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Revealing value from bioderived polymers: effects of locally sourced polysaccharides on the rheology of limestone mixtures

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Abstract

Admixtures are important constituents to enhance the performance of concrete. They allow for more efficient use of binders which can mitigate negative environmental impacts from producing cement-based materials. Commonly used rheology modifying agents like polycarboxylate ethers or cellulose ethers are synthetic or semi-synthetic, respectively. This requires additional energy consumption for their production and global supply chains particularly for many developing regions, which will be large consumers of concrete in the future. However, many locally available bio-based polysaccharides could be effectively used instead. These polymers are often overlooked by engineers and scientists due to their limited distribution and inherent complexity, yet they represent an under-leveraged source of precursors for admixtures. This study investigates the action mechanisms of some bio-based rheology modifying agents, i.e., acacia gum and miscanthus gum, and provides a comparison to a conventionally modified starch. The results show that the mechanism of action of these polymers is closely related to the composition of the mixture, mixing regime, and the composition of the aqueous phase. Depending on the agent, either plasticizing or stabilizing effects on rheology can be revealed.

Keywords: Polysaccharides, superplasticizers, hydration, cement

27 **1. Introduction**

28 Enhanced durability properties and mechanical behavior of concrete have enabled the
29 construction of high-performance structures and development of a more resilient built environment [1–
30 3]. Over the course of several decades, chemical admixtures have become a key tool to control the fresh
31 properties and the related quality of concrete [4]. These admixtures have enabled workable, higher
32 strength concretes with fewer internal defects [5,6]. These higher-strength and higher quality concretes
33 can allow for more efficient material use and, thus, increase the sustainability of concrete [2,4].
34 However, standard chemical admixtures are expensive and inaccessible to producers in the Global South
35 [7,8]. In this work, the rheological effects are evaluated for limestone slurries with a variety of gums
36 derived from different regions in the world.

37 As future regions across the Global South develop, the consumption of building materials, and
38 especially concrete, will increase. Global concrete consumption is inevitably accompanied by a large
39 amount of greenhouse gas emissions [9]. As the availability of supplementary cementitious materials is
40 already restricted [10,11], access to regionally available and affordable chemical admixtures could be
41 one of the few levers available to drive higher quality concrete production and enable more-sustainable
42 future developments. Furthermore, many established admixtures are based on naphtha and thus depend
43 on global value chains. Hence, alternative admixture feedstocks will be needed to make the products and
44 their supply chains less energy and carbon intensive [12,13].

45 Acacia gum and miscanthus gums are two bioderived admixtures evaluated in this work. Acacia
46 gum (which consists to a large extent of gum Arabic) is a complex polysaccharide derived from the sap
47 of acacia trees [14,15]. Literature describes them as slightly acidic, water-soluble, and containing a mix
48 of mineral salts [14–16]. Predominantly grown in Africa, Senegal and Sudan is the largest exporters of
49 acacia gums [17]. Acacia gums can have both plasticizing and stabilizing effects depending on the

dosage, gum composition, and paste system [18–20]. Other works have investigated acacia gum to modify the workability of cement-based systems (e.g., [21–23]) and as a dispersant (e.g., [23,24]). However, the industrial use of acacia gums is largely limited to the food and cosmetic industries [15,24].

Miscanthus grass is composed of cellulose, hemicellulose, and lignin [25]. Research has primarily focused on miscanthus and other lignocellulosic biomass as an alternative to petroleum-based fuels (e.g. [26–28]). Miscanthus, specifically, is of great interest because it requires relatively low amounts of input and management. As a C4 plant, meaning it is more efficient at photosynthesis in hot climates with restricted water access, miscanthus has relatively high biomass yields in adverse environments [25,29,30]. Valorizing this biomass into fuels or petrochemical resources requires lignin extraction and then bio-refinement through fermentation or hydrolysis. These processes are typically done at elevated temperatures and often with hazardous reagents to maximize extraction and conversion [31,32]. Currently, most of this processing remains at laboratory scale, but the environmental and economic implications of these systems need to be considered [27,33]. In rheological studies have investigated carboxymethylcelluloses derived from miscanthus feedstocks [34] and nanofilms made with cellulose nanocrystals derived from miscanthus fibers [35]. However, little attention has been given to miscanthus gums in cement-based systems, though initial work by Schmidt et al., has shown that miscanthus gums could reduce the dynamic and static yield stress in cement pastes [17]. In this study minimally processed acacia gums and miscanthus gums are evaluated in limestone slurries using rheological measurements to better understand the behavior of these compounds.

69

2. Materials and Methods

2.1. Materials

72 The behavior of bioderived acacia gum and miscanthus gum were evaluated using a shear
 73 rheometer to determine the effect of the biopolymers in a particle-liquid systems. For rheological
 74 evaluation, slurries were made using limestone powder, deionized (DI) water, and polycarboxylate
 75 ethers (PCE). The water to limestone powder ratio was set to 0.22, which corresponds to the minimum
 76 water demand according to the Punkte test [36]. The PCE, Melflux AP 101F (BASF; Ludwigshafen,
 77 Germany), was used to disperse the slurry and provide a consistency that can be tested in a cylinder
 78 system in a rheometer. A hydroxypropylated starch with a degree of substitution of 0.6, was selected so
 79 that the behavior of the unmodified bio-based admixtures could be compared to an industrially modified
 80 admixture. Admixture dosages and slurry mixture IDs can be found in Table 1.

81
 82 **Table 1.** Limestone slurry mixture IDs and admixture dosages used to make slurry mixtures for
 83 rheological evaluation.

ID	Bio-based admixture	Admixture dose (% limestone mass)	PCE dose (% limestone mass)
REF	-	-	
Ac	Acacia gum		
Mi	Miscanthus gum	0.042	0.062
St6	Hydroxypropylated starch		
0.5xSt6	Hydroxypropylated starch	0.021	

84

85 Acacia gum, in solid form, was ground with a mortar and pestle into a powder. The water-
 86 soluble fraction of miscanthus was extracted from 2 cm long pieces of dried miscanthus by soaking in
 87 DI water for 72 h. A non-bleached coffee filter, pre-soaked in DI water, was used to separate the liquid
 88 and solid fractions. Then the residual miscanthus was soaked for an additional 24 h and, again, the
 89 leachate was collected using the same filter. Both leachates were combined and then dried in a 40 °C
 90 oven for 24 h, until only the extracted solid fraction remained.

91

92 2.2. Methods

93 Limestone slurries were mixed using an STARVISC 200-2.5 control measuring mixer (IKA;
94 Staufen, Germany). To mix the slurry, the PCE and limestone powder were combined, then water was
95 poured in the mixture and mixed at 250 RPMs for 45 s. Then the starch, acacia gum, or miscanthus gum
96 were added to the mixture and mixed for a final 45 s at 250 RPM before being loaded into the testing
97 cell. Three replicates were tested for each slurry mixture.

98 All testing was performed using a concentric cylinder cell (CC27) with cup dimensions of
99 28.895 mm (d) x 120.2 mm (height) and a bob measured 26.665 mm (d) x 72.5 mm (height) in a MCR
100 502 WESP shear rheometer (Anton Paar; Graz, Austria). A three-part testing protocol was employed to
101 evaluate the performance of the admixtures dynamic shearing, to indicate different conditions during
102 mixing and casting, and to measure the effect of pre-shearing. The initial pre-shear ramp was performed
103 by linearly increasing shear rate from 1/s to one of three maximum shear rates over a 60 s interval,
104 maintaining the maximum as a constant for 120 s, and then ramping down linearly over a 60 s interval
105 from the maximum shear rate to 1/s (Figure 1, **region I**). The maximum shear rates of 50/s, 100/s, or
106 150/s were measured for each admixture to understand how pre-shearing affected the structural build-up
107 and static yield stress measured in later regions. Step two involved a resting phase with low amplitude
108 oscillation. This oscillation phase was performed with a constant strain rate of 0.008% and a linear
109 angular frequency ramp from 1 rad/s to 10 rad/s (Figure 1, **region II**). The constant strain rate of 0.008%
110 was determined in preliminary tests to be within the viscoelastic region of the St6 slurry. Finally, an
111 amplitude sweep was performed with a constant angular frequency of 2 rad/s and a linear shear strain
112 ramp from 0.008% to 0.1% (Figure 1, **region III**).

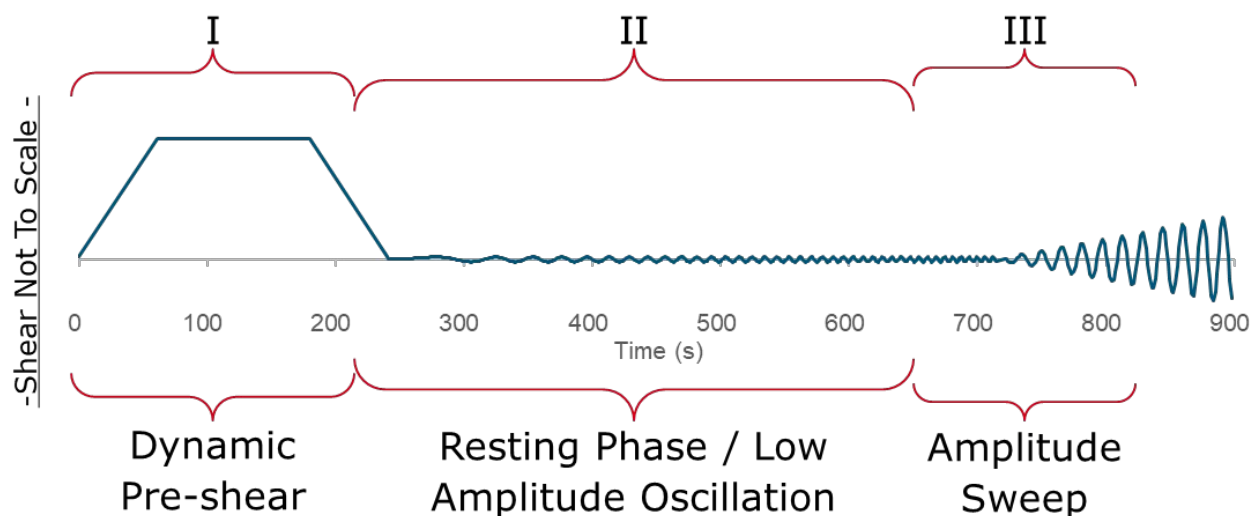


Figure 1. Illustration of the testing profile for rheological assessment of gums in a limestone slurry showing (I) the dynamic pre-shearing region and (II) the small amplitude oscillatory shear region.

3. Results and Discussion

3.1. Dynamic pre-shearing

To understand how the studied bio-derived admixture behave in a slurry under dynamic shearing, which can be an indicator of workability properties in a cementitious material, shear stress was measured over a shear ramp (Figure 2). Increasing the maximum shear rate led to an expected increase in the shear stresses, with St6 showing very large increases across the three shear rates (Figure 2A-C). During the dynamic pre-shearing region, the shear stresses trends in the Mi and Ac slurries are similar to the lower dosage starch slurry, 0.5xSt6 (Figure 2 A-C). For the REF, Mi, Ac, and 0.5xSt6 slurries, the measured shear stresses for a given strain rate remained similar regardless of the maximum shear rate used. Notably, St6 shows a shear thickening behavior triggered at a shear rate of approximately 50 1/s which increased as shear rate increased (Figure 3A-B). This led to a large viscosity increase at higher maximum shear rates, which maintained even when the shear rate was reduced below 50/s. On a mass basis, the starch has stronger viscosity modifying affect compared to the other polymers [37]. The strong

viscosity increase and shear thickening behavior can be caused by the better dispersed large amylopectin molecules, causing a higher viscosity of the liquid phase and more particle interactions between cement particles, hydrates, and amylopectin, respectively. The hydroxypropylation might improve the viscosity efficiency of starch [38].

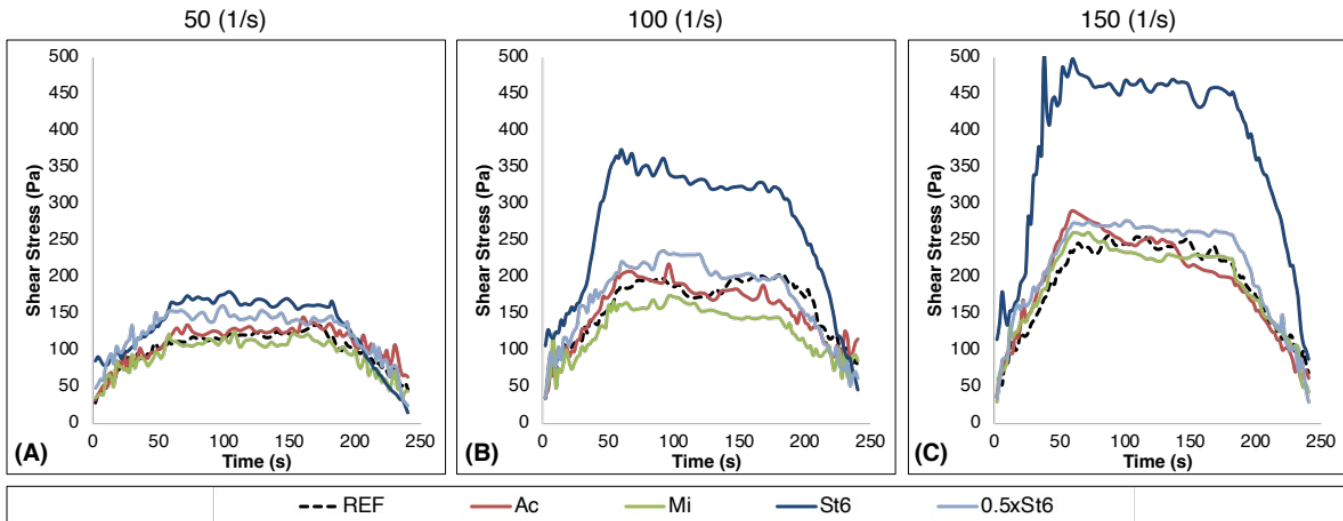


Figure 2. Shear stress vs. time and shear stress vs. shear rate over the pre-shear ramp phase of testing with A showing results for 50/s maximum shear rate; B showing results for 100/s maximum shear rate; and C showing results for 150/s maximum shear rate.

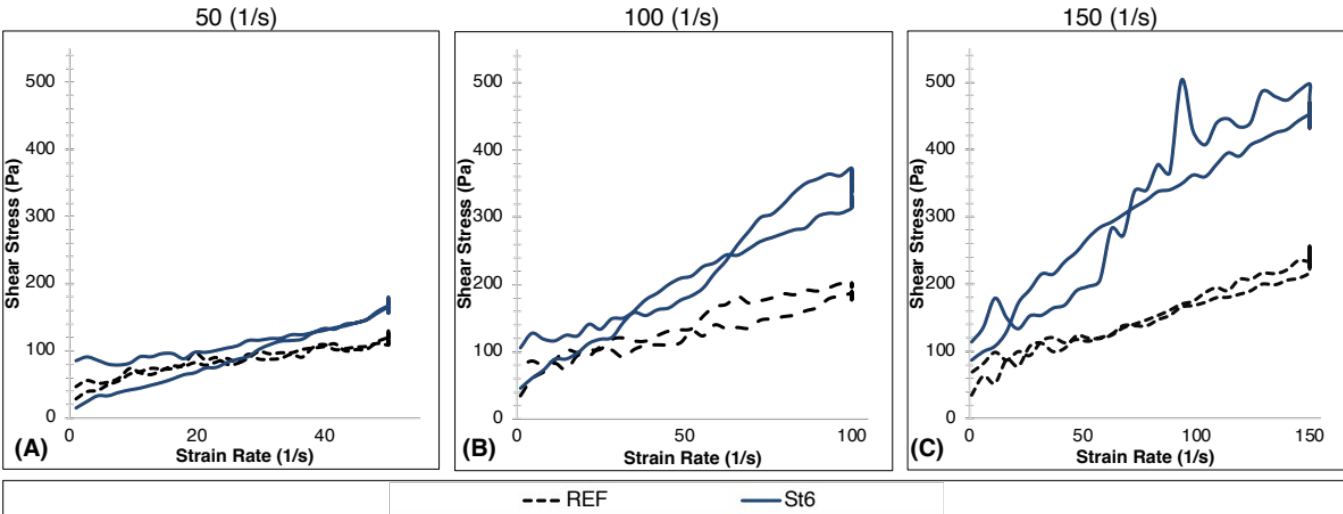
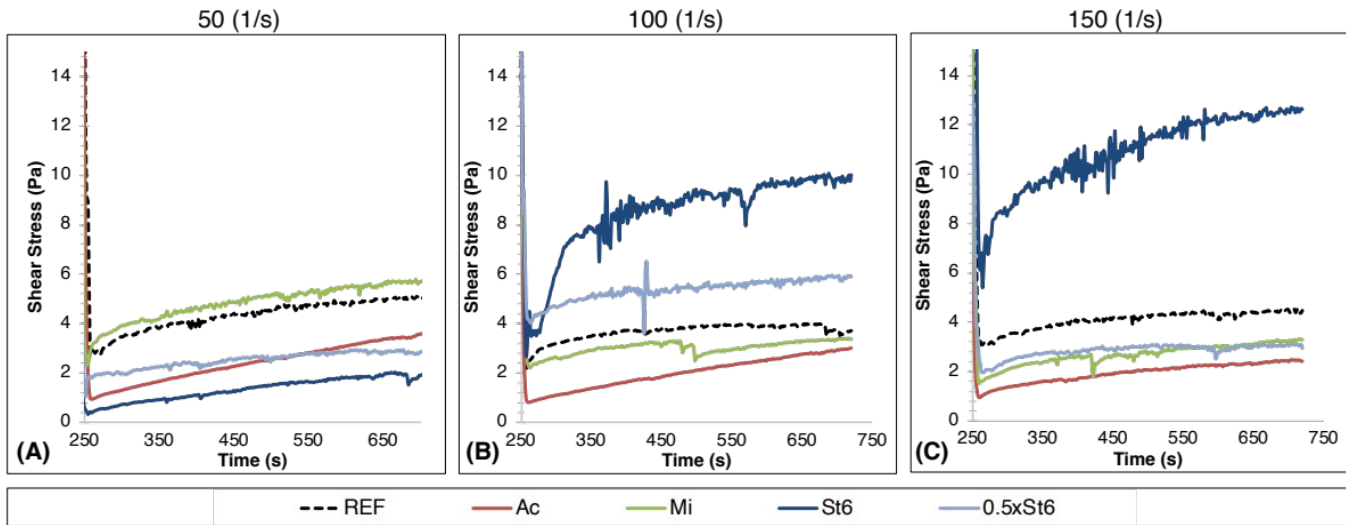


Figure 3. Shear stress vs strain rate of the full ramp interval in Region I for REF and St6 slurry mixtures.

143 The relationship between shear stress and strain rate measured during the downward ramp at the
 144 end of Region I was observed to follow a linear trend for shear stresses greater than 10 Pa. Thus, a
 145 Bingham regression was applied to this region to determine the yield stress and plastic viscosity of the
 146 slurry mixtures and these values are presented and discussed below.

147
 148 **3.2. Low Amplitude Oscillation**

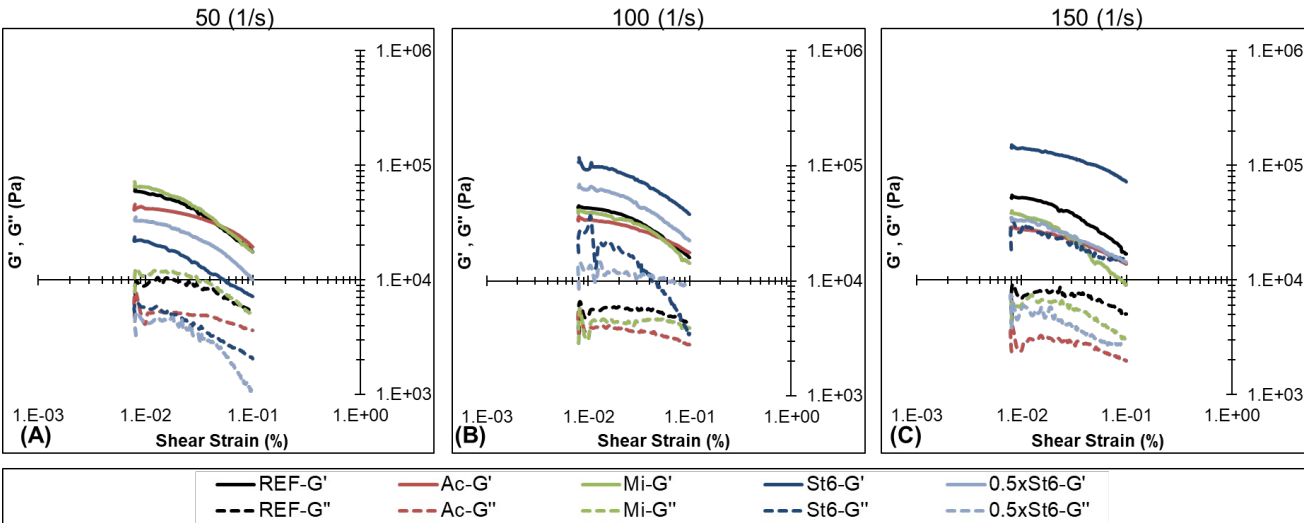
149 The slurry mixtures were evaluated with low amplitude oscillation to measure the shear stress
 150 and structural build up after pre-shearing at different maximum shear rates (Figure 4). The control
 151 slurry, REF, shows little change with very small decreases as pre-shearing increases. As the pre-shearing
 152 increased, St6 showed an increase in shear stress across the shearing conditions. However, 0.5xSt6
 153 shows an initial increase in shear stress values from 50/s to 100/s pre-shearing conditions, but this was
 154 followed by lower shear stresses at 150/s. Ac and Mi both show smaller shear stress curves as the pre-
 155 shearing increased.



156
 157 **Figure 4.** The shear stress over time of slurry mixtures after (A) 50 /s maximum shear rate, (B) 100 /s
 158 maximum shear rate, and (C) 150 /s maximum shear rate.

161 **3.3. Amplitude Sweep**

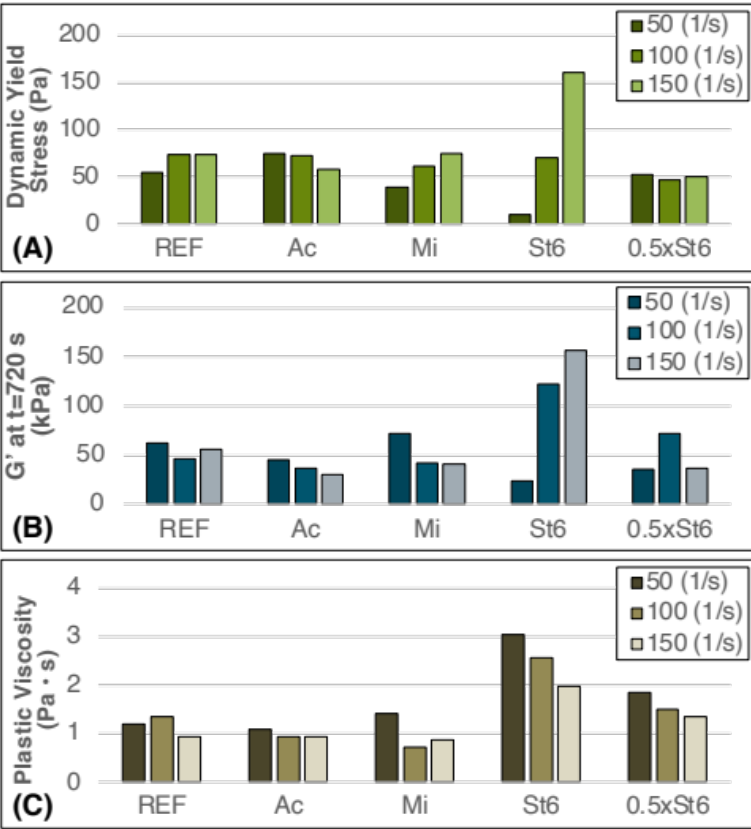
162 The measurements of the amplitude sweep (Figure 1, **Region III**) did not enter the linear
163 viscoelastic regime. Likewise, as the shear stresses in Figure 4 show a plateauing behavior, with the
164 potential exception of Ac, the shear stresses at the beginning of the Amplitude Sweep (~720 s) can be
165 interpreted as an indicator static behavior. The corresponding storage moduli (G') values were
166 determined and are show in Figure 6B along with the dynamic yield stress (Figure 6A) and plastic
167 viscosity (Figure 6C) determined earlier for the dynamic pre-shearing regime.



168 **Figure 5.** The storage and loss moduli versus shear strain for the amplitude sweep testing (regime III)
169 for 50/s, 100/s, and 150/s pre-shearing conditions.
170
171

172 For dynamic yield stress, St6 and Mi increased with increased shear rate. REF increases initially
173 approximately 30% from 50/s to 100/s, but then remains the approximately the same at 150/s.
174 Conversely, from 50/s to 100/s Ac shows little change, but then shows a moderate decrease when pre-
175 shearing is increased to 150/s. While the increase in yields stress of Mi appears linear (i.e., increasing
176 approximately 20 Pa for each 50/s increase in shear rate), St6 shows a sharp increase as maximum shear
177 rate increased (i.e., increasing ~60 Pa from 50/s to 100/s and then increasing ~90 Pa from 100/s to
178 150/s). However, 0.5xSt6 shows little change across shear rates (ranging from 47-52 Pa) This indicates

179 that the starch dosage influences the observed behavior and that there may be a minimum dose required
 180 effectively modify the yields stress. Likewise, higher shear rates appear to improve the effectiveness of
 181 the starch. Possibly the starch molecules, when first introduced into the system, are agglomerated and
 182 higher shearing aids in breaking up the agglomerants and better dispersing the starch in the system.



183 **Figure 6.** The (A) yield stress calculated using the Bingham regression for the downward ramp in
 184 Region I, (B) the storage modulus at t = 720 s for the tested slurry samples at pre-shearing rates of 50/s,
 185 100/s, and 150/s and (C) plastic viscosity calculated using the Bingham regression for the downward
 186 ramp in Region I. n = 3.
 187
 188

189 As with the results of dynamic yield stress, the Ac and Mi slurries shows a gradual decrease in
 190 structural build up at higher pre-shearing rates (Figure 6B). The REF and 0.5xSt6 slurries exhibit mix
 191 results at different pre-shearing conditions. And St6 shows a sharp increase, indicating a significant
 192 increase in structure build for increase pre-shearing conditions, matching the previous observations of
 193 improved starch efficiency at higher pre-shearing rates.

194 The REF, Ac, and Mi slurries, the plastic viscosity showed mixed effects in relation to the shear
195 rate (Figure 6C). However, both St6 and 0.5xSt6 slurries showed a decreasing viscosity with increasing
196 maximum shear rate. These differences observed with the strong change of St6 compared to the 0.5xSt6
197 (with half the mass of starch) and other admixtures is likely related to the starch having a larger impact
198 in higher solid-volume systems [18]. These results also show that miscanthus gum has plasticizing
199 properties in the system under shear, but at rest leads to structural development like the REF system.
200 Acacia gum, on the other hand, shows an increasing yield stress, but decreases plastic viscosity meaning
201 the structural build up is slower compared to the REF.

202

203 4. Outlook

204 In this work, acacia gum and miscanthus gums are compared to a hydroxypropylated starch in
205 limestone slurries with different maximum pre-shearing rates. Herein, we demonstrate how increasing
206 pre-shearing led to larger storage moduli for the starch admixtures, but also coincided with lower moduli
207 values or mixed effects for the slurries with miscanthus or acacia gums. This shows that higher shearing
208 rates caused the polymers to be more effective in the mixtures. Literature shows that the properties of the
209 polysaccharides and processing (e.g., hydroxypropylation) affect the efficiency of the admixture in the
210 liquid-particle systems. Likewise, higher shearing may help break up agglomerated starch and better
211 disperse the starch in a system. At higher shear, miscanthus gums were observed to exhibit plasticizing
212 behaviors and acacia gum increased yield stress. At rest, Mi developed structure similar to the REF
213 slurry, but Ac developed structure slower.

214 Future work to determine the molecular weight or polymer content of the bioderived admixture
215 could allow for comparison on a polymer weight basis instead of a material mass basis. Additionally,
216 improved processing and purification could increase the effects observed from the bioderived materials.

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Likewise, observing these admixtures in slurries with ionic solutions or mixtures with cement is imperative future step to identify the behavior of the bioderived admixtures in cement-based systems.

219

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References

- [1] G. Lai, X. Liu, S. Li, Y. Xu, Y. Zheng, J. Guan, R. Gao, Z. Wei, Z. Wang, S. Cui, Development of chemical admixtures for green and environmentally friendly concrete: A review, *J. Clean. Prod.* 389 (2023) 136116. <https://doi.org/10.1016/j.jclepro.2023.136116>.
- [2] A. Kunhi Mohamed, S.A. Weckwerth, R.K. Mishra, H. Heinz, R.J. Flatt, Molecular modeling of chemical admixtures; opportunities and challenges, *Cem. Concr. Res.* 156 (2022) 106783. <https://doi.org/10.1016/j.cemconres.2022.106783>.
- [3] W. Schmidt, M. Alexander, V. John, Education for sustainable use of cement based materials, *Cem. Concr. Res.* 114 (2018) 103–114. <https://doi.org/10.1016/j.cemconres.2017.08.009>.
- [4] J. Cheung, L. Roberts, J. Liu, Admixtures and sustainability, *Cem. Concr. Res.* 114 (2018) 79–89. <https://doi.org/10.1016/j.cemconres.2017.04.011>.
- [5] J. Plank, E. Sakai, C.W. Miao, C. Yu, J.X. Hong, Chemical admixtures - Chemistry, applications and their impact on concrete microstructure and durability, *Cem. Concr. Res.* 78 (2015) 81–99. <https://doi.org/10.1016/j.cemconres.2015.05.016>.
- [6] W. Schmidt, H.J.H. Brouwers, H.C. Kühne, B. Meng, The working mechanism of starch and diutan gum in cementitious and limestone dispersions in presence of polycarboxylate ether superplasticizers, *Appl. Rheol.* 23 (2013) 1–12. <https://doi.org/10.3933/ApplRheol-23-52903>.
- [7] W. Schmidt, Why Africa can spearhead innovative and sustainable cement and concrete technologies globally, *Proc. Second KEYS Symp. Knowl. Exch. Young Sci.* (2016).
- [8] W. Schmidt, K.A. Olonade, Optimised processes for the production of performance concrete constituents based on agricultural wastes, (n.d.).
- [9] S.A. Miller, G. Habert, R.J. Myers, J.T. Harvey, Achieving net zero greenhouse gas emissions in the cement industry via value chain mitigation strategies, *One Earth.* 4 (2021) 1398–1411. <https://doi.org/10.1016/j.oneear.2021.09.011>.
- [10] Caltrans, Fly Ash: Current and Future Supply. A Joint Effort Between Concrete Task Group of the Caltrans Rock Products Committee and Industry, 2016. <https://globalpozz.com/wp-content/uploads/2021/02/Caltrans-Fly-Ash-Future-and-Alternatives.pdf>.
- [11] P.R. Cunningham, L. Wang, P. Thy, B.M. Jenkins, S.A. Miller, Effects of Leaching Method and Ashing Temperature of Rice Residues for Energy Production and Construction Materials, *ACS Sustain. Chem. Eng.* (2021) acssuschemeng.0c07919. <https://doi.org/10.1021/acssuschemeng.0c07919>.
- [12] W. Schmidt, N.S. Msinjili, H.C. Kühne, Materials and technology solutions to tackle the

- 259 challenges in daily concrete construction for housing and infrastructure in sub-Saharan Africa,
 260 African J. Sci. Technol. Innov. Dev. 11 (2019) 401–415.
 261 <https://doi.org/10.1080/20421338.2017.1380582>.
- 262 [13] W. Schmidt, M. Commeh, K. Olonade, G.L. Schiewer, D. Dodoo-Arhin, R. Dauda, S. Fataei,
 263 A.T. Tawiah, F. Mohamed, M. Thiedeitz, N.W. Radebe, A. Rogge, Sustainable circular value
 264 chains: From rural waste to feasible urban construction materials solutions, Dev. Built Environ. 6
 265 (2021) 100047. <https://doi.org/10.1016/j.dibe.2021.100047>.
- 266 [14] D. Renard, L. Lavenant-Gourgeon, M.C. Ralet, C. Sanchez, Acacia senegal gum: Continuum of
 267 molecular species differing by their protein to sugar ratio, molecular weight, and charges,
 268 Biomacromolecules. 7 (2006) 2637–2649. <https://doi.org/10.1021/bm060145j>.
- 269 [15] C. Sanchez, M. Nigen, V. Mejia Tamayo, T. Doco, P. Williams, C. Amine, D. Renard, Acacia
 270 gum: History of the future, Food Hydrocoll. 78 (2018) 140–160.
 271 <https://doi.org/10.1016/j.foodhyd.2017.04.008>.
- 272 [16] M. Elmanan, S. Al-Assaf, G.O. Phillips, P.A. Williams, Studies on Acacia exudate gums: Part VI.
 273 Interfacial rheology of Acacia senegal and Acacia seyal, Food Hydrocoll. 22 (2008) 682–689.
 274 <https://doi.org/10.1016/j.foodhyd.2007.02.008>.
- 275 [17] W. Schmidt, Effect of calcium ions on bio-based polymers for rheology control, Am. Concr.
 276 Institute, ACI Spec. Publ. SP-354 (2022) 75–86. <https://doi.org/10.14359/51736063>.
- 277 [18] W. Schmidt, H.J.H. Brouwers, H.-C. Kühne, B. Meng, Interactions of polysaccharide stabilising
 278 agents with early cement hydration without and in the presence of superplasticizers, Constr.
 279 Build. Mater. 139 (2017) 584–593. <https://doi.org/10.1016/j.conbuildmat.2016.11.022>.
- 280 [19] W. Schmidt, M. Otieno, K.A. Olonade, N.W. Radebe, H. van Damme, P. Tunji-olayeni, S. Kenai,
 281 A.T. Tawiah, K. Manful, A. Akinwale, R.N. Mbugua, A. Rogge, Innovation potentials for
 282 construction materials with specific focus on the challenges in Africa, RILEM Tech. Lett. 5
 283 (2020) 63–74. <https://doi.org/10.21809/rilemtechlett.2020.112>.
- 284 [20] W. Schmidt, I.L. Tchegnina Ngassam, K.A. Olonade, R. Mbugua, H.C. Kühne, Plant based
 285 chemical admixtures – potentials and effects on the performance of cementitious materials,
 286 RILEM Tech. Lett. 3 (2018) 124–128. <https://doi.org/10.21809/rilemtechlett.2018.83>.
- 287 [21] R. Mbugua, R. Salim, J. Ndambuki, Effect of gum arabic karroo as a water-reducing admixture in
 288 concrete, Materials (Basel). 9 (2016) 1–16. <https://doi.org/10.3390/ma9020080>.
- 289 [22] A.U. Elinwa, M. Umar, X-ray diffraction and microstructure studies of gum Arabic-cement
 290 concrete, Constr. Build. Mater. 156 (2017) 632–638.
 291 <https://doi.org/10.1016/j.conbuildmat.2017.08.162>.
- 292 [23] W. Schmidt, K.A. Olonade, R.N. Mbugua, F.J. Lenz, I.T. Ngassam, Bio-Based Rheology
 293 Modifiers for High Performance Concrete – Possible Modes of Actions and Case Study for
 294 Cassava Starch in West Africa, in: 2020: pp. 158–166. https://doi.org/10.1007/978-3-030-33342-3_17.
- 295
- 296 [24] C. Zhao, Q. Zhao, Y. Zhang, M. Zhou, The Effect of Gum Arabic on the Dispersion of Cement
 297 Pastes, in: 2015: pp. 483–494. https://doi.org/10.1007/978-3-319-13948-7_47.
- 298 [25] N. Brosse, A. Dufour, X. Meng, Q. Sun, A. Ragauskas, Miscanthus : a fast-growing crop for
 299 biofuels and chemicals production, Biofuels, Bioprod. Biorefining. 6 (2012) 580–598.
 300 <https://doi.org/10.1002/bbb.1353>.
- 301 [26] T.R. Sarker, F. Pattnaik, S. Nanda, A.K. Dalai, V. Meda, S. Naik, Hydrothermal pretreatment
 302 technologies for lignocellulosic biomass: A review of steam explosion and subcritical water
 303 hydrolysis, Chemosphere. 284 (2021) 131372.
 304 <https://doi.org/10.1016/j.chemosphere.2021.131372>.

- 305 [27] J. Zhang, D. Cai, Y. Qin, D. Liu, X. Zhao, High value-added monomer chemicals and functional
 306 bio-based materials derived from polymeric components of lignocellulose by organosolv
 307 fractionation, *Biofuels, Bioprod. Biorefining.* 14 (2020) 371–401.
 308 <https://doi.org/10.1002/bbb.2057>.
- 309 [28] J. Baruah, B.K. Nath, R. Sharma, S. Kumar, R.C. Deka, D.C. Baruah, E. Kalita, Recent Trends in
 310 the Pretreatment of Lignocellulosic Biomass for Value-Added Products, *Front. Energy Res.* 6
 311 (2018). <https://doi.org/10.3389/fenrg.2018.00141>.
- 312 [29] L. Serrano, I. Egües, M.G. Alriols, R. Llano-Ponte, J. Labidi, *Miscanthus sinensis* fractionation
 313 by different reagents, *Chem. Eng. J.* 156 (2010) 49–55. <https://doi.org/10.1016/j.cej.2009.09.032>.
- 314 [30] S. Irmak, B. Meryemoglu, A. Sandip, J. Subbiah, R.B. Mitchell, G. Sarath, Microwave
 315 pretreatment effects on switchgrass and miscanthus solubilization in subcritical water and
 316 hydrolysate utilization for hydrogen production, *Biomass and Bioenergy.* 108 (2018) 48–54.
 317 <https://doi.org/10.1016/j.biombioe.2017.10.039>.
- 318 [31] M.P. Yadav, K.B. Hicks, Isolation, characterization and functionalities of bio-fiber gums isolated
 319 from grain processing by-products, agricultural residues and energy crops, *Food Hydrocoll.* 78
 320 (2018) 120–127. <https://doi.org/10.1016/j.foodhyd.2017.04.009>.
- 321 [32] S. Rivas, C. Vila, J.L. Alonso, V. Santos, J.C. Parajó, J.J. Leahy, Biorefinery processes for the
 322 valorization of *Miscanthus* polysaccharides: from constituent sugars to platform chemicals, *Ind.*
 323 *Crops Prod.* 134 (2019) 309–317. <https://doi.org/10.1016/j.indcrop.2019.04.005>.
- 324 [33] S. Periyasamy, V. Karthik, P. Senthil Kumar, J.B. Isabel, T. Temesgen, B.M. Hunegnaw, B.B.
 325 Melese, B.A. Mohamed, D.-V.N. Vo, Chemical, physical and biological methods to convert
 326 lignocellulosic waste into value-added products. A review, *Environ. Chem. Lett.* 20 (2022) 1129–
 327 1152. <https://doi.org/10.1007/s10311-021-01374-w>.
- 328 [34] C. Barba, D. Montané, X. Farriol, J. Desbrières, M. Rinaudo, Synthesis and characterization of
 329 carboxymethylcelluloses from non-wood pulps II. Rheological behavior of CMC in aqueous
 330 solution, *Cellulose.* 9 (2002) 327–335. <https://doi.org/10.1023/A:1021136626028>.
- 331 [35] M. El Achaby, N. El Miri, H. Hannache, S. Gmouh, V. Trabadelo, A. Aboulkas, H. Ben Youcef,
 332 Cellulose nanocrystals from *Miscanthus* fibers: insights into rheological, physico-chemical
 333 properties and polymer reinforcing ability, *Cellulose.* 25 (2018) 6603–6619.
 334 <https://doi.org/10.1007/s10570-018-2047-1>.
- 335 [36] W. Puntke, Wasseranspruch von feinen Kornhaufwerken, *Beton-Dusseldorf.* 5 (2002) 242–249.
- 336 [37] K. Zhang, W. Schmidt, A. Mezhev, Influence of the Hydroxypropylation of Starch on its
 337 Performance as Viscosity Modifying Agent, in: *SP-354 Superplast. Other Chem. Admixtures*
 338 *Concr. - Conf. Proc.*, American Concrete Institute, 2022: pp. 209–2018.
 339 <https://doi.org/10.14359/51736074>.
- 340 [38] M.C. Vieira, D. Klemm, L. Einfeldt, G. Albrecht, Dispersing agents for cement based on
 341 modified polysaccharides, *Cem. Concr. Res.* 35 (2005) 883–890.
 342 <https://doi.org/10.1016/j.cemconres.2004.09.022>.
- 343 [39] K. Zhang, A. Mezhev, W. Schmidt, Chemical and thixotropic contribution to the structural build-
 344 up of cementitious materials, *Constr. Build. Mater.* 345 (2022) 128307.
 345 <https://doi.org/10.1016/j.conbuildmat.2022.128307>.
- 346