agent.

Increasing the HEMC use level yielded moderate increases in zero-shear viscosity at the expense of higher cost-in-use and undesired texture, so this option was not pursued further. For the second strategy, blends with xanthan gum and carrageenan from CP Kelco were explored (0.75% HEMC with/without 0.15% natural gums). At these use levels only xanthan gum (XG) yielded improved suspension so only these formulations are shown in this article.

Figure 6 shows the shear rate curves and rheology parameters of the experimental formulations used for the suspension study as well as three commercial shampoos used as benchmarks. The RMs used in the commerical shampoos were sodium chloride and PVP for sample #3, sodium chloride and carbomer for sample #4, and sodium chloride, stearyl alcohol and cetyl alcohol for sample #5 (hence the opaque color in Figure 7). Regarding zero-shear viscosity, sample #1 (HEMC only) had a similar value as benchmarks #3 and #4 and since it was below 20 Pa-s, poor suspension performance was expected. Sample #2 (HEMC + XG) had a higher zero-shear viscosity, even higher than benchmark #5, so suspension was expected. The mid- and high-shear rate viscosity values for the experimental samples was comparable or lower than those of the benchmarks, and so was the shear rate index. In terms of texture, the experimental samples were still liquid-like but they did not flow as easily as the benchmarks (as evidenced by tan delta >1 but below that of the benchmarks).



	RM	Shear rate index	Zero-shear viscosity (Pa-s)	Viscosity at 1 s^{-1} (Pa-s)	Tan delta
#1	HEMC	0.649	11.88	5.54	1.72
#2	HEMC + XG	0.651	84.63	11.93	1.04
#3	Commercial	0.853	7.75	6.53	4.32
#4	Commercial	1.092	13.34	12.01	7.72
#5	Commercial	0.885	33.22	19.12	3.29

#1 – HEMC 0.75%, #2 – HEMC 0.75%, Xanthan Gum 0.15%

Figure 6: Shear rate sweep curves of suspension study samples (left) and rheology parameters (right)

Suspension was assesed using a glitter test and taking photos at set intervals. As shown in the top row of Figure 7, the addition of low concentrations of xanthan gum to HEMC clearly improved suspension. The glitter on sample #2 remained well suspended for at least 10 days while the glitter on sample #1 (without xanthan gum) settled after a several days. Further studies are needed to determine the minimum use level of xanthan gum needed to achieve stability for different particulates (natural oils, silicone oils, anti-dandruff actives, etc.) and maintain adequate formulation clarity. The glitter test was performed with the commerical shampoos as well, and only sample #5 showed suspension benefits. The glitter quickly settled for samples #3 and #4, which was surprising since sample #4 contained carbomer. The suspension benefits for sample #5 arose from lamellae formed by the fatty alcohols present, which also turned the formulation opaque.

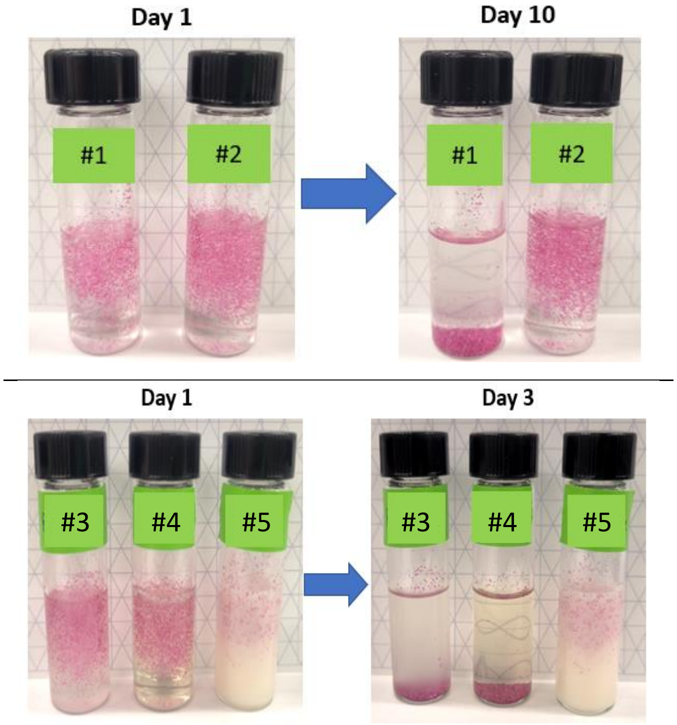


Figure 7: Timed photos to visually assess suspension performance

Discussion. This study introduced a new cellulose-based rheology modifier that is suitable for a wide range of personal care formats, from surfactant-containing formulations like shampoo and body wash, to emulsified formulations such as conditioners, skin lotions and creams. In addition to showing a better biodegradability than HEC and other cellulosic RMs, the HEMC polymer showed higher thickening efficiency and emulsifying benefits in formulation. As compared to natural gums and biopolymers, the HEMC was broadly compatible in surfactant systems and had a wider use level range before the onset of undesired textures. And when compared to synthetic RMs, the textures achieved were slightly different and the efficiency was lower. If the goal is to match the viscosities of existing formulations with carbomer and other acrylate RMs, then the use level of HEMC needs be adjusted. As these synthetic RMs are being phased out, the new HEMC RM is a suitable and versatile alternative with a high amount of biobased carbon and biodegradability given that it is a cellulose derivative.

Conclusion. This article introduced a new biodegradable rheology modifier polymer based on cellulose chemistry. This HEMC polymer showed good thickening and suspension performance in a variety of rinse-off and leave-in formats containing surfactants and emulsified oils. It showed good pH and electrolyte tolerance as compared to acrylate benchmarks. To further boost the suspension benefits of HEMC shampoos, blends with natural gums were explored. It was found that the addition of low amounts of xanthan gum to HEMC formulations resulted in great suspension without negatively affecting the viscosity or texture of the formulation. In summary, HEMC is a suitable and more sustainable alternative to acrylate based RMs.

Acknowledgments. Thank you to Beth Johnson, Isabelle Van Reeth, Sandro Sato, Deepak Dandekar, Greg Cardoen and Blondine Van Roy for their technical guidance, formulation suggestions and support of the work. Thank you to Alexandra Hild and Joerg Neubaeuer for their collaboration. All are colleagues at Dow North America, Europe, and India.

Conflict of Interest Statement. NONE.

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