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
CMC improves redispersibility and reduces aggregation of MFC microfibrils

NMR relaxation measurements give an insight into the mechanisms of redispersibility

Polymer aggregation dominates the $T_2$ value and NMR behaviour of suspensions

Improved re-dispersion is correlated with higher shear viscosity and increased $T_2$

Unique microstructures relevant to foods have been created

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

1. **Introduction**

Cellulose is the most abundant natural structural polymer in nature and provides mechanical properties such as strength and stiffness to the plant cell wall of higher plants. Important components of this natural fibre strength and stiffness are the microfibrils within the cellulose structure. The fibrous cell wall is essentially a composite material consisting of a framework of cellulose (micro-) fibrils organised into strands of cellulose which are embedded in a matrix of hemicelluloses and lignin. Cellulose microfibrils in the cell wall are intertwined fibrils with a diameter of approx. 2-20nm and a length of 100-40,000nm depending on the source (Kirk and Othmer, 1967; Kocherbitov, Ulvenland, Kober and Jarring, 2008). These cellulose fibres can be broken down into their structural micro/nano-scale units by various chemical and mechanical processes (Henriksson, Berglund and Lindstrom, 2007). Production and characterisation of microfibrillar cellulose (MFC) from wood fibres have been described by Turbak *et al.* 1983 and Herrick *et al.* 1983, where MFC suspensions were obtained by disintegrating cellulose fibres at high shear. The resultant highly entangled MFC network consists of micro/nano size elements with a gel-like behaviour for water suspensions at 1% or lower concentrations of MFC (Turbak *et al*., 1983, Herrick *et al*., 1983, Nakagaito and Yano 2004, Nishiyama, 2009). During the last decade, microfibrillar cellulose (MFC) has been 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 (Quievy 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
aggregation or agglomeration occurs to varying extents depending on the drying process. To protect the microfibrils from collapse and agglomeration, a number of hydrocolloids, e.g. low and high methoxyl pectin, CMC, and sodium polyacrylate, as well as salts e.g. sodium chloride (Lowys, Desbrieres & Rinaudo, 2001; Tandjawa et al., 2012; Missoum, Bras & Belgacem, 2012), have been used to stabilise the fibrils. Lowys (2001) demonstrated an interaction between MFC and polymeric additives such as sodium-CMC and pectins, where the additives were homogeneously distributed and formed weak bonds with MFC fibres improving the redispersibility of MFC in water. This interaction between the additive and MFC tends to stabilise the fibrils against collapse or agglomeration during the drying process. The objective of the current publication is to provide an insight into the impact of drying (hornification) on the state of the polymer and the apparent water mobility in the MFC matrix.

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

It has been suggested that proton nuclear magnetic resonance (NMR) parameters such as spin-lattice-relaxation time ($T_1$) and spin-spin relaxation time ($T_2$) are sensitive to water state and mobility in polymeric suspensions/dispersions (Ono, Inamoto and Okajima, 1997; Rachocki, Markiewicz and Tritt, 2005, Vackier, Hills and Rutledge, 1999). The spin-spin relaxation time
T₂ is generally measured using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence (Meiboom and Gill, 1958). The CPMG sequence provides a more accurate measure of the liquid transverse free-induction decay time (T₂) and is free of artefacts such as magnetic inhomogeneity. In a study by Ono (1997), an MCC suspension was shown to contain both free-water and water-associated to the polymer with a mutual exchange of protons resulting in shorter overall T₂ compared to pure distilled water, where a typical T₂ is of the order of 2 seconds.

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

2. Materials and methods

2.1. Materials

Microfibrillar cellulose (MFC) from spruce cellulose (8.97%w/w MFC paste) was provided by Borregaard AS (Sarpsborg, Norway). Cellulose was obtained from 100% spruce. The charge density of pure cellulose changes noticeably during the pre-treatment and finishing process to 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 5 minutes. 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.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>% w/w in suspension</th>
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<tr>
<td></td>
<td>MFC (%)</td>
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<tr>
<td>MFC100</td>
<td>2</td>
</tr>
<tr>
<td>CMC15</td>
<td>1.7</td>
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<tr>
<td>CMC25</td>
<td>1.5</td>
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<tr>
<td>CMC50</td>
<td>1</td>
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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 5 minutes. The mixtures were stored overnight at room temperature for equilibration and the pH was re-measured. For
re-dispersion studies, an approximately 1mm thin layer of the suspension was layered on an aluminium plate and dried at 50°C for 12 hours using a conventional oven (Gallenkamp hotbox oven, size 2).

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

2.3. Rheological measurements

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

2.4. Pulsed ¹H-NMR measurements
Time domain measurements were carried out at 25MHz using a Resonance Instruments (RI) Maran benchtop NMR spectrometer (Oxford-Instruments Plc, UK). This type of instrument is used routinely in the food industry for fat and moisture measurements. The temperature was regulated at 20±1°C by a conventional gas flow system calibrated with an external thermocouple and controlled with a standard R.I. temperature unit. All measurements were made in 10mm outer diameter (OD) NMR tubes. Spin-spin relaxation times (T$_2$) were recorded using the CPMG (Curr-Purcell-Meiboom-Gill) pulse sequence (Meiboom and Gill, 1958), 90°$_x$--- (---τ---180°$_y$---τ---echo---)$_n$ with τ = 2048µs. Typical 90° pulse lengths were of the order of 5µs and 180° pulse length was 10µs. The recycle delay time was fixed at 10 seconds ensuring that all samples were relaxed before the next pulse sequence was applied. 64 scans were recorded. All samples were left at a constant temperature for 15min to ensure the temperature was equilibrated and consistent for all data points (see McConville, Pope, 2001). All relaxation curves obtained by the CPMG method showed a single exponential decay.

2.5. Microscopic analysis

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

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 (|Ƞ*|) 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 $\eta^*$ 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
is identical to that present in an MFC/CMC formulation. At 0% CMC concentration the MFC concentration is 2% and at a CMC concentration of 50% the MFC concentration is 1%. Solid symbols represent the (ND) suspensions and open symbols the (D) suspensions.

A noticeable difference in complex viscosity was observed on comparing the MFC100 (ND) and MFC/CMC (ND) suspension (Figure 1B), this behaviour can be explained by the dilution effect of CMC on MFC producing the different ratios. Diluting the MFC network structure with CMC to make up the formulation (as per Table 1), results in less microfibril entanglement in the network structure and is also seen in the microscopy images presented in Figure 2A, resulting in a lower complex viscosity as compared with comparable concentrations of MFC100 (ND) (Figure 1B). A slightly lower complex viscosity was observed when comparing MFC/CMC (ND) and MFC/CMC (D) formulations, but this reduction was minimal in the case of CMC50 (Figure 1B). However, the CMC50 suspension showed weaker gel-like behaviour.

The slight frequency dependence of the moduli and the relatively large value of tan δ (G”/G’ > 0.1) defines so-called weak gel behaviour (Ikeda and Nishinari, 2001) as evident in Figure 1A. Tan δ values are also presented later in Figure 4. When the negatively charged CMC was added at higher levels, the CMC adsorption to MFC increased significantly. Similar behaviour was reported with bacterial cellulose/CMC systems where changes in zeta-potential were shown (Veen et al., 2014). The increase in the charge for all ratios of CMC leads to better redispersibility of the MFC/CMC formulations in water with higher complex viscosity values. Lower values of G’ where Tan δ > 0.1 for CMC50 suspensions can be explained by a dilution effect. As the dense network of microfibrils plays an important role in maintaining viscoelastic gel-like behaviour, when MFC is diluted with 50% CMC the MFC is at 1%, which without additives shows an order of magnitude decrease in G’ and G” (Figure 1B), and the MFC forms a weaker entangled network structure.
Figure 2 Light microscopy images of 2% w/w aqueous suspensions of (A) never dried, (B) dried and redispersed suspensions of MFC100 and MFC/CMC at CMC levels of 15, 25 and 50%. (C) Fluorescence microscopy images of 2% w/w redispersed suspension of CMC15, and CMC50, scale bar 200μm, where CMC is tagged with FITC (green fluorescence).

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

3.2. Temperature dependence of the viscoelastic moduli

The temperature dependence of G’ and G” for 2% w/w aqueous suspensions of MFC/CMC mixtures is shown in Figure 3. All the samples showed stable viscoelastic gel-like behaviour where the storage modulus was higher than the loss modulus throughout the temperature range 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.
Figure 3 Temperature dependency (20° to 90°C at a heating rate 1°C/min) of the viscoelastic moduli of 2% w/w aqueous suspensions of MFC100 (D) and MFC/CMC (D) acquired at 1Hz frequency and 1% strain. Solid symbols represent storage modulus (G’) and open symbols represent loss modulus (G”).

3.3. Relaxation time (T₂) of MFC/CMC suspensions

Figure 4 shows the spin-spin relaxation time (T₂) as a function of the amount of CMC present in the MFC/CMC formulations. At higher levels of CMC in the formulation, the T₂ (ms) value and the Tan δ of the suspension increased, the latter implying that the suspension was behaving in a more viscous or liquid-like fashion. Lower T₂ values for the redispersed MFC100 (CMC=0) suspensions are most likely due to the rigid network structure formed by strong intra- or intermolecular H-bond within the microfibrils and a consequently reduced T₂ value for the polymeric component. It appears to be the presence of these rigid structures in case the of MFC100 (D) suspensions which dominate the T₂ values at all concentrations. In this case, the overall T₂ value of the suspensions are driven by the T₂ value of the polymer “1/T₂p” (see equation 1) assuming the water is behaving as bulk water and has not been perturbed in any way. The fraction of water which is proposed to be perturbed in such systems is normally low (~2%, McConnell & Pope 2001).

\[
\frac{1}{T_2} = a \times \left( \frac{1}{T_{2p}} \right) + (1-a) \times \left( \frac{1}{T_{2w}} \right) \tag{Equation 1}
\]

Equations of the form of equation 1 describe the effect of protons exchanging between a polymer site with the polymer present at a weight fraction \( a \) and having a T₂ value of T₂p and water at a weight fraction (1-\( a \)) having a T₂ value of T₂w under conditions of a CPMG Tau value which allows exchange to be rapid. To examine the effect of drying on the overall apparent water mobility in the microfibrillar network in the presence and absence of CMC, the T₂ values and shear viscosities as a function of concentration were plotted for aqueous
suspensions of CMC15 (ND) which had not been dried, CMC15 (D) which had been dried but then redispersed and compared with MFC100 (ND) and MFC100 (D) (Figure 5A and 5B).

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

As suggested earlier, the drying of MFC without CMC results in the formation of strong intermolecular H-bonds between the microfibrils resulting in rigid fibre bundles or aggregates of MFC, which limits the polymer mobility within the microfibril network resulting in lower redispersibility. Effectively this reduces the $T_{2p}$ value of the polymer and consequently increases the $1/T_{2p}$ value reducing the overall measured $T_2$ as can be seen in figure 5B. As the concentration increases, this effect becomes more pronounced however now it is mediated by increases in the value of $\alpha$. The net result is a further decrease in the value of $T_2$. If the polymer is not dried then the bonding between the fibrillar complex is not as strong and the $T_2$ values are higher by similar arguments to the above. Figure 5A shows that the addition of CMC to MFC i.e. CMC15 (D) significantly increases the shear viscosity of the redispersed suspension compared to MFC100 (D). Similarly, the overall $T_2$ values of the redispersed CMC15 (D) were
higher compared to MFC100(D) (Figure 5B). The CMC15(ND) suspensions showed highest T₂ values of all.

Figure 5 (A) Shear viscosity (at 50 s⁻¹ shear rate); and (B) Spin-spin relaxation time T₂ (ms) as a function of concentration at 20°C for (-•-) MFC100 (ND) solid diamonds, (D) unfilled diamonds; (-○-) CMC15 (ND) solid circles, (D) unfilled circles.
The addition of CMC appears to prevent the formation of strong hydrogen bonds between MFC fibres, resulting in improved redispersibility of the CMC15. The reduced amount of aggregates and fibres bundles in the redispersed suspension increases polymer mobility and hence increases the polymer T₂ value in the CMC15. There may also be a direct effect of the CMC on the polymer via an altered ionic environment. The result of these changes is that the interactions between fibrils are weaker and the overall measured T₂ increases. If this interpretation is correct then whilst the NMR T₂ value is sometimes loosely referred to as the water signal it is in fact actually only the apparent overall water mobility. Equation 1 gives a more accurate description of mobility in the system. In addition, because the bonds are now weakened by CMC, the difference in T₂ values between the dried and non-dried CMC containing materials is reduced as can be seen in Figure 5B. Drying the MFC100 systems results in tighter bonding which impairs redispersibility and results in substantial differences between dried and non-dried MFC100.

4. Conclusions

The influence of CMC on the rheological properties of MFC suspension is consistent with an exchange based NMR interpretation of spin-spin relaxation times (T₂) for polymer and water. Rheological measurements show that addition of CMC to MFC increases complex viscosity and shear viscosity of the suspension compared to dried MFC without additives. Fluorescence microscopy showed that the CMC tends to interact homogenously with MFC possibly on the surface of the microfibrils present in the network. This prevents the formation of H-bonds between the MFC’s microfibrils, hence making dried MFC/CMC easier to re-disperse in water. The lower T₂-values of the single component MFC100 suspensions result from the rigid structures formed upon drying and the lower polymer mobility. The addition of CMC to the MFC suspensions improved redispersibility of MFC after drying and produces stable and
highly fibrillated microstructures, hence increasing apparent water mobility ($T_2$ values) within the matrix.

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