



- 26 • CMC improves redispersibility and reduces aggregation of MFC microfibrils
- 27 • NMR relaxation measurements give an insight into the mechanisms of redispersibility
- 28 • Polymer aggregation dominates the  $T_2$  value and NMR behaviour of suspensions
- 29 • Improved re-dispersion is correlated with higher shear viscosity and increased  $T_2$
- 30 • Unique microstructures relevant to foods have been created

31 **Keywords:** Microfibrillar cellulose; carboxymethyl cellulose; low-field NMR; relaxation time;  
32 rheology

### 33 **1. Introduction**

34 Cellulose is the most abundant natural structural polymer in nature and provides mechanical  
35 properties such as strength and stiffness to the plant cell wall of higher plants. Important  
36 components of this natural fibre strength and stiffness are the microfibrils within the cellulose  
37 structure. The fibrous cell wall is essentially a composite material consisting of a framework  
38 of cellulose (micro-) fibrils organised into strands of cellulose which are embedded in a matrix  
39 of hemicelluloses and lignin. Cellulose microfibrils in the cell wall are intertwined fibrils with  
40 a diameter of approx. 2-20nm and a length of 100-40,000nm depending on the source (Kirk  
41 and Othmer, 1967; Kocherbitov, Ulvenland, Kober and Jarring, 2008). These cellulose fibres  
42 can be broken down into their structural micro/nano-scale units by various chemical and  
43 mechanical processes (Henriksson, Berglund and Lindstrom, 2007). Production and  
44 characterisation of microfibrillar cellulose (MFC) from wood fibres have been described by  
45 Turbak *et al.* 1983 and Herrick *et al.* 1983, where MFC suspensions were obtained by  
46 disintegrating cellulose fibres at high shear. The resultant highly entangled MFC network  
47 consists of micro/nano size elements with a gel-like behaviour for water suspensions at 1% or  
48 lower concentrations of MFC (Turbak *et al.*, 1983, Herrick *et al.*, 1983, Nakagaito and Yano  
49 2004, Nishiyama, 2009). During the last decade, microfibrillar cellulose (MFC) has been  
50 produced by using more aggressive, high shear or high energy mechanical treatments such as

51 homogenisers or microfluidisers which led to highly entangled, fibril aggregates and  
52 mechanically strong networks (Frone *et al.*, 2011, Lavoine *et al.*, 2012). Depending on the  
53 pressure, flow rate, temperature, and the design and diameter of the chambers used in high-  
54 pressure homogenisers or microfluidisers, different particle size distributions and microfibrillar  
55 networks can be produced (Lavoine *et al.*, 2012). Several publications have shown applications  
56 of these highly networked MFC microfibrils for various purposes, such as reinforcement in  
57 nanocomposites (Malainine, Mahrouz and Dufresne 2005, Lopez-Rubio *et al.*, 2007, Bruce *et*  
58 *al.*, 2005), dispersion stabilization (Oza and Frank 1986, Ougiya *et al.*, 1997, Khopade and Jain  
59 1990), media filtration (Burger, Hsiao and Chu 2006), antimicrobial action in films (Andresen  
60 *et al.*, 2007) and oxygen barrier production in food and pharmaceuticals (Syverud and Stenius  
61 2009). The rheological properties of these MFC suspensions have been widely studied by a  
62 number of researchers. In general, the rheological properties of aqueous MFC suspensions  
63 isolated from softwood, sugar beet pulp, corn cobs and cotton show gel-like behaviour where  
64 the storage modulus ( $G'$ ) is higher than the loss modulus ( $G''$ ) over a wide concentration range  
65 (Pääkkö *et al.*, 2007, Tanjawa *et al.*, 2010, Cordabo *et al.*, 2010, Tatsumi *et al.*, 2002, Tatsumi  
66 *et al.*, 2007).

67 Homogenisation modifies the structure of the starting materials by releasing microfibrils into  
68 the suspension. Drying the MFC is also known to modify the defibrillated state primarily by  
69 increased hydrogen bonding but possibly also other forms of bonding such as van der Waals  
70 between the microfibrils, leading to the formation of bundles and agglomerates (Quiévy *et al.*,  
71 2010). These fibre bundles and aggregates are difficult to redisperse in water in order to form  
72 homogeneous suspensions, a consequence being a reduction in the values of rheological  
73 parameters such as  $G'$ ,  $G''$  and the shear viscosity of the suspension. This process of irreversible  
74 or partial irreversible agglomeration of cellulosic fibres and stiffening of the polymer structure  
75 during drying is known in the literature as hornification. It is a technical term widely used in  
76 the paper-making industry (Smook 1990, Kato *et al.*, 1999, Fernandes *et al.*, 2004). The

77 aggregation or agglomeration occurs to varying extents depending on the drying process. To  
78 protect the microfibrils from collapse and agglomeration, a number of hydrocolloids, *e.g.* low  
79 and high methoxyl pectin, CMC, and sodium polyacrylate, as well as salts *e.g.* sodium chloride  
80 (Lowys, Desbrieres & Rinaudo, 2001; Tandjawa *et al.*, 2012; Missoum, Bras & Belgacem,  
81 2012), have been used to stabilise the fibrils. Lowys (2001) demonstrated an interaction  
82 between MFC and polymeric additives such as sodium-CMC and pectins, where the additives  
83 were homogeneously distributed and formed weak bonds with MFC fibres improving the  
84 redispersibility of MFC in water. This interaction between the additive and MFC tends to  
85 stabilise the fibrils against collapse or agglomeration during the drying process. The objective  
86 of the current publication is to provide an insight into the impact of drying (hornification) on  
87 the state of the polymer and the apparent water mobility in the MFC matrix.

88 Rheological properties of aqueous suspensions of MFC with or without additives show  
89 viscoelastic gel-like behaviour and high viscosity (Cordabo *et al.*, 2010, Agoda-Tandjawa *et*  
90 *al.*, 2010). Such properties of aqueous suspensions at 1% (w/w) and lower concentrations, make  
91 MFC valuable in a wide range of industrial applications such as food, cosmetics, paints and  
92 composites, *etc.* The strong interactions between the MFC fibres in aqueous media are the  
93 driving force behind rheological characteristics, such as water binding and viscosity. Agoda-  
94 Tandjawa (2012) reported that in the presence of calcium ions, low methoxyl pectin exhibited  
95 a synergistic effect with MFC fibres leading to increased shear and complex viscosities of the  
96 composites. In the present study, the impact of carboxymethyl cellulose on rheological  
97 properties of a dried and redispersed MFC suspension was studied.

98 It has been suggested that proton nuclear magnetic resonance (NMR) parameters such as spin-  
99 lattice-relaxation time ( $T_1$ ) and spin-spin relaxation time ( $T_2$ ) are sensitive to water state and  
100 mobility in polymeric suspensions/dispersions (Ono, Inamoto and Okajima, 1997; Rachocki,  
101 Markiewicz and Tritt, 2005, Vackier, Hills and Rutledge, 1999). The spin-spin relaxation time

102 T<sub>2</sub> is generally measured using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence  
103 (Meiboom and Gill, 1958). The CPMG sequence provides a more accurate measure of the  
104 liquid transverse free-induction decay time (T<sub>2</sub>) and is free of artefacts such as magnetic  
105 inhomogeneity. In a study by Ono (1997), an MCC suspension was shown to contain both free-  
106 water and water-associated to the polymer with a mutual exchange of protons resulting in  
107 shorter overall T<sub>2</sub> compared to pure distilled water, where a typical T<sub>2</sub> is of the order of 2  
108 seconds.

109 The primary aim of this study then is focused on understanding the impact of CMC on the  
110 redispersibility of MFC in water and its impact on rheological properties of the suspension. It  
111 is hoped that this understanding will shed light on the occurrence of aggregation of MFC and  
112 the technical problems that ensue from this in various industries from food to paper-making. A  
113 detailed study of rheological behaviour and the NMR determined apparent water mobility of  
114 the redispersed MFC/CMC system, when correlated with fluorescence microscopy, as  
115 presented here, will enable important structural features of these cellulosic materials which are  
116 of relevance to the food and personal care industries to be determined. The hypothesis  
117 underpinning this research is that the addition of CMC to an MFC suspension improves the  
118 redispersibility of MFC after drying, by increasing the repulsion between polymer chains due  
119 to the charge on the added polymer, and that the effects on the apparent water mobility in the  
120 matrix are ultimately due to this.

## 121 **2. Materials and methods**

### 122 *2.1. Materials*

123 Microfibrillar cellulose (MFC) from spruce cellulose (8.97% w/w MFC paste) was provided by  
124 Borregaard AS (Sarpsborg, Norway). Cellulose was obtained from 100% spruce. The charge  
125 density of pure cellulose changes noticeably during the pre-treatment and finishing process to  
126 produce MFC (Ribitsch *et al.*, 2001). From the information provided by the supplier, the charge

127 density on the microfibrillar cellulose will be low. Carboxymethyl cellulose (CMC) with a  
 128 degree of substitution of 0.71 was supplied by CP Kelco (Norway). Reverse osmosis (RO)  
 129 water was used for all experiments. Light mineral oil density 0.838 g/mL at 25°C (Sigma-  
 130 Aldrich, UK) was used during the rheological measurements to prevent sample dehydration.

131 *2.2. Sample preparation and biopolymer mixtures*

132 2% w/w aqueous suspensions of microfibrillar cellulose were prepared by diluting the MFC  
 133 stock solution (8.97%w/w MFC paste) with RO water using a high shear overhead mixer  
 134 (Silverson, UK) at 8000rpm for 5minutes. An aqueous solution of CMC (2% w/w) was  
 135 prepared separately and added to a 2%w/w MFC suspension according to the formulations  
 136 shown in Table 1, to produce an overall concentration including both components of 2%. The  
 137 CMC sample was dissolved by dispersing in RO water (2%w/w) under gentle stirring (IKA  
 138 Eurostar 20 Digital Overhead Stirrer) at room temperature for 2h. The pH of the solution was  
 139 adjusted to 6.8 and left overnight at 4°C before mixing with the MFC stock suspension. Sodium  
 140 azide solution (0.02% w/w) was added to prevent bacterial contamination. The concentration  
 141 of stock samples was determined by evaporating to dryness and measuring the dry solids  
 142 content.

143 *Table 1: Composition of the MFC/CMC model systems used in this study.*

Sample Code	% w/w in suspension	
	MFC (%)	CMC (%)
MFC100	2	0
CMC15	1.7	0.3
CMC25	1.5	0.5
CMC50	1	1

144 MFC/CMC solutions were mixed in different proportions as shown in Table 1 at room  
 145 temperature in water and at an overall concentration of 2% w/w. All samples were mixed  
 146 thoroughly using an overhead stirrer (Silverson, UK) at 8000rpm for 5minutes. The mixtures  
 147 were stored overnight at room temperature for equilibration and the pH was re-measured. For

148 re-dispersion studies, an approximately 1mm thin layer of the suspension was layered on an  
149 aluminium plate and dried at 50°C for 12 hours using a conventional oven (Gallenkamp hotbox  
150 oven, size 2).

151 For rheological and relaxation NMR measurements all dry samples were redispersed at 2% w/w  
152 concentration in water by using high shear (T25 digital Ultra-Turrax®) at 15000rpm for  
153 4minutes at room temperature. Samples were stored overnight at room temperature on a roller  
154 bed (Stuart Digital tube rollers - SRT6D) at a speed 60rpm in order to achieve a homogeneous  
155 suspension. For relaxation NMR v/s shear viscosity curves, MFC100 and CMC15 “never-dry”  
156 (ND) and “dried” (D) suspensions at 0.2-2% w/w were prepared in RO-water using high shear  
157 (T25 digital Ultra-Turrax®) at 15000rpm for 4minutes at room temperature. The pH of all  
158 suspensions was maintained at 6.8.

### 159 2.3. *Rheological measurements*

160 The rheological measurements were carried out on a stress-controlled rheometer (Physica MCR  
161 301, Anton Paar, Austria) with a serrated parallel plate geometry (50mm diameter with a gap  
162 of 1mm) at 20±1°C, controlled by a Peltier system. Small oscillatory amplitude sweeps were  
163 generated by log ramping strain 0.01 to 100% at a constant frequency of 1Hz. Frequency  
164 sweeps were performed over the frequency range of 0.1-15Hz at a constant strain of 0.2%  
165 which lay within the linear viscoelastic region. Shear viscosity was measured at constant shear  
166 rate *i.e.* at 50s<sup>-1</sup> at 20±1°C. Temperature sweeps were generated by heating the sample between  
167 the plates from 20°C to 90°C at the rate of 1°C/min. During these experiments, the strain was  
168 fixed at 1% and the frequency at 1Hz. A light mineral oil barrier was used to prevent water  
169 evaporation. Data presented are an average of four replicates.

### 170 2.4. *Pulsed <sup>1</sup>H-NMR measurements*

171 Time domain measurements were carried out at 25MHz using a Resonance Instruments (RI)  
172 Maran benchtop NMR spectrometer (Oxford-Instruments Plc, UK). This type of instrument is  
173 used routinely in the food industry for fat and moisture measurements. The temperature was  
174 regulated at  $20\pm 1^{\circ}\text{C}$  by a conventional gas flow system calibrated with an external  
175 thermocouple and controlled with a standard R.I. temperature unit. All measurements were  
176 made in 10mm outer diameter (OD) NMR tubes. Spin-spin relaxation times ( $T_2$ ) were recorded  
177 using the CPMG (Carr-Purcell-Meiboom-Gill) pulse sequence (Meiboom and Gill, 1958),  
178  $90^{\circ}_x - (\tau - 180^{\circ}_y - \tau - \text{echo})_n$  with  $\tau = 2048\mu\text{s}$ . Typical  $90^{\circ}$  pulse lengths were of the order  
179 of  $5\mu\text{s}$  and  $180^{\circ}$  pulse length was  $10\mu\text{s}$ . The recycle delay time was fixed at 10 seconds ensuring  
180 that all samples were relaxed before the next pulse sequence was applied. 64 scans were  
181 recorded. All samples were left at a constant temperature for 15min to ensure the temperature  
182 was equilibrated and consistent for all data points (see McConville, Pope, 2001). All relaxation  
183 curves obtained by the CPMG method showed a single exponential decay.

#### 184 2.5. Microscopic analysis

185 Light microscopy of aqueous suspensions of samples was performed using an Olympus BX5  
186 bright field light microscope at 20X magnification with a scale bar of  $200\mu\text{m}$ . The fibres were  
187 dyed using Congo red dye (Sigma-Aldrich). Fluorescence microscopy was carried out using an  
188 EVOS microscopy system in fluorescence mode with a 20X objective. As both MFC and CMC  
189 do not fluoresce, it was necessary to attach a fluorescence label to one of them. In the current  
190 study, CMC was tagged with FITC fluorescent dye. 1g of CMC was dissolved in 10ml of  
191 dimethyl sulphoxide containing a few drops of pyridine. 0.1g of Isothiocyanate -fluorescein  
192 was added to 20mg dibutyltin dilaurate and the whole mixture was heated at  $95^{\circ}\text{C}$  for 2hours.  
193 Free dye was removed from the system by a number of precipitations in ethanol, then the FITC-  
194 CMC was filtered and dried at  $80^{\circ}\text{C}$ . The protocol used is the same as that published by Belder  
195 *et al.*, 1973.

### 196 3. Results and Discussion



197 3.1. Viscoelastic properties of MFC/CMC suspensions

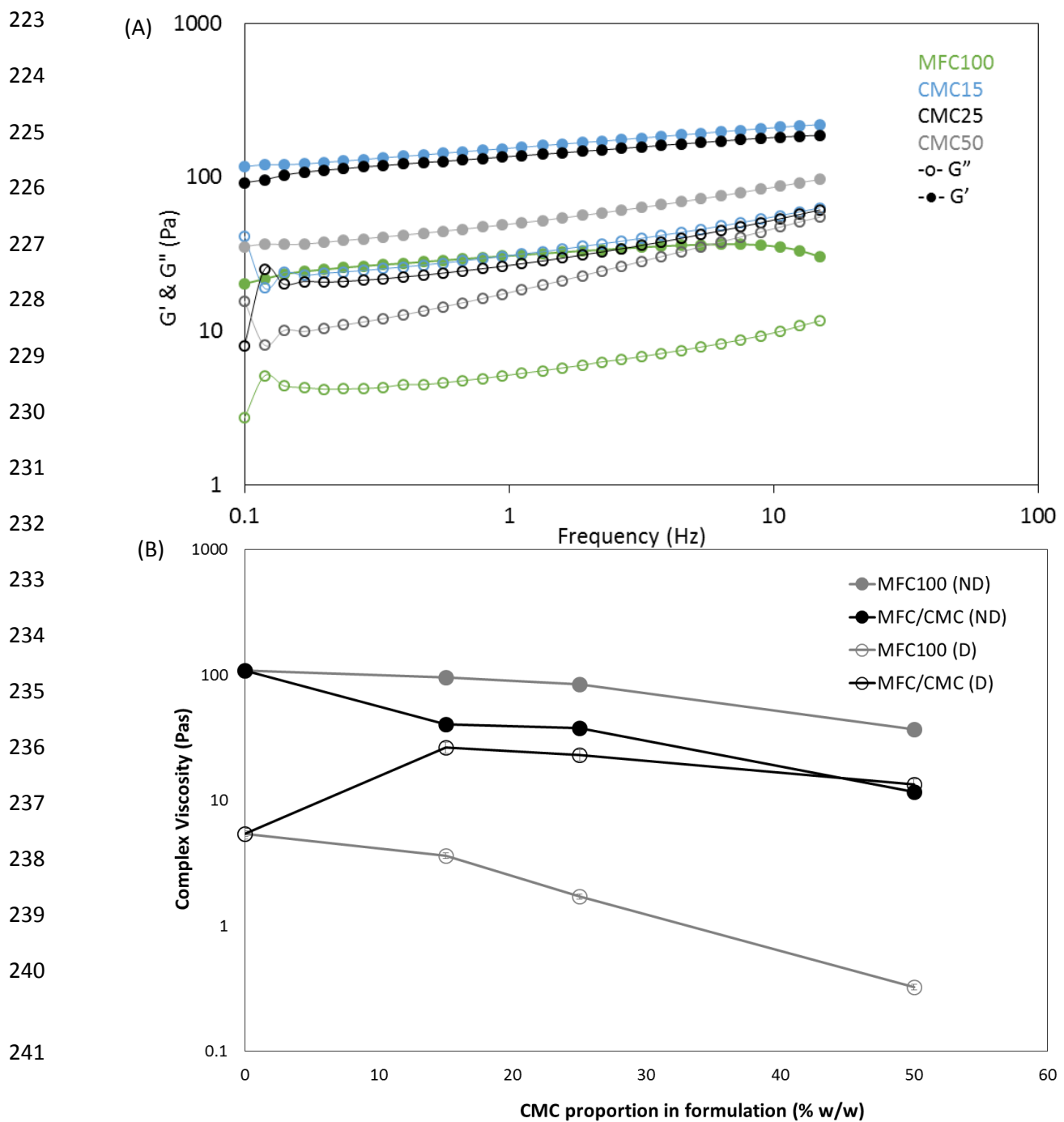
198 Figure 1A shows the viscoelastic properties as a function of frequency at 20°C for rehydrated  
199 aqueous suspensions of MFC/CMC with various contents of CMC (CMC15, CMC25 and  
200 CMC50), at a total biopolymer concentration of 2%w/w. The storage modulus ( $G'$ ) of the  
201 suspension was higher than the loss modulus ( $G''$ ) with little dependency on frequency  
202 indicating viscoelastic gel-like behaviour. Both moduli increased with increasing frequency,  
203 indicating that the network structure formed by the microfibrils is in the dynamic mode of  
204 forming entanglements resulting in a stable network of fibres. Similar viscoelastic gel-like  
205 behaviour was also observed with never-dried MFC100 and MFC/CMC suspensions.  
206 Frequency sweep data for these systems are not shown. Similar viscoelastic behaviour was  
207 observed with aqueous suspensions of softwood MFC containing polymeric additives such as  
208 pectin, cationic starch *etc.* (Lowys, Desbrieres and Rinaudo, 2001; Tandjawa *et al.*, 2012).  
209 Redispersed MFC/CMC suspensions showed noticeably higher values for  $G'$  and  $G''$  compared  
210 with MFC100 (Figure 1A). Visually, it was observed that the addition of CMC improved the  
211 redispersibility of the MFC in water and a homogenous suspension was produced using a high  
212 shear mixing process. Figure 1B shows the change in complex viscosity measured at 0.2%  
213 strain and 1Hz frequency for pure MFC100 (D) without additives and MFC/CMC mixtures, as  
214 a function of CMC proportion in the mixture. In Figure 1B, the concentration for pure MFC100  
215 is identical to that present in MFC/CMC mixtures. It was observed that the complex viscosity  
216 ( $|\eta^*|$ ) of the redispersed suspension increased with an increase in CMC proportion in the  
217 formulation, indicating that the MFC forms entangled networks crosslinked with CMC,  
218 resulting in higher complex viscosity (Figure 1B) and higher values for  $G'$  and  $G''$  (Figure 1A).

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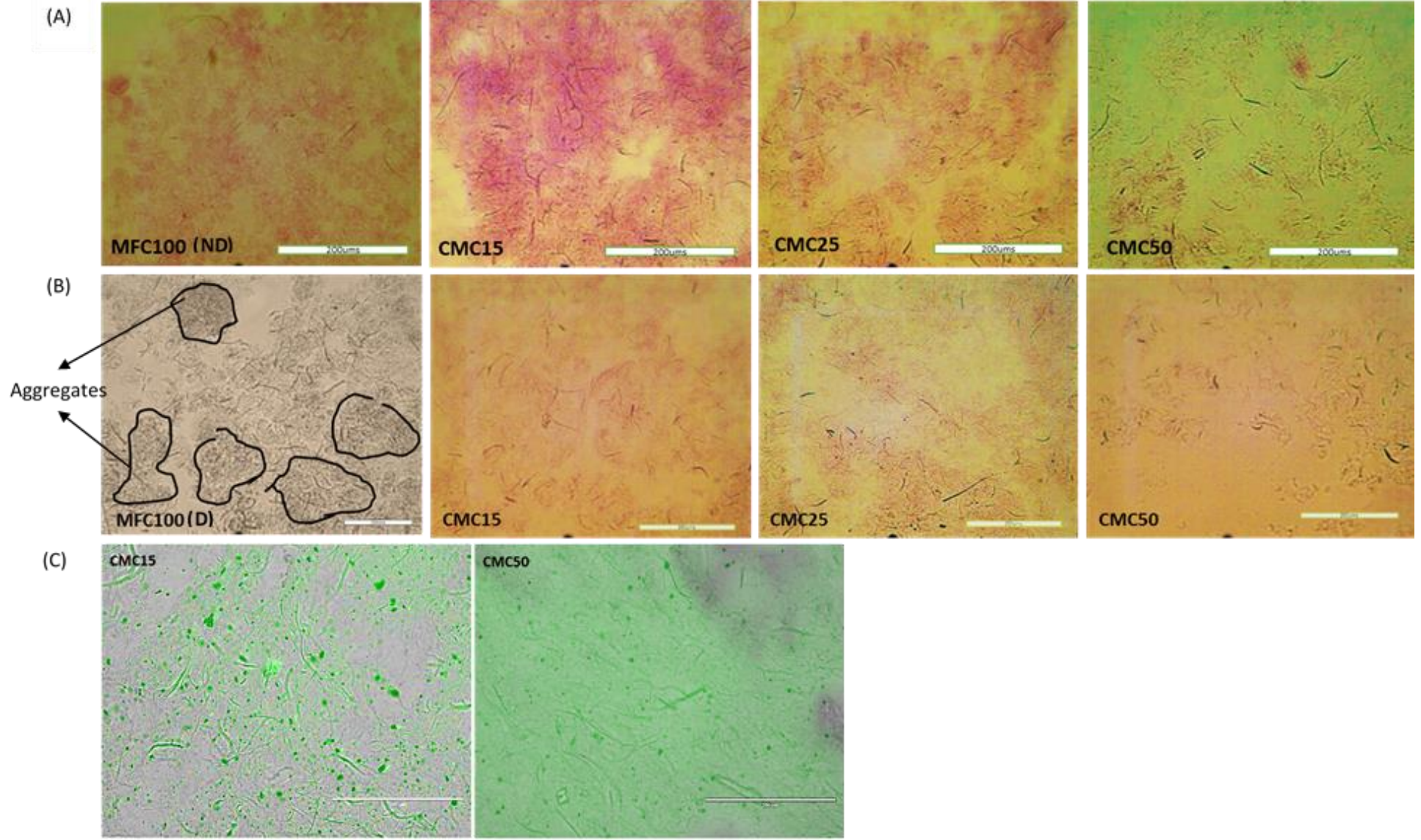


243 **Figure 1** (A) Frequency dependency of viscoelastic moduli for MFC/CMC mixtures dried and  
 244 redispersed in aqueous media. Data were acquired at 0.2% strain and 20°C. Solid symbols  
 245 represent the storage modulus ( $G'$ ) and open symbols the loss modulus ( $G''$ ). (B) Complex  
 246 viscosity  $\eta^*$  measured at a frequency of 1Hz and 0.2% strain as a function of CMC  
 247 concentration in an aqueous suspension of MFC:CMC and also for MFC100 alone. For each  
 248 point the MFC concentrations are matched therefore the percentage of MFC in a pure solution

249 *is identical to that present in an MFC/CMC formulation. At 0% CMC concentration the MFC*  
250 *concentration is 2% and at a CMC concentration of 50% the MFC concentration is 1%. Solid*  
251 *symbols represent the (ND) suspensions and open symbols the (D) suspensions.*

252 A noticeable difference in complex viscosity was observed on comparing the MFC100 (ND)  
253 and MFC/CMC (ND) suspension (Figure 1B), this behaviour can be explained by the dilution  
254 effect of CMC on MFC producing the different ratios. Diluting the MFC network structure  
255 with CMC to make up the formulation (as per Table 1), results in less microfibril entanglement  
256 in the network structure and is also seen in the microscopy images presented in Figure 2A,  
257 resulting in a lower complex viscosity as compared with comparable concentrations of  
258 MFC100 (ND) (Figure 1B). A slightly lower complex viscosity was observed when comparing  
259 MFC/CMC (ND) and MFC/CMC (D) formulations, but this reduction was minimal in the case  
260 of CMC50 (Figure 1B). However, the CMC50 suspension showed weaker gel-like behaviour.  
261 The slight frequency dependence of the moduli and the relatively large value of  $\tan \delta$  ( $G''/G' > 0.1$ )  
262 defines so-called weak gel behaviour (Ikeda and Nishinari, 2001) as evident in Figure  
263 1A.  $\tan \delta$  values are also presented later in Figure 4. When the negatively charged CMC was  
264 added at higher levels, the CMC adsorption to MFC increased significantly. Similar behaviour  
265 was reported with bacterial cellulose/CMC systems where changes in zeta-potential were  
266 shown (Veen *et al.*, 2014). The increase in the charge for all ratios of CMC leads to better  
267 redispersibility of the MFC/CMC formulations in water with higher complex viscosity values.  
268 Lower values of  $G'$  where  $\tan \delta > 0.1$  for CMC50 suspensions can be explained by a dilution  
269 effect. As the dense network of microfibrils plays an important role in maintaining viscoelastic  
270 gel-like behaviour, when MFC is diluted with 50% CMC the MFC is at 1%, which without  
271 additives shows an order of magnitude decrease in  $G'$  and  $G''$  (Figure 1B), and the MFC forms  
272 a weaker entangled network structure.

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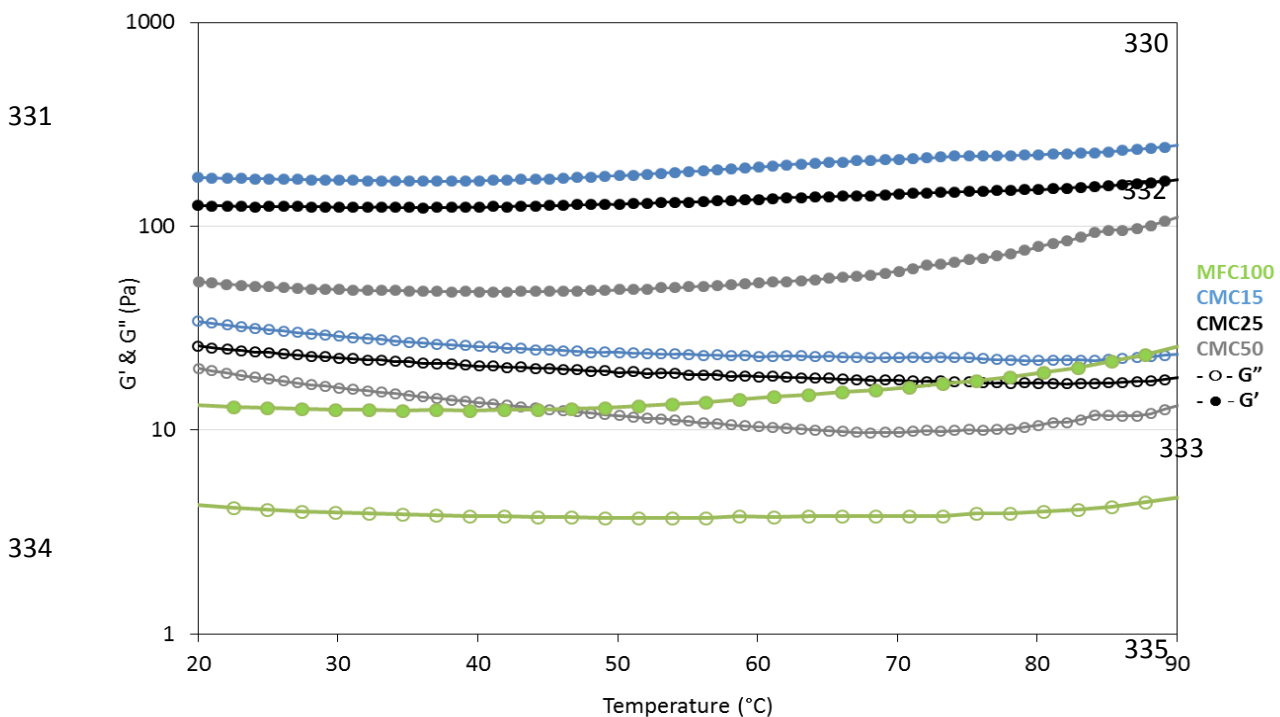
289 **Figure 2** *Light microscopy images of 2% w/w aqueous suspensions of (A) never dried, (B)*  
290 *dried and redispersed suspensions of MFC100 and MFC/CMC at CMC levels of 15, 25 and*  
291 *50%. (C) Fluorescence microscopy images of 2% w/w redispersed suspension of CMC15, and*  
292 *CMC50, scale bar 200 $\mu$ m, where CMC is tagged with FITC (green fluorescence).*

293 Light microscopy images of never-dried MFC with different levels of CMC indicated that the  
294 addition of CMC does not affect microfibrillar entangled network except at high levels (Figure  
295 2A). A lower level of entanglement was observed in the case of CMC50. This can be explained  
296 by dilution effect of CMC on the MFC network structure as outlined for the case of complex  
297 viscosity earlier. Microscopy images of dried and redispersed MFC/CMC (i.e., CMC15,  
298 CMC25 & CMC50) indicate that the addition of CMC reduced the microfibrillar aggregate or  
299 fibre bundle formation as compared to MFC100 (D) (Figure 2B). Drying MFC without CMC  
300 resulted in a large amount of microfibrillar aggregates due to the formation of strong inter- and  
301 intramolecular hydrogen bonds during the drying process (Figure 2B). These were difficult to  
302 redisperse in water and reduced the values of viscoelastic parameters such as  $G'$ ,  $G''$  and  
303 complex viscosities due to poor network formation. From fluorescence microscopy images  
304 (Figure 2C) it cannot be said with certainty that fluorescently tagged-CMC interacted at a  
305 molecular level with the surface of MFC microfibrils. It is strongly implied however from the  
306 comparison in Figure 2C of CMC15 and CMC50 that as the amount of CMC increased, either  
307 the surface coverage of MFC by CMC increased or there was a general build-up of the labelled  
308 CMC in the solution surrounding the fibres.

### 309 *3.2. Temperature dependence of the viscoelastic moduli*

310 The temperature dependence of  $G'$  and  $G''$  for 2% w/w aqueous suspensions of MFC/CMC  
311 mixtures is shown in Figure 3. All the samples showed stable viscoelastic gel-like behaviour  
312 where the storage modulus was higher than the loss modulus throughout the temperature range  
313 20°C - 90°C at a heating rate of 1°C/min. It was observed that the  $G'$  and  $G''$  for all suspensions

314 showed an initial slight decrease from 20°C to 40°C, however above 40°C the suspensions  
 315 showed an increase in  $G'$  and  $G''$  up to 90°C. Similar behaviour was observed with cellulose  
 316 nanofibers from poplar wood by Chen *et al.*, 2013. The first slight decrease in modulus may be  
 317 due to thermal agitation/thermal motion of microfibrils, resulting in loosening of the fibrils  
 318 within the network structure. However, the swelling of microfibrils with an increase in  
 319 temperature, while interacting with CMC in the matrix, may strengthen the gel-like structure,  
 320 resulting in an increased  $G'$  and  $G''$  of suspensions above 40°C. As the amount of CMC  
 321 increased in the formulation,  $G'$  and  $G''$  increase to a greater extent above 40°C suggesting  
 322 synergistic interactions between MFC/CMC. It is well known that polymeric solutions such as  
 323 HPMC (hydroxyl propyl methyl cellulose), exhibit an increased thermal motion upon heating,  
 324 leading to a weaker network and sometimes a decrease in viscosity, however the viscosity of  
 325 these systems tends to increase above the gelation temperature depending on concentration  
 326 (Silva *et al.*, 2008). The fact that the MFC/CMC suspensions do not lose structure upon heating,  
 327 even when the MFC proportion is lowered, indicates an interaction beyond the surface  
 328 stabilisation of the microfibrils by CMC, although it is not yet clear which mechanisms are  
 329 involved.



336 **Figure 3** *Temperature dependency (20° to 90°C at a heating rate 1°C/min) of the viscoelastic*  
337 *moduli of 2% w/w aqueous suspensions of MFC100 (D) and MFC/CMC (D) acquired at 1Hz*  
338 *frequency and 1% strain. Solid symbols represent storage modulus (G') and open symbols*  
339 *represent loss modulus (G'').*

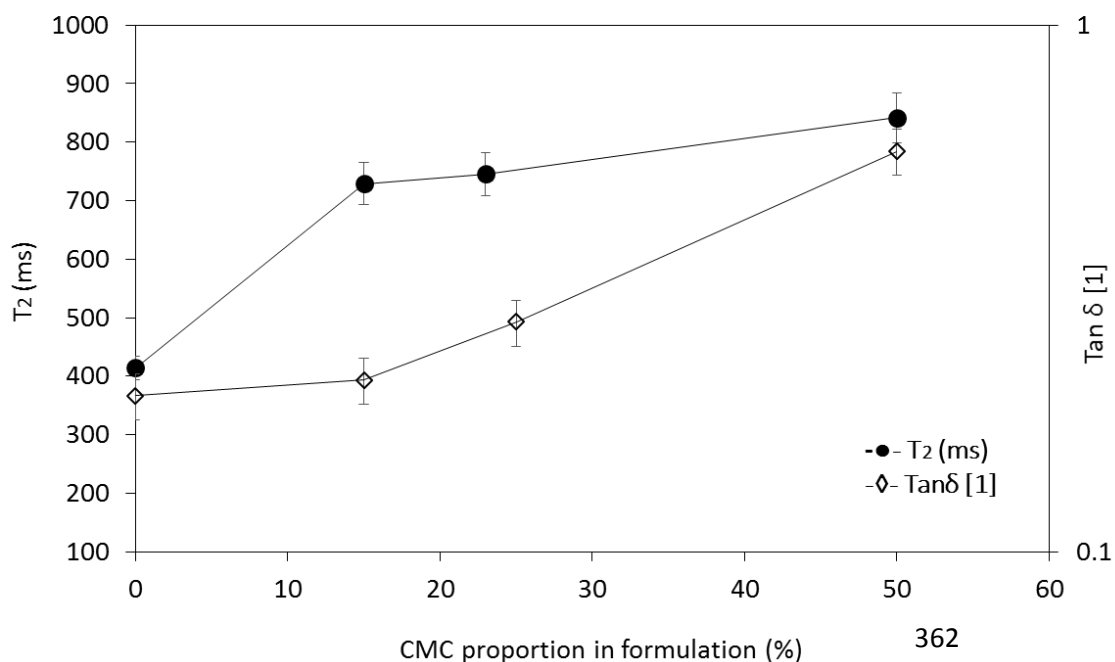
### 340 3.3. Relaxation time ( $T_2$ ) of MFC/CMC suspensions

341 Figure 4 shows the spin-spin relaxation time ( $T_2$ ) as a function of the amount of CMC present  
342 in the MFC/CMC formulations. At higher levels of CMC in the formulation, the  $T_2$  (ms) value  
343 and the  $\tan \delta$  of the suspension increased, the latter implying that the suspension was behaving  
344 in a more viscous or liquid-like fashion. Lower  $T_2$  values for the redispersed MFC100  
345 (CMC=0) suspensions are most likely due to the rigid network structure formed by strong intra-  
346 or intermolecular H-bond within the microfibrils and a consequently reduced  $T_2$  value for the  
347 polymeric component. It appears to be the presence of these rigid structures in case the of  
348 MFC100 (D) suspensions which dominate the  $T_2$  values at all concentrations. In this case, the  
349 overall  $T_2$  value of the suspensions are driven by the  $T_2$  value of the polymer “ $1/T_{2p}$ ” (see  
350 equation 1) assuming the water is behaving as bulk water and has not been perturbed in any  
351 way. The fraction of water which is proposed to be perturbed in such systems is normally low  
352 (~2%, McConnell & Pope 2001).

$$353 \quad 1/T_2 = a*(1/T_{2p}) + (1-a)*(1/T_{2w}) \quad \text{Equation (1)}$$

354 Equations of the form of equation 1 describe the effect of protons exchanging between a  
355 polymer site with the polymer present at a weight fraction  $a$  and having a  $T_2$  value of  $T_{2p}$  and  
356 water at a weight fraction  $(1-a)$  having a  $T_2$  value of  $T_{2w}$  under conditions of a CPMG Tau  
357 value which allows exchange to be rapid. To examine the effect of drying on the overall  
358 apparent water mobility in the microfibrillar network in the presence and absence of CMC, the  
359  $T_2$  values and shear viscosities as a function of concentration were plotted for aqueous

360 suspensions of CMC15 (ND) which had not been dried, CMC15 (D) which had been dried but  
 361 then redispersed and compared with MFC100 (ND) and MFC100 (D) (Figure 5A and 5B).

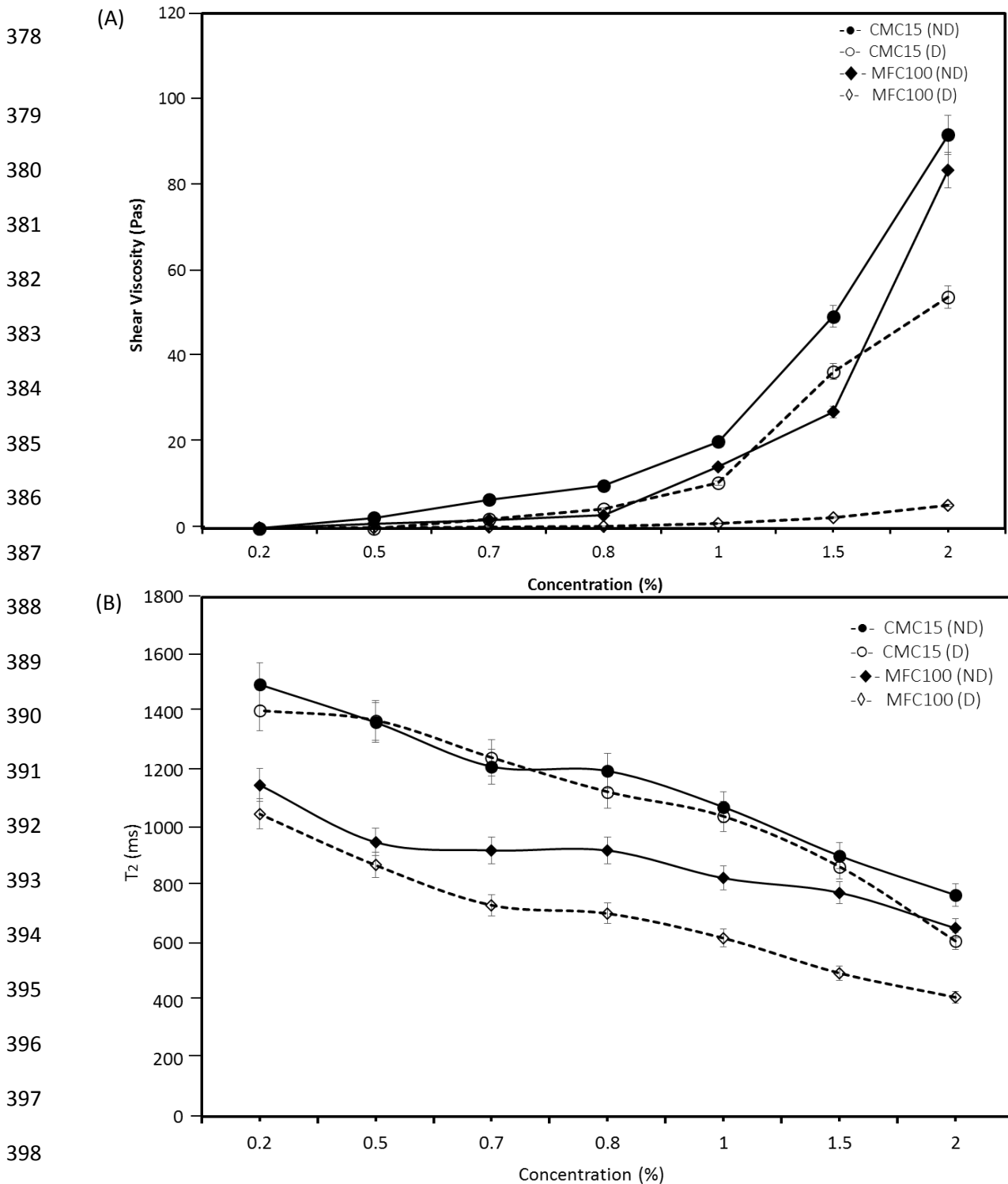


363 **Figure 4** Change in  $T_2$  (ms) and  $\tan \delta$  (measured at a frequency of 1 Hz and a strain of 0.2%)  
 364 plotted against increasing proportion of CMC in the suspension at 20°C.

365 As suggested earlier, the drying of MFC without CMC results in the formation of strong  
 366 intermolecular H-bonds between the microfibrils resulting in rigid fibre bundles or aggregates  
 367 of MFC, which limits the polymer mobility within the microfibril network resulting in lower  
 368 redispersibility. Effectively this reduces the  $T_{2p}$  value of the polymer and consequently  
 369 increases the  $1/T_{2p}$  value reducing the overall measured  $T_2$  as can be seen in figure 5B. As the  
 370 concentration increases, this effect becomes more pronounced however now it is mediated by  
 371 increases in the value of  $a$ . The net result is a further decrease in the value of  $T_2$ . If the polymer  
 372 is not dried then the bonding between the fibrillar complex is not as strong and the  $T_2$  values  
 373 are higher by similar arguments to the above. Figure 5A shows that the addition of CMC to  
 374 MFC *i.e.* CMC15 (D) significantly increases the shear viscosity of the redispersed suspension  
 375 compared to MFC100 (D). Similarly, the overall  $T_2$  values of the redispersed CMC15 (D) were



376 higher compared to MFC100(D) (Figure 5B). The CMC15(ND) suspensions showed highest  
 377  $T_2$  values of all.



399 **Figure 5** (A) Shear viscosity (at  $50s^{-1}$  shear rate); and (B) Spin-spin relaxation time  $T_2$  (ms) as  
 400 a function of concentration at  $20^\circ C$  for (- $\diamond$ -) MFC100 (ND) solid diamonds, (D) unfilled  
 401 diamonds; (- $\circ$ -) CMC15 (ND) solid circles, (D) unfilled circles.

402 The addition of CMC appears to prevent the formation of strong hydrogen bonds between MFC  
403 fibres, resulting in improved redispersibility of the CMC15. The reduced amount of aggregates  
404 and fibres bundles in the redispersed suspension increases polymer mobility and hence  
405 increases the polymer  $T_2$  value in the CMC15. There may also be a direct effect of the CMC  
406 on the polymer via an altered ionic environment. The result of these changes is that the  
407 interactions between fibrils are weaker and the overall measured  $T_2$  increases. If this  
408 interpretation is correct then whilst the NMR  $T_2$  value is sometimes loosely referred to as the  
409 water signal it is in fact actually only the apparent overall water mobility. Equation 1 gives a  
410 more accurate description of mobility in the system. In addition, because the bonds are now  
411 weakened by CMC, the difference in  $T_2$  values between the dried and non-dried CMC  
412 containing materials is reduced as can be seen in Figure 5B. Drying the MFC100 systems  
413 results in tighter bonding which impairs redispersibility and results in substantial differences  
414 between dried and non-dried MFC100.

#### 415 **4. Conclusions**

416 The influence of CMC on the rheological properties of MFC suspension is consistent with an  
417 exchange based NMR interpretation of spin-spin relaxation times ( $T_2$ ) for polymer and water.  
418 Rheological measurements show that addition of CMC to MFC increases complex viscosity  
419 and shear viscosity of the suspension compared to dried MFC without additives. Fluorescence  
420 microscopy showed that the CMC tends to interact homogeneously with MFC possibly on the  
421 surface of the microfibrils present in the network. This prevents the formation of H-bonds  
422 between the MFC's microfibrils, hence making dried MFC/CMC easier to redisperse in water.  
423 The lower  $T_2$ -values of the single component MFC100 suspensions result from the rigid  
424 structures formed upon drying and the lower polymer mobility. The addition of CMC to the  
425 MFC suspensions improved redispersibility of MFC after drying and produces stable and

426 highly fibrillated microstructures, hence increasing apparent water mobility ( $T_2$  values) within  
427 the matrix.

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