Interactions between microfibrillar cellulose and carboxymethyl cellulose in an aqueous suspension

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Abstract

New microstructures with interesting, unique and stable textures, particularly relevant to food systems were created by redispersing Microfibrillar cellulose (MFC). This paper reports the interactions between microfibrillar cellulose and carboxymethyl cellulose (CMC) in redispersed aqueous suspensions, by using rheological measurements on variable ratios of MFC/CMC and correlating these with apparent water mobility as determined by time domain NMR. MFC is a network of cellulose fibrils produced by subjecting pure cellulose pulp to high-pressure mechanical homogenisation. A charged polymer such as CMC reduces the aggregation of microfibrillar/fibre bundles upon drying. Small amplitude oscillatory rheological analysis showed the viscoelastic gel-like behaviour of suspensions which was independent of the CMC content in the MFC suspension. A viscous synergistic effect was observed when CMC was added to MFC before drying, leading to improved redispersibility of the suspension. Novel measurements of NMR relaxation suggested that the aggregated microfibrillar/fibre bundles normally dominate the relaxation times (T_2). The dense microfibrillar network plays an important role in generating stable rheological properties and controlling the mobility of the polymer and hence the apparent mobility of the water in the suspensions.

Highlights

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

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

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

3

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_2 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_2) 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_2 compared to pure distilled water, where a typical T_2 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

density on the microfibrillar cellulose will be low. Carboxymethyl cellulose (CMC) with a

degree of substitution of 0.71 was supplied by CP Kelco (Norway). Reverse osmosis (RO)

water was used for all experiments. Light mineral oil density 0.838 g/mL at 25°C (Sigma-

Aldrich, UK) was used during the rheological measurements to prevent sample dehydration.

2.2. Sample preparation and biopolymer mixtures

2% w/w aqueous suspensions of microfibrillar cellulose were prepared by diluting the MFC

stock solution (8.97%w/w MFC paste) with RO water using a high shear overhead mixer

(Silverson, UK) at 8000rpm for 5minutes. An aqueous solution of CMC (2% w/w) was

prepared separately and added to a 2%w/w MFC suspension according to the formulations

shown in Table 1, to produce an overall concentration including both components of 2%. The

CMC sample was dissolved by dispersing in RO water (2%w/w) under gentle stirring (IKA

Eurostar 20 Digital Overhead Stirrer) at room temperature for 2h. The pH of the solution was

adjusted to 6.8 and left overnight at 4°C before mixing with the MFC stock suspension. Sodium

azide solution (0.02% w/w) was added to prevent bacterial contamination. The concentration

of stock samples was determined by evaporating to dryness and measuring the dry solids

content.

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

MFC/CMC solutions were mixed in different proportions as shown in Table 1 at room

temperature in water and at an overall concentration of 2% w/w. All samples were mixed

thoroughly using an overhead stirrer (Silverson, UK) at 8000rpm for 5minutes. The mixtures

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 $50s^{-1}$ at 20±1°C. Temperature sweeps were generated by heating the sample between

167 the plates from 20℃ 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 ^{1}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 $20\pm1°C$ 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 (Curr-Purcell-Meiboom-Gill) pulse sequence (Meiboom and Gill, 1958),

178    $90°_x$--- $(--\tau--180°_y—\tau—echo--)_{ns}$ with $\tau = 2048\mu s$. Typical $90°$ pulse lengths were of the order

179   of $5\mu s$ and $180°$ pulse length was $10\mu s$. 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 $200\mu m$. 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 $95°C$ 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 $80°C$. The protocol used is the same as that published by Belder

195   *et al.,* 1973.

196   **3. Results and Discussion**

3.1. *Viscoelastic properties of MFC/CMC suspensions*

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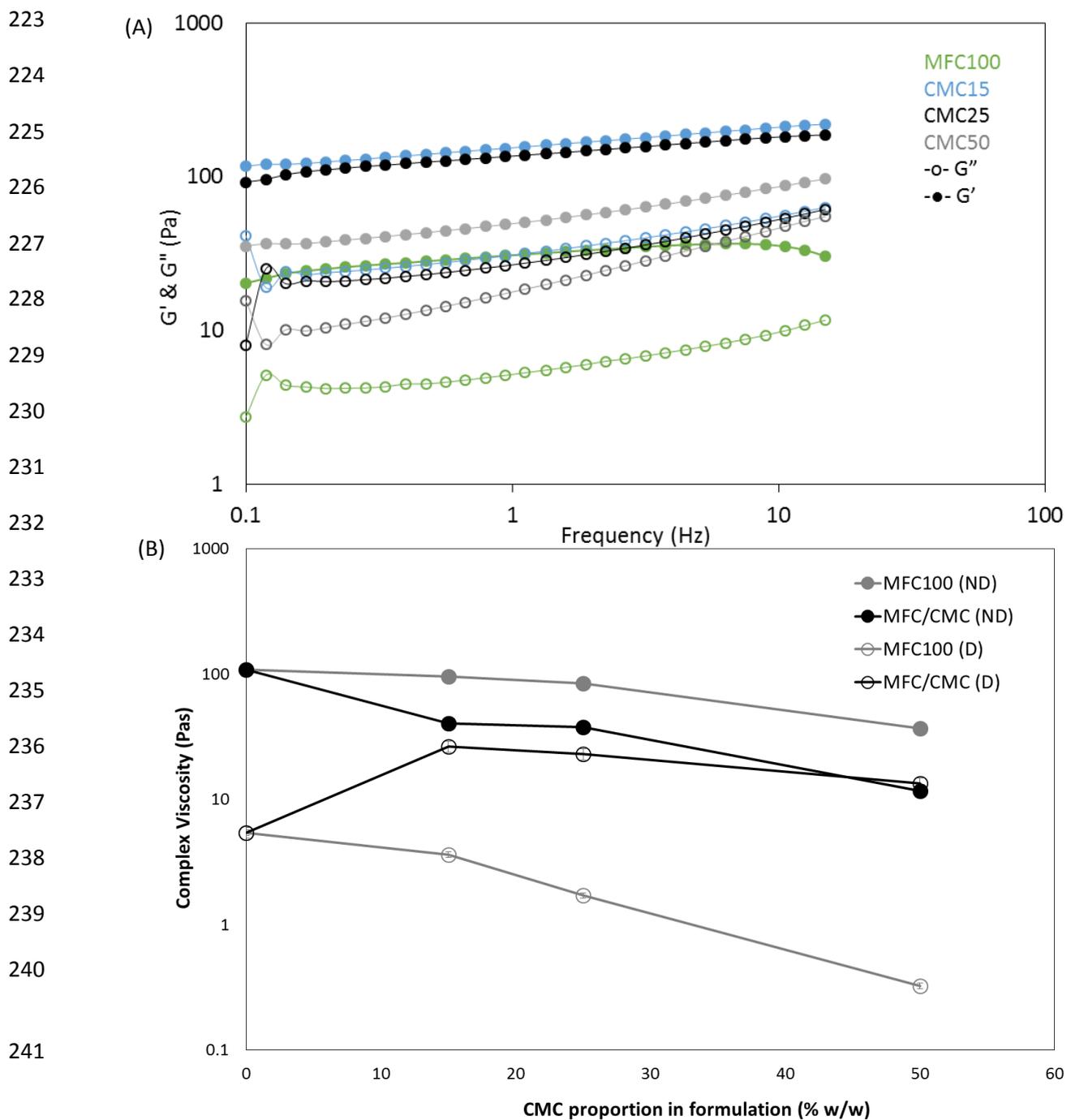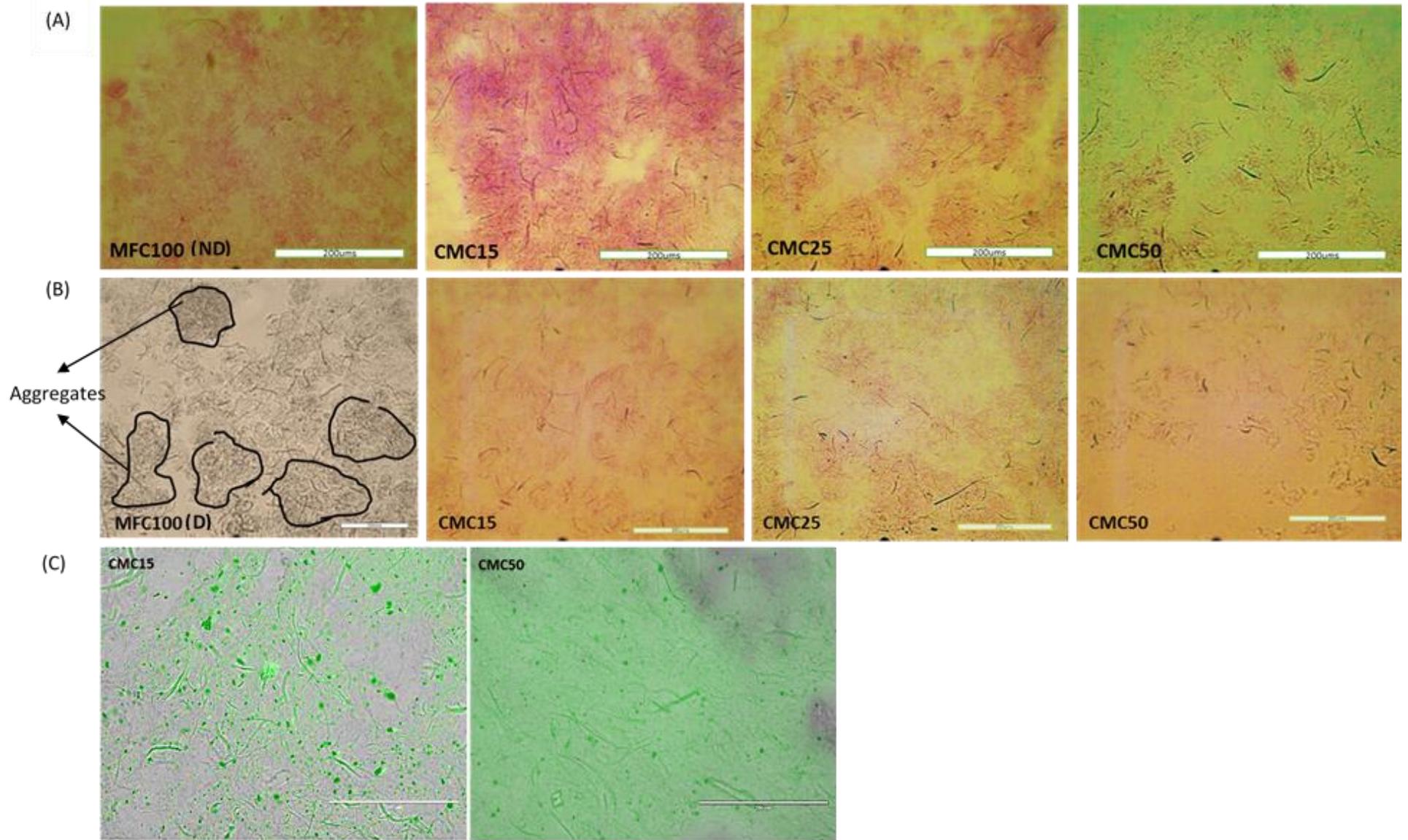
Figure 1 *(A) Frequency dependency of viscoelastic moduli for MFC/CMC mixtures dried and redispersed in aqueous media. Data were acquired at 0.2% strain and 20°C. Solid symbols represent the storage modulus (G') and open symbols the loss modulus (G''). (B) Complex viscosity η* measured at a frequency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

262 > 0.1) defines so-called weak gel behaviour (Ikeda and Nishinari, 2001) as evident in Figure

263 1A. Tan δ 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 δ > 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.

(A) MFC100 (ND)   CMC15   CMC25   CMC50

(B) Aggregates   MFC100 (D)   CMC15   CMC25   CMC50

(C) CMC15   CMC50

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 200µm, 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

showed an initial slight decrease from 20°C to 40°C, however above 40°C the suspensions showed an increase in G' and G" up to 90°C. Similar behaviour was observed with cellulose nanofibers from poplar wood by Chen *et al.,* 2013. The first slight decrease in modulus may be due to thermal agitation/thermal motion of microfibrils, resulting in loosening of the fibrils within the network structure. However, the swelling of microfibrils with an increase in temperature, while interacting with CMC in the matrix, may strengthen the gel-like structure, resulting in an increased G' and G" of suspensions above 40°C. As the amount of CMC increased in the formulation, G' and G" increase to a greater extent above 40°C suggesting synergistic interactions between MFC/CMC. It is well known that polymeric solutions such as HPMC (hydroxyl propyl methyl cellulose), exhibit an increased thermal motion upon heating, leading to a weaker network and sometimes a decrease in viscosity, however the viscosity of these systems tends to increase above the gelation temperature depending on concentration (Silva *et al.,* 2008). The fact that the MFC/CMC suspensions do not lose structure upon heating, even when the MFC proportion is lowered, indicates an interaction beyond the surface stabilisation of the microfibrils by CMC, although it is not yet clear which mechanisms are involved.
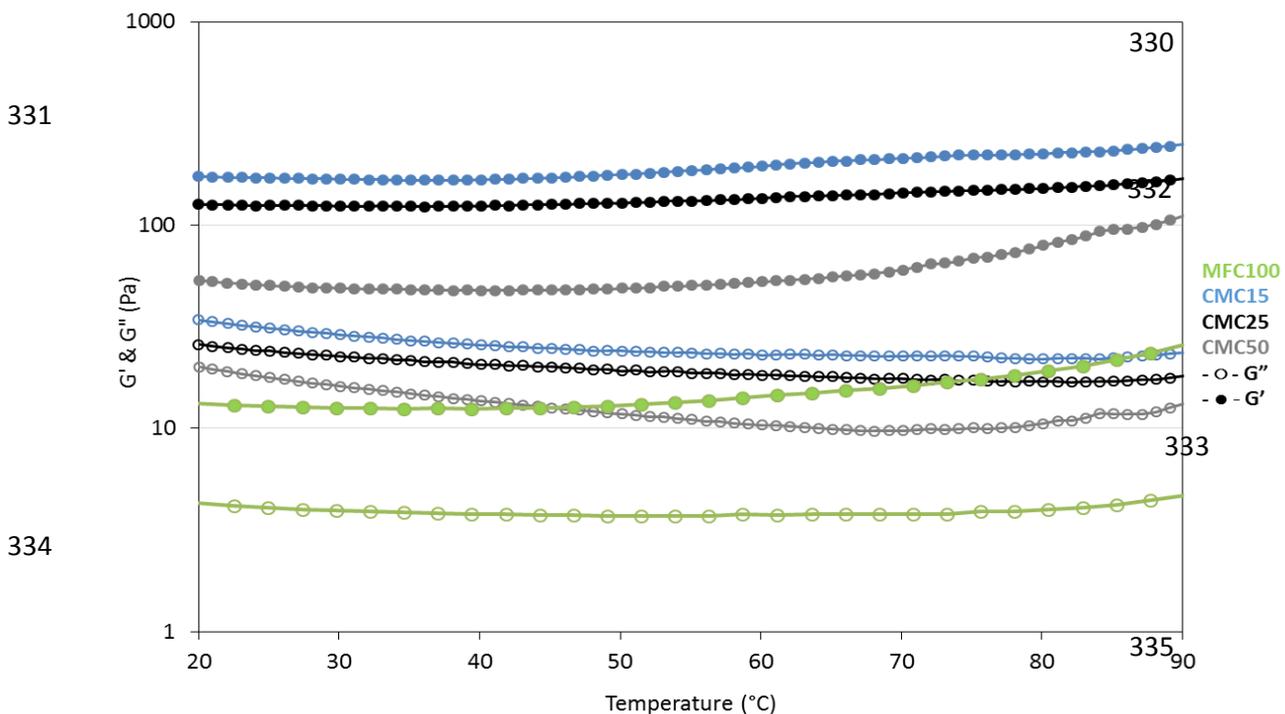
336 **Figure 3** *Temperature dependency (20° to 90°C at a heating rate 1°C/min) of the viscoelastic*

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 δ 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 $$1/T_2 = a*(1/T_{2P}) + (1-a)*(1/T_{2w}) \qquad \text{Equation (1)}$$

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).

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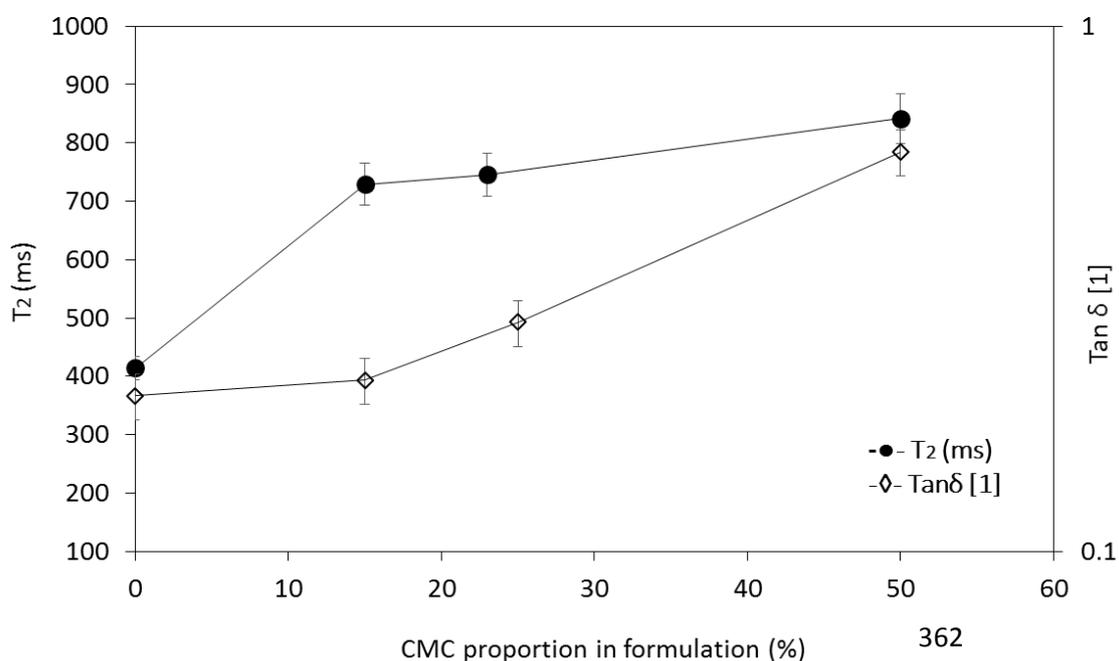
363   **Figure 4** *Change in T_2 (ms) and Tanδ (measured at a frequency of 1 Hz and a strain of 0.2%)*

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.
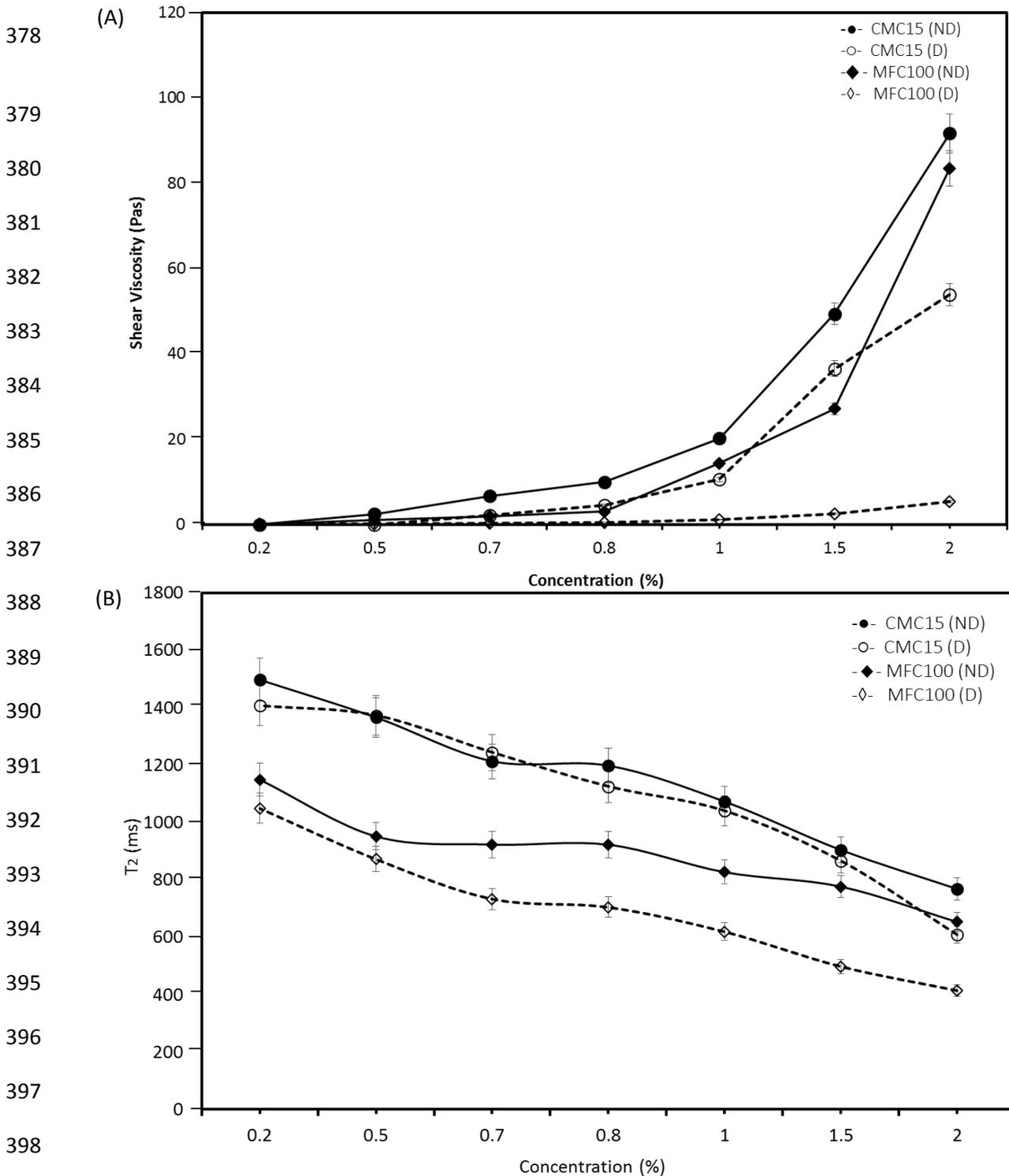
Figure 5 *(A) Shear viscosity (at 50s^{-1} shear rate); and (B) Spin-spin relaxation time T$_2$ (ms) as a function of concentration at 20°C for (-◇-) MFC100 (ND) solid diamonds, (D) unfilled diamonds; (-○-) CMC15 (ND) solid circles, (D) unfilled circles.*

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 homogenously 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.

428 **Acknowledgement**

430 **References**

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