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# Predicting effect of fibers on thermal gelation of methylcellulose using Bayesian optimization

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#### Abstract

Understanding of the viscoelastic behavior of a polymer is a prerequisite for its thermomechanical processing beyond laboratory scale. Utilizing rheological characterization is a powerful tool to comprehend the complex nature and time-dependent properties of macromolecular materials. Nevertheless, it consumes time as rheometry involves iterating experiments under several conditions to visualize the non-linear behavior of materials under varying conditions. The work hereunder examines the rheology of cellulosic aqueous suspensions prepared using cellulose fibers as the dispersed phase (Refcell and Storacell) and methylcellulose (MC) as the polymeric matrix. Interfacial phenomena between MC and cellulose fibers arise in particle laden systems with supramolecular structures formed by non-covalent interactions. Therefore, this study elucidates the rheological evolution of these interactions as a function of temperature and fiber concentration. This study displays how researchers may reduce the number of rheological experiments and save time utilizing a novel method based on a Bayesian optimization with Gaussian processes.

*Keywords:* fibers, methylcellulose, rheology, Bayesian optimization *PACS:* 0000, 1111 2000 MSC: 0000, 1111



Figure 1: Illustration of (a) a FoamWood prototype block (Reichler et al., 2021) and (b) a commercial packaging plastic foam.

# 1 **Introduction**

Cellulose is a key market driver in the present and future bioeconomy of 2 polymers. As a material, cellulose has multiple benefits, such as being re-3 cyclable, chemically modifiable, and naturally available in enormous quan-4 tities (Klemm et al., 2005). Its supramolecular structure and crystallinity, 5 together with its high surface area, make of cellulose a perfect additive to cre-6 ate advanced materials and structures (Kontturi et al., 2018). For instance, 7 we have recently created a cellulose-based foam (Reichler et al., 2021) which 8 is an alternative to replace plastics (Fig. 1). The "FoamWood" solution is 9 a cellular and lightweight material created after drying a gel suspension of 10 methylcellulose (MC) and cellulose fibers. Others have prepared similar com-11 posites using methylcellulose and cellulose nanofibers instead of macroscopic 12 fibers (Church et al., 2021; Voisin et al., 2018). Then, to better understand 13 the mechanical properties of such materials, the rheological properties of the 14 MC suspensions must be characterized under varying stimuli (e.g., tempera-15 ture and shear forces). 16

Fabricating the FoamWood relies on the capacity of MC to form hydrogels
upon heating due to fibril network formation (Lott et al., 2013). In the solgel transition the fluid becomes turbid and the relaxation timescales increase

two to three orders of magnitude (Desbrieres et al., 2000). The transition is 20 thermoreversible and the process depends on the heating/cooling rate and 21 the MC concentration (Kobayashi et al., 1999; Li et al., 2001). In addition, it 22 has been shown that an small stress can have a significantly effect on the MC 23 structure, which affects the gel temperature  $T_{qel}$  and, consequently, its me-24 chanical properties (Nelson et al., 2022). We then study the rheology of two 25 types of particle suspensions. Those systems consist of a continuous aqueous 26 phase of MC and a dispersed phase of cellulose fibers (never-dried or dried 27 pulp). In rheological studies, it is well established that  $T_{ael}$  is determined by 28 looking the interception between the loss and storage modulus (Mcallister 29 et al., 2015). However, as a consequence of the dispersed matrix in the par-30 ticle laden suspension, such cross-over is not visible. Instead we introduce a 31 new way to compute the gelation temperature by using the phase shift angle. 32 The macrostructure of cellulose possesses dipole-dipole associations (hy-33 drogen bonding), which create a supramolecular system (Ioelovich, 2016). 34 In cellulose, the dipole-dipole interactions between OH groups are additive; 35 thus, the orientation between two dipoles affects all the surrounding medium. 36 The idea of combining cellulose and MC involves taking advantage of the 37 hydrogen bonding between these two. Hence, the interfaces between both 38 materials are compatible and physically bonded to one another. In addition 39 to the interactions arising from the OH groups, cellulose chains have hy-40 drophobic sites. Hydrophobic interactions take more relevance for MC than 41 cellulose since MC becomes an amphiphilic molecule (Nasatto et al., 2015). 42 The reduction in the number of hydrogen bonds allows the solubilization of 43 the cellulose ether in water. However, the polymer-polymer (hydrophobic) 44 interactions among carbon chains and methyl groups make the system form a 45 gel above room temperature (Nasatto et al., 2015). The gel transition of MC 46 is essential for certain manufacturing processes, such as 3D printing and the 47 FoamWood process, which allows the material to hold the 3D structure of the 48 hydrogel during drying. The storage modulus during the solution/hydrogel 49 transition have been shown to alter with added materials such as cellulose 50 nanocrystals (Hynninen et al., 2018) and kappa carrageenan (Almeida et al., 51 2018). Here we test using rheological methods similar with macroscopic 52 cellulose fibers. Previous research suggest that cellulose nanocrystals con-53 tribute to the percolation network of the MC fibers forming in the thermal 54 gelation (Hynninen et al., 2018), however such result does not generalize 55 automaticly to macroscopic fibers studied here. 56

A considerable amount of experimental effort has been devoted to char-

acterizing the gelation of methylcellulose (Coughlin et al., 2021; Mcallister 58 et al., 2015). The rheological method is well known to be the most direct 59 and reliable way to determine gelation transition. However, this characteri-60 zation ends up to be time consuming and requires dozens of experiments. To 61 ease the experiment load, computer simulations (Huang et al., 2014; Quey-62 roy et al., 2004) and phenomenological laws (Li, 2002) are the common ways 63 to study the problem. Over the last years, significant results have been 64 achieved with the help of the machine learning methods. Machine learning 65 approaches have become powerful tools for revealing hidden information (Gao 66 et al., 2022). One recent example applied neural networks that use known 67 constitutive realtions in predicting rheological response of silica suspension in 68 various experimental protocols (Mahmoudabadbozchelou et al., 2022). Here 69 in particular, we use a "semi-active learning" method (Tian et al., 2021) 70 using Bayesian optimization (Shahriari et al., 2016). 71

Therefore, this study aims to (i) study the rheology of methylcellulose and its gelation temperature, (ii) introduce a new way to determine the gelation temperature using the phase shift angle, and (iii) develop a Bayesian optimization approach which will reduce experiment load. We hypothesize that Bayesian optimization method utilizing Gaussian processes could capture rheological properties of cellulose materials with minimal experimental effort.

# 79 2 Materials and Methods

#### 80 2.1 Materials

We used cellulose ether "Benecel MX MC-50000 cP" (50 Pa·s) from Ashland 81 Specialties Belgium. This MC is a food-grade cellulose ether complying with 82 the standard E461 (JECFA, 2006). According to the latter standard, the DS 83 of methyl  $(CH_3)$  groups of the Benecel cellulose ether (BC) must be between 84 1.45 and 2.00. Furthermore, the maximum content of hydroxypropyl groups 85 is 5%. BC's average molecular weight  $(M_w)$  and polydispersity index (PDI)86 were inspected via size exclusion chromatography (SEC) using an 1260 Infin-87 ity II Multi-Detector GPC/SEC system. We used  $0.1 \text{ M NaNO}_3$  as solvent 88 and pollulan standard with  $M_w$  of 110 kg/mol. SEC analysis of BC exhibited 89 a macromolecular structure with  $M_w = 534$  kg/mol and PDI = 1.5. Com-90 plementing the structural characterization, BC functional groups, product of 91

cellulose etherification, were identified through Raman spectroscopy  $\lambda = 532$ 92 nm (Renishaw inVia<sup>™</sup> Qontor, United Kingdom, see supplementary infor-93 mation Figure S1). Characteristic Raman signals of MC were detected in 94 the wavenumber range 2750-3100 cm<sup>-1</sup> (i.e.,  $v(CH_3)$ ,  $v(CH_2)$ , and v(CH)). 95 Here, two cellulose pulps were formulated as Refcell (RC) and Storacell (SC) 96 to prepare the particle laden suspensions. Refcell is never-dried and bleached 97 pine and spruce Kraft pulps. Storacell is a dried "Supreme Strong" bleached 98 softwood Kraft pulp produced by Stora Enso Oyj (Finland). The pulps were 99 in the form of 5% solid content aqueous suspensions. 100



Figure 2: (a) Arithmetic fiber length  $\ell$  and width w distributions. (b-c) Optical microscope images of (b) Refcell, and (c) Storacell fibers. The images display the materials' morphologies.

Figure 2a shows the fiber length and width distributions for Refcell and Storacell obtained with a Valmet Fiber Image Analyzer. While the number-average width of both fibers are similar,  $w_{RC} = 28.23 \ \mu \text{m}$  and  $w_{SC} =$ 

Formulation	Concentration in water (wt.%)		
Sample	BC	Pulp	Water
BC	1.5	0.0	98.50
		Refcell	
BC-RC-25	1.5	0.25	98.25
BC-RC-50	1.5	0.50	98.0
		Storacell	
BC-SC-25	1.5	0.25	98.25
BC-SC-50	1.5	0.50	98.0

Table 1: Formulations used for preparing the particle laden suspensions.

27.2  $\mu$ m, the number-average fiber length for Refcell is longer ( $\ell_{RC} = 1.1 \text{ mm}$ ) 104 than Storacell ( $\ell_{SC} = 0.73$  mm). Figure 2b and c show optical microscope 105 images of the materials at  $100 \times$  magnification using a B120C Siedentopf 106 Binocular Compound Microscope (AmScope, USA) with a digital camera 107 Canon EOS M3. A clear morphology difference can be depicted between 108 the employed materials. Finally, the preparation of samples used high pu-109 rity Finnish tap water (pH 8.4 at 23°C) (further details about the water 110 composition in supplementary information Table S1). 111

#### <sup>112</sup> 2.2 Preparation of particle laden suspension

The experiments use two particle laden suspensions with different pulp con-113 tent of each type. Furthermore, the rheological study involves characterizing 114 the BC matrix for having a comparison reference. Table 1 summarizes the 115 formulations employed for each sample. The following process was used for 116 the sample preparation. First, the respective amounts of BC powder and 117 pulp suspension were mixed in a glass beaker. Then, reaching the desired 118 mass fraction percentage in the aqueous dispersion comprised the addition 119 of water (at 70°C). Finally, the samples' mixing involved placing the glass 120 containers in an ice bath and mixing them with a magnetic stirrer for one 121 hour at 700 rpm. The suspensions were then stored overnight at 3°C before 122 characterization. 123

#### 124 2.3 Rheometry

Rheological characterization took place using a rheometer Physica MCR 302. 125 Anton Paar (Austria). The geometry for the analysis consisted of a modified 126 concentric cylinder: a cup (CC27) and a bob (CC17/P6), both with serrated 127 walls to minimize wall slip issues during measurements. Figure 3 shows the 128 setup used in the characterization. The objective of the camera was to mon-129 itor the experiment and record sources of error. Rheological measurements 130 occurred utilizing oscillatory tests of the type Dynamic Mechanical Thermal 131 Analysis (DMTA) and a flow curve with shear rate between 0.01 to 100  $s^{-1}$ . 132 DMTA examines the effect of temperature T on the rheological properties.

133 In DMTA test, a sinusoidal oscillatory strain  $\gamma = \gamma_0 \sin(\omega t)$  rises in the 134 sinusoidal material stress  $\tau = \tau_0 \sin(\omega t + \delta)$  with a phase shift angle  $\delta$  and 135 angular frequency  $\omega$ . The phase shift angle is a parameter measuring the 136 dominant type of behavior in the material, being an elastic material if  $\delta = 0$ 137 and a perfect viscous liquid if  $\delta = \pi/2$ . A viscoelastic material has a  $\delta$ 138 between 0 and  $\pi/2$ . Accordingly, the change of  $\delta$  in an oscillatory experiment 139 may be used as an indicator for the transition of MC from a viscoelastic liquid 140 to a gel. This assumes it is possible to deconvolve the shear stress signal into 141 in-phase and out-of-phase components (Morrison, 2001) 142

$$\tau(\omega, t) = G' \sin(\omega t) + G'' \cos(\omega t) \tag{1}$$

Here the elastic and viscous behaviors of the material are represented by the 143 storage modulus G' and loss modulus G'', respectively. In MC, when G' is 144 greater than G'', the molecular conformation is a hydrogel (i.e., a 3D hydrated 145 network). The in-phase and out-of-phase responses may be expressed using 146 complex notation, and then the complex elastic modulus is  $G^* = \sqrt{G'^2 + G''^2}$ . 147 Moreover, the phase shift in terms of G' and G'' is defined as  $\tan \delta = G''/G'$ . 148 To the best of our knowledge, this work proposes for the first time to use the 149 phase shift  $\delta$  as a parameter to identify the gelation temperature  $T_{qel}$  of a 150 particle laden suspension such as the one prepared for this manuscript. 151

<sup>152</sup> We use a strain  $\gamma_0$  of 1% in the Linear Viscoelastic region (LVR) that <sup>153</sup> deforms the suspensions at constant angular frequency  $\omega$  while heating the <sup>154</sup> samples at 1°C/min (from 25 to 60°C). The characterization comprised re-<sup>155</sup> peating the test at three different angular frequencies (0.63, 6.30, and 63.00 <sup>156</sup> rad/s). Every DMTA test employed a new sample, and  $T_{gel}$  is determined <sup>157</sup> from the intercept of two slopes of the phase shift  $\delta$  (see supplementary infor-<sup>158</sup> mation Figure S2), which is compared to the intercept temperature between 159 G' and G''.



Figure 3: Illustration of the experimental assembly using (a) an Anton Paar rheometer MCR 302, (b) a serrated concentric cylinder geometry, and (c) a digital camera Canon EOS R.

In addition to DMTA, dynamic viscosity  $(\eta)$  experiments complemented 160 the characterization. Isothermal flow curves of viscosity  $\eta$  as a function 161 of shear rate  $\dot{\gamma}$  characterize the molecular structure of a polymer through 162 the interpretation of its resistance to flow. In particular, for the cellu-163 lose/methylcellulose system, these curves provide information about the in-164 teraction within the mixture. Isothermal analyses carried out from 25 to 165 40°C (5°C stepwise) allowed to obtain flow curves. The flow curves resulted 166 from deforming each suspension using a  $\dot{\gamma}$  interval from 0.01 to 100 s<sup>-1</sup> set-167 ting the measuring time as the reciprocal of  $\dot{\gamma}$ . These tests were performed 168 using the same assembly described in Fig. 3. 169

#### 170 2.4 Bayesian optimization

Bayesian optimization allows us to obtain an objective functions that take 171 a long time to evaluate, which in our case it corresponds to rheology curve. 172 It builds a surrogate for the objective and quantifies its uncertainty using a 173 Gaussian process regression (see supplementary information for mathemati-174 cal details) (Shahriari et al., 2016). The Bayesian optimization ran using an 175 in-house developed Python 3.8 based code. The optimization came from a 176 regression utilizing Gaussian processes (GP) with kernels k ConstantKernel, 177 RBF, and WhiteKernel from Scikit-learn (Pedregosa et al., 2011). 178

This report discusses the results from rheometry after Bayesian optimization to explore the code's feasibility in future experiments. Therefore, the values of  $\eta$  obtained from rotational tests and the outcomes of  $G^*$  and  $\delta$  from DMTA tests were used to train and generate 3D surfaces. The outcomes of the regression process assisted in discussing the rheological properties and interactions between cellulose and BC qualitatively.

# **3** Results and Discussion

The Bayesian optimization used the samples' dynamic viscosity  $\eta$  to generate 186 the 3D surfaces in Fig. 4 (the data without fit is shown in supplementary 187 information Figure S3). First, the mathematical process demonstrated the 188 possibility of using machine learning (ML) instead of empirical rheological 189 models. Nevertheless, a question arises about the physical meaning of the 190 length-scale parameter (l) (Pedregosa et al., 2011) in the material's be-191 havior. Assigning a physical meaning to parameters is a common problem 192 when working with such high abstraction level models. Despite the previous 193 problem, to our knowledge, this manuscript reports a Bayesian optimiza-194 tion of rheological properties for the first time. ML combined with rheology 195 concepts suggests being a powerful tool in materials characterization. With 196 further investigation, predicting the rheological properties of any system from 197 an experimental data set can achieve savings in time and effort. Addition-198 ally, as Fig. 5 illustrates, the optimization boundaries open fitting different 199 rheological properties such as  $G^*$  (for measurement data see Figure S4 in 200 supplementary information). Accordingly, the Bayesian optimization could 201 also fit similar viscoelastic responses, including the polymer's electrical and 202 magnetic rheological responses (e.g., complex dielectric permittivity). 203

It is known from the provider that this BC forms a gel at temperatures 204 above 40°C. Figure 4a illustrates the behavior of the matrix: BC viscosity 205 initially follows an Arrhenius decay and then after 30°C, it starts increasing. 206 BC's formation of a gel structure stems from hydrophobic polymer-polymer 207 interactions via methyl groups (Nasatto et al., 2015). The hydrophobic inter-208 actions reduce the molecular mobility of the polymer, and as a consequence, 209 the viscosity increases. It is worth mentioning that all the systems showed 210 a shear-thinning behavior. The pseudoplastic behavior suggests the forma-211 tion of no chemical cross-links; alternatively, the hydrophobic associations 212 cause physical entanglements with relative conformational mobility and flex-213 ibility. Adding cellulose fibers to the BC matrix modifies, as expected, the 214 suspensions' viscosity. The hornification's effect in SC fibers is remarkable 215

when comparing samples BC-SC-25 (Figure 4d) with BC-RC-25 (Figure 4b). 216 Over the experimental conditions, sample BC-SC-25 presented a viscosity 217 no higher than  $\sim 100$  Pa·s; meanwhile, sample BC-RC-25 reached viscosity 218 values one order of magnitude higher. This difference is because RC fibers' 219 internal volume is open, and they can create more physical interactions with 220 the unmodified OH groups of BC (Giacomozzi and Joutsimo, 2015). There-221 fore, inducing shear flow in sample BC-RC-25 requires a more elevated force 222 input than in sample BC-SC-25. 223

Modifying the fiber concentration to 0.50% increased  $\eta$  at temperatures 224 no higher than 35°C for sample BC-RC-50 and at all the temperatures in the 225 SC sample (Figure 4c and 4e, respectively). The viscosity increased because 226 the free volume in the suspension is less after loading the system with more 227 fibers, which start reflecting their rheological behavior in the particle laden 228 system. Moreover, the number of cooperative interactions between cellulose 220 fibers increased since they formed hydrogen bonding with the components of 230 the surrounding medium (water, BC, and other fibers). RC sample's viscosity 231 profile (Figure 4c) is similar to the ones reported by Karppinen et al. (2012). 232 The difference in the viscosity's behavior observed in specimens carrying RC 233 and SC fibers can be explained by the number of supramolecular interactions. 234 Sample BC-RC-50 (Figure 4c) contains more cooperative interactions than 235 the SC sample (Figure 4e). At a temperature higher than 35°C (Figure 4c), 236 the effect of RC fibers in viscosity seemed unclear since the viscosity is lower 237 than for sample BC-RC-25. By recalling the experiments' videos, sample 238 BC-RC-50 presented apparent wall slip in a higher degree than sample BC-239 RC-25. Therefore, it is possible to conclude that at temperatures close to 240  $T_{ael}$  the apparent wall slip affects the measurements' accuracy. 241

Figure 5 presents experimental data (dots) together with the Bayesian 242 optimization (surface) of  $G^*$  and  $\delta$  as a function of fiber concentration c and 243 temperature T. In Fig. 5a and 5b, at a concentration of 0.25 wt.%, RC 244 and SC fibers affected  $G^*$  alike: they increased the shear elastic modulus 245 of BC. Additionally, the behavior of  $\delta$  (Fig. 5c and d) at 0.25 wt.% was 246 opposite to the one of  $G^*$ . The modulus increased after adding both types 247 of fibers since they induced an effect comparable to the one observed in 248 fibrillated all-cellulose composites (Baghaei and Skrifvars, 2020). The fibers' 249 influence becomes noticeable after increasing c to 0.50 wt.<sup>%</sup>, and when BC 250 develops a gel structure ( $T > 40^{\circ}$ C). The BC matrix may immobilize the 251 fibers and therefore reinforce the elastic properties. Figures 5c and d support 252 the last statement since the phase shift angle decays due to increasing c and T253



Figure 4: Samples' dynamic viscosity as a function of  $\dot{\gamma}$  and T fitted with a Bayesian optimization (surfaces) of the experimental data (scatter points). (a) BC, (b) BC-RC-25, (c) BC-RC-50, (d) BC-SC-25, (e) BC-SC-50. The scales of  $\dot{\gamma}$  and  $\eta$  are logarithmic. The data without the surface fit is shown in Figure S3 in supplementary information.

	0	
Sample	$T_{gel}$	$T_{gel}$
	G' and $G''$ intercept	$\delta$ slopes intercept
BC	$50.17^{\circ}\mathrm{C}$	49.20°C
BC-RC-25	42.14°C	44.23°C
BC-RC-50	No intercept	$43.53^{\circ}\mathrm{C}$
BC-SC-25	44.16°C	$45.35^{\circ}\mathrm{C}$
BC-SC-50	No intercept	$44.75^{\circ}\mathrm{C}$

Table 2: Gelation temperature of the particle laden suspensions estimated utilizing two methodologies.

(i.e., the material turns gradually more elastic than viscous). Regarding the fiber type effect, it is more evident at 0.50 wt.%. RC fibers create a stiffer material since the increment of  $G^*$  (Fig. 5a) and decrement of  $\delta$  (Fig. 5c) were more significant than the ones observed with SC fibers. The viscosity discussion also explains these differences; the RC-BC interface possesses more cooperative associations than the SC-BC.

Table 2 collects the  $T_{gel}$  of the examined suspensions. The intercept of 260 G' and G'' is traditionally the best route to determine the gel transition. 261 However, in the particle laden suspensions, no intercept can be identified as 262 a consequence of the dispersed phase effects on the matrix. Cellulose fibers 263 increase the elastic component of  $G^*$  and hide the transition as the G' and 264 G'' curves never intercept. Here, we used  $\delta$  to determine  $T_{ael}$  (see Figure S2). 265 Considering that  $\delta$  defines the viscoelastic behavior, the exponential decay of 266 this parameter could assist in elucidating the gel transition. Identifying  $T_{qel}$ 267 from  $\delta$  imitates the methodology used to determine the glass transition using 268 the exponential decay of G' (see Figure S2 in supplementary information). 269 In general, adding both types of fibers reduced  $T_{qel}$ . The fibers' hydrophobic 270 and OH sites may work as heterogeneous nucleation segments for BC. Adding 271 more fibers decreased  $T_{gel}$ , this fact supports the idea about their nucleant 272 effect since more fibers represent more nucleation segments. Respect the 273 difference between RC and SC fibers, RC fibers induced a lower  $T_{qel}$  than 274 SC ones. The cooperative associations arising between RC-BC and SC-BC 275 interfaces are again a possible explanation to the differences in  $T_{qel}$ . 276

Finally, the new method to define  $T_{gel}$  and fitted surfaces provide a methodology to deduce the dependency of  $T_{gel}$  of the fiber concentration. Fitting the lines as shown in Figure S2 to the predicted  $\delta$  values for vari-



Figure 5: Samples'  $G^*$  and  $\delta$  (at  $\omega = 6.30$  rad/s) as a function of fiber concentration and T fitted with a Bayesian optimization (surfaces) of the experimental data (scatter points). (a) and (c) belong to the samples containing BC and RC. (b) and (d) belong to samples containing BC and SC. The scale of  $G^*$  is logarithmic. The data without the surface fit is shown in Figure S4 in supplementary information.



Figure 6: (a) The values for  $T_{gel}$  may be defined at concentrations that have not been measured using the GP regressor fitted surface. The surface is the same as in Fig. 5d and the solid line shows the position of gelation. (b) The gelation temperature with respect to the fiber concentration c of the Storacell fibers determined using the GP fitted surface. The circles show the values determined from the measurements.

ous values of c result in estimates of  $T_{ael}$  that were not actually measured. 280 Figure 6a shows the same surface as in the Fig. 5d with a line showing the 281 estimated  $T_{qel}$  for suspensions with c from 0.0 to 0.5 %. The Figure 6b then 282 displays the estimated gel temperature with the concentration. The circles 283 in Fig. 6b are the values actually determined from the measurements. The 284 estimate accords with the three points; however, these points alone do not 285 contain enough data for such complete estimate for gel temperature. Supple-286 mentary Figure S5 shows similar plots with increasing Refcell concentration 287 where the outcome accords with Figure 6. The examples demonstrates the 288 power of GP regressor in successfully estimating material properties with 289 incomplete data sets without laborious extra measurements. 290

### <sup>291</sup> 4 Conclusion

Methylcellulose demonstrated being an alternative to utilizing solubilized cellulose for the manufacture of cellulosic composites. Nevertheless, the compatibility between the cellulose derivative and fibers depended on the number of supramolecular interactions. This manuscript revealed that enhancing the

interface matrix-fiber hangs on the degree of substitution of MC and fibers? 296 morphology. For instance, never-dried fibers possessed an uncollapsed inner 297 structure abundant in OH groups, while dried fibers lacked it. The differ-298 ence in morphology defined the properties of the particle laden suspensions, 299 which was why RC could create more cooperative associations with the cel-300 lulose ether than SC. Accordingly, raising the concentration of RC fibers 301 overall increased the viscosity and reinforced the mechanical properties to a 302 higher degree when compared to SC samples. 303

In brief, rheology was an adequate tool to elucidate the interfacial phe-304 nomena in the studied particle laden suspensions under different stimuli and 305 conditions  $(c, \dot{\gamma}, \text{ and } T)$ . Assisted with Bayesian optimization, the spectra 306 of rheological characterization exhibited having unexplored frontiers. Our 307 approach has effectively fill the gap between the different experimental mea-308 surements, reducing in this way the number of experimental required. Here 300 we have used experimental data to determine the 3D surfaces, but it can 310 be easily extrapolate to be used in simulation and reduce the computational 311 time. It is unmistakable that using Bayesian optimization will lead to saving 312 resources in materials characterization and research development. 313

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