Elsevier Editorial System(tm) for
Carbohydrate Polymers
Manuscript Draft

Manuscript Number: CARBPOL-D-18-04779R1

Title: Effect of moisture content on thermal and dynamic mechanical properties of microfibrillar cellulose with polymeric additives.

Article Type: Research Paper

Keywords: Carboxymethyl cellulose; Locust bean gum; MFC; TGA; DSC; DVS.

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Abstract: The aim of this study was 1) to investigate the influence of polymeric additives such as carboxyl methyl cellulose (CMC) and locust bean gum (LBG) added before and after homogenisation on the moisture uptake of microfibrillar cellulose (MFC) in the dry and semi-wet state; and 2) to further understand the thermally induced structural transitions of low moisture MFC in the presence of the polymeric additives. A higher moisture content in the highly dense MFC network maintains the fibrillated network structure, which is lost during the drying process resulting in MFC aggregates. The addition of polymeric additives results in the regaining of the structure upon redispersion of the dry material with CMC being more effective than LBG). Results also indicated that CMC has a high level of compatibility with MFC, whereas LBG appears to have limited distribution in the MFC dense microfibrillar network and probably exists as a separate phase when added after homogenisation, however co-processing of LBG and cellulose significantly changed this behaviour. The presence of low-temperature transitions in MFC/additives/water mixtures indicates the involvement of these semi-flexible polymeric additives in the formation of liquid crystals when added to MFC in low moisture environments (2% and 20% w/w). An insight is offered into the theory of surface interactions between MFC and polymeric additives, which prevents the agglomeration of microfibrils present in the highly fibrillated suspension upon drying.

Highlights

- Point of addition of polymeric additives impacts the thermal properties of MFC.
- CMC & LBG ~~improves~~ increases moisture sorption and desorption in an MFC ~~microfibrils~~ network.
- Co-processing of MFC and polymeric additives ~~enhance~~ increase molecular interactions.
- Co-processing of MFC and LBG ~~results in improved~~ significantly changed the thermal properties of MFC.

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15th Feb 2019

Dear Sir/Madam,

We would like to thank the reviewers for their comments which we believe will improve the manuscript. We have taken all the reviewers' comments into account and made all the corrections.

We now deal specifically with the reviewers' detailed points as follows:

Reviewer #1: Minor Revisions for acceptance This is a well written paper on effects of moisture content on thermal and dynamic mechanical behaviour of microfibrillar cellulose mixed with other hydrocolloids. Experiments are well designed and data interpretation is of high quality.
I have no major remarks. Minor remarks

- please provide shear conditions used for high pressure processing (give at least pressure level), page 6

Done in materials and methods. We have given details for pressure used in microfluidics homogeniser:

All samples were mixed thoroughly, then these mixtures were passed through a Microfluidics homogeniser (Microfluidics Processor M-700) with a z-chamber at a pressure of 2000 bar.

- please provide arguments for the drying conditions chosen, page 6

Done in materials and methods.

The drying conditions were selected from the preliminary trials (results are not shown), which indicated that relatively less MFC aggregates were observed upon drying under these conditions in comparison with other oven drying conditions.

- please explain rationale for use of CMC and locust bean gum in the context of this study?

We have included a rationale very briefly on why we used CMC and LBG in the current study.

In the current study, CMC and Locust bean gum (LBG) were used as polymeric additives to protect against the aggregation of MFC upon drying. The rationale for using CMC and LBG as polymeric additives are: CMC showed a positive surface interaction with MFC with a high degree of recovery of rheological properties upon drying (Agarwal, MacNaughtan, Foster

2018). It has also previously been reported that some galactomannans and glucomannans, such as LBG and Konjac glucomannan show positive interactions with cellulose (Whitney et al., 1998, Newman and Hemmingson 1998).

Reviewer #2: Accept

- Please explain what is meant by "whereas LBG appears to have limited solubility in the MFC" ? Is it solubility of LBG in water in the presence of CMF?

Yes we agree this is confusing and hope that the added sentence to the text and abstract shown below clarifies the situation.

Figure 2 demonstrates that CMC has a high level of compatibility with MFC, whereas LBG appears to have limited ~~solubility~~ distribution in the MFC dense microfibrillar network and probably exists as a separate phase when these polymers are added *after homogenisation*.

In the abstract we have included the correction:

Results also indicated that CMC has a high level of compatibility with MFC, whereas LBG appears to have limited ~~solubility~~ distribution in the MFC dense microfibrillar network and probably exists as a separate phase when added after homogenisation, however co-processing of LBG and cellulose significantly changed this behaviour.

We have also now included the additional references which are included in the text.

Finally, we have also made some minor corrections and some rephrasing to make sentences much clearer.

We hope that the above answers cover most of the reviewers' comments. Once again we are grateful for the feedback which we have received from the reviewers which we believe will render the manuscript more easily understandable and relevant.

Dr Deepa Agarwal

Effect of moisture content on thermal and dynamic mechanical properties of microfibrillar cellulose with polymeric additives.

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Abstract

The aim of this study was 1) to investigate the influence of polymeric additives such as carboxyl methyl cellulose (CMC) and locust bean gum (LBG) added *before* and *after homogenisation* on the moisture uptake of microfibrillar cellulose (MFC) in the dry and semi-wet state; and 2) to further understand the thermally induced structural transitions of low moisture MFC in the presence of the polymeric additives. A higher moisture content in the highly dense MFC network maintains the fibrillated network structure, which is lost during the drying process resulting in MFC aggregates. The addition of polymeric additives results in the regaining of the structure upon redispersion of the dry material with CMC being more effective than ~~followed by~~ LBG). Results also indicated that CMC has a high level of compatibility with MFC, whereas LBG appears to have limited ~~solubility~~ distribution in the MFC dense microfibrillar network and probably exists as a separate phase when added after homogenisation, however co-processing of LBG and cellulose significantly changed this behaviour. The presence of low-temperature transitions in MFC/additives/water mixtures indicates the involvement of these semi-flexible polymeric additives in the formation of liquid crystals when added to MFC in low moisture environments (2% and 20% w/w). ~~and offers~~ ~~a~~An insight is offered into the theory of surface interactions between MFC and

polymeric additives, which prevents the agglomeration of microfibrils present in the highly fibrillated suspension upon drying.

Keyword: Carboxymethyl cellulose; Locust bean gum; MFC; TGA; DSC; DVS.

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- Co-processing of MFC and LBG ~~results in improved~~ significantly changed the thermal properties of MFC.

1. Introduction

Cellulose is the most abundant natural polymer. It is a linear, high molecular weight ~~and most abundant natural~~ polymer consisting of repeating β-D-glucopyranose units linked by 1→4 glycosidic bonds (Kirk and Othmer, 1967). It also forms both inter- and intramolecular hydrogen bonds due to a large number of polar hydrogen and oxygen atoms. The two intramolecular hydrogen bonds, OH-3··O5 and OH-2···O6 binds neighbouring glucose units providing high stiffness to natural cellulose chains. As it is a renewable and biodegradable polymer, cellulose is a promising feedstock for the production of chemicals and is also used in various commercial applications such as papermaking, paints, composites, pharma~~ceutical~~, food and cosmetics ~~*etc*~~. Cellulose fibres are assembled in a hierarchically ordered structure. Cellulose chains aggregate together in alternate crystalline and amorphous domains in the form of elementary fibrils. These elementary fibrils are aligned and further aggregate into larger microfibrils or macrofibrils (Siró and Plackett, 2010, O'Sullivan 1997, Atalla and VanderHart 1984, Lavoine, Desloges, Dufresne & Bras 2012). The cellulose fibres can be broken down into their structural micro-scale units (such as microfibrillar units) by various chemical and mechanical processes (Henriksson, Henriksson G, Berglund and Lindstrom, 2007). Intensive mechanical treatments such as high-pressure homogenisation, microfluidisation or grinding result in highly entangled networks of microfibrillar cellulose (MFC) (Leitner *et al.*, 2007, Lavoine *et al.*, 2012, Saarinen, Lille & Seppala 2009, Nechyporchuk, Belgacem & Bras 2016). Carrasco (2011) defined an MFC suspension as a material composed of nanofibrils, fibrillar fines, fibre fragments and fibres; however, MFC with a high degree of fibrillation (properly produced) may contain nano-structures with diameters less than 40nm as a main component.

An MFC suspension in water shows a number of unique physical and mechanical properties. Rheological properties such as coating and thickening agent are some of the key characteristics which influence a wide range of commercial applications ~~such as~~ in food, cosmetics. ~~pharmaceuticals, paints and composites~~ Typically, a highly entangled network of microfibrillar cellulose shows a gel-like behaviour in water dispersions, where the storage modulus (G’) is higher than the loss modulus (G”) (Pääkkö *et al.*, 2007, Cordabo *et al.*, 2010, Nishiyama, 2009). However, drying the MFC is known to modify the highly fibrillated MFC into fibre bundles and aggregates caused by hydrogen bonds between the microfibrils. These aggregates are difficult to rehydrate in water, which leads to impaired rheological properties compared to never-dried MFC (Quiévy *et al.*, 2010). To protect the microfibrils from aggregation, hydrocolloids, *e.g.* low and high methoxyl pectin, carboxymethylcellulose (CMC), and sodium polyacrylate, as well as salts *e.g.* sodium chloride, are used to stabilise the microfibrils by forming weak bonds and blocking H-bond formation, leading to improved redispersbility of the MFC in water, with improved rheological properties (higher G’, G” and shear viscosity) compared to MFC dried without additives (Lowys, Desbrieres & Rinaudo, 2001; Agoda-Tandjawa *et al.*, 2012; Missoum, Bras & Belgacem, 2012). In the current study, CMC and Locust bean gum (LBG) were used as polymeric additives to protect against the aggregation of MFC upon drying. The rationale for using CMC and LBG as a polymeric additives are: CMC showed a positive surface interaction with MFC with a high degree of recovery of rheological properties upon drying (Agarwal, MacNaughtan, Foster 2018). It has also, previously been reported that some galactomannans and glucomannans, such as LBG and Konjac glucomannan show positive interactions with cellulose (Whitney *et al.*, 1998, Newman and Hemmingson 1998).

It is important to understand the interactions between the water and MFC for all critical processing stages such as drying, and rehydration. Cellulose interacts with water due to the presence of hydroxyl groups and water sorption in the dry material is closely related to the crystallinity of the material, as water pre-dominantly penetrates the amorphous region of cellulose whereas a negligible amount of water sorption occurs in crystalline regions (basically filling the voids and interstitial spaces) (Mihranyan *et al.*, 2004, Kachrimanis *et al.*, 2006). The addition of polymeric additives in the MFC suspension (to stabilise the MFC during the drying process) potentially influences the interaction between cellulose-water and the overall functional properties of the redispersed MFC suspensions. While a number of papers have shown the impact of additives on the rheological properties of MFC, there is limited information ~~has been reported~~ concerning the impact of polymeric additives on the thermal properties of MFC in low moisture systems (2-25% moisture content), and importantly, how the additives facilitate the moisture sorption and desorption in a dried MFC network. This can then be correlated with redispersibility of MFC/additive mixed systems at higher water contents.

The primary aim of this study is understanding the impact of different polymeric additives such as carboxymethylcellulose (CMC) and locust bean gum (LBG) on the interaction between the MFC and water in a low moisture environment. It is hoped that this understanding will shed light on the interactions between the polymeric additives and the microfibrillar cellulosic material and the technical problems that ensue from these interactions in various commercial applications. A detailed study of low-temperature structural changes and degradation in MFC/additive systems by using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) and correlation with moisture sorption and desorption by using Dynamic Vapour Sorption (DVS), has been carried out. The hypothesis underpinning this research is that the structural properties of MFC (or cellulose) can be altered or modified by ~~different~~ polymeric additives such as CMC and LBG, and by co-processing cellulose with these additives, ~~to produce MFC, with modified structures to enable~~ different levels of moisture sorption in the MFC matrix occur, which ultimately affect the redispersibility and rheological properties of MFC ~~in a high moisture environment~~.

2. Materials and methods

2.1. Materials

Microfibrillar cellulose (MFC) and Non-fibrillated cellulose from spruce cellulose 8.98% w/w paste were provided by Borregaard AS (Norway) and used at a concentration of 2% w/w. From the information provided by the supplier, the charge density on the MFC will be low. Carboxymethylcellulose (CMC) with a degree of substitution (DS) of 0.71 was supplied by CP Kelco (Norway). Locust bean gum (Grindsted LBG®246) was provided by Danisco Ltd. (Denmark). Phosphorus pentoxide (P_2O_5) and Potassium nitrate (KNO_3) was supplied by Sigma-Aldrich, Merck (UK). Reverse osmosis (RO) water was used for all experiments.

2.2. Sample preparation

2.2.1. Preparation of Carboxymethylcellulose (CMC): The CMC sample was dissolved in RO water (at 2% w/w) by dispersing under gentle stirring (1600 rpm) at room temperature for 2 h using an overhead stirrer (IKA Eurostar 20 Digital Overhead Stirrer) ~~at room temperature for 2 h~~. The pH of the solution was adjusted to 6.8 and left overnight before mixing with the MFC stock suspension. The concentration of stock samples was determined by evaporating to dryness and measuring the dry solids content. Sodium azide solution (0.02% w/w) was added to prevent bacterial contamination.

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

Sample Code	% w/w in suspension		
	MFC (%)	CMC (%)	LBG (%)
MFC100	2	0	0
CMC100	0	2	0
LBG100	0	0	2
CMC15	1.7	0.3	0
CMC25	1.5	0.5	0
CMC50	1	1	0
LBG15	1.7	0	0.3
LBG25	1.5	0	0.5
LBG35	1.3	0	0.7
LBG50	1	0	1

2.2.2. Preparation of Locust bean gum (LBG): The LBG samples were dissolved by dispersing in RO water (at 2% w/w) for 1 h at 20 °C using a magnetic stirrer (IKA® RET Control-visc, Germany) ~~for 1 h at 20 °C~~, ~~then heated~~ and heating for 30 mins at 80 °C and later cooled at 20 °C. The pH of the solution was adjusted to 6.8 and left overnight before mixing with the MFC stock suspension. Sodium azide solution (0.02% w/w) was added to prevent bacterial growth ~~contamination~~. The concentration of stock samples was determined by evaporating to dryness and measuring the dry solids content.

2.3. *Preparation of MFC/additive*

2.3.1. The addition of additives after homogenisation: MFC/CMC and MFC/LBG 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 8000 rpm for 5mins.

2.3.2. The addition of additives before homogenisation: Mixtures of cellulose and polymeric additives were prepared by adding CMC and LBG separately at 85:15 ratio (MFC: additive) at room temperature in water and at an overall concentration of 2% w/w. All samples were mixed thoroughly, then these mixtures were passed through a Microfluidics homogeniser

(Microfluidics Processor M-700) with a z-chamber at a pressure of 2000 bar. All the mixtures were passed through the homogeniser from one to three times and coded as MFC/CMC (1P, 2P and 3P) and MFC/LBG (1P, 2P and 3P), where "P" represents a number of passes through the homogeniser.

All the mixtures were stored overnight at room temperature for equilibration and the pH was re-measured before the drying process. The concentration of all samples was determined by evaporating to dryness and measuring the dry solids content. To avoid bacterial growth ~~contamination~~, 0.02% w/v sodium azide solution was added. A dried product was obtained by preparing an approximately 1 mm thin layer of the suspension on an aluminium plate which was subsequently dried at 50 °C for 12 h using a conventional oven (Gallenkamp hotbox oven, size 2). The drying conditions were selected from the preliminary trials (results are not shown), which indicated that relatively less MFC aggregates were observed upon drying under these conditions in comparison with other oven drying conditions. All samples were ground to a smaller particle size using a conventional grinder (De'Longhi KG49 grinder, UK) at maximum speed for 2 mins. Moisture content was maintained at 2% w/w for low moisture (LM: low moisture samples) analysis. All samples were then stored in P_2O_5 desiccator for 7 days to dry samples to 0% moisture. They were then stored ~~followed by storing~~ under controlled relative humidity (air circulated RH: 93%) for 7 days at 20 °C which ~~have~~ resulted in a sample moisture content of 20% w/w (HM: high moisture samples). Both DSC and TGA analyses were performed on both sets of samples *i.e.*, MFC/additives powders with 2% (LM) and 20% w/w (HM) moisture content.

2.4. Differential scanning calorimetry (DSC)

The DSC thermograms were recorded using a Differential scanning calorimeter (Mettler Toledo, DSC823e, Leicester UK). Approx. 10-20 mg of MFC/additive (at both 2% and 20% w/w moisture content) were weighed into sealed stainless steel pans, and an empty steel pan was used as reference sample. The samples were first cooled up to -30 °C then heated from -30 °C to 120 °C at 5 °C/min, followed by cooling the sample from 120 °C to -30 °C at 40 °C/min followed by a re-heat from -30 °C to 200 °C. Different peaks associated with thermal transitions occurring in the sample were monitored by using STARe Thermal Analysis software.

2.5. Differential Thermo-gravimetric analysis (DTGA)

Thermal stability of ~~different~~ dried MFC/additives samples (both 2% and 20% w/w moisture content) and were studied by using a Mettler Toledo model TGA/SDTA851e/LF1600 (Mettler Toledo, Leicester UK). Approximately 5–10 mg of the sample was heated under a Nitrogen environment from 20 °C to 450 °C at a rate of 10 °C/min. The initial and final degradation temperatures, corresponding percentage weight loss and the 1st derivative using a smoothing function with a third order polynomial and a running average of 75 points ~~with order of 3 & number of points 75) for the samples~~ were calculated using STARe Thermal Analysis Software.

2.6. Dynamic Vapour Sorption (DVS)

The moisture sorption and desorption of MFC/additive powder were studied using a Dynamic Vapour Sorption Analyser (DVS-1, Surface Measurements Systems Ltd., London, UK) equipped with a microbalance (Cahn D200, UK) capable of measuring a change in sample mass of 10^{-7} g. Approximately 8 mg of the sample were loaded into the sample pan and dried for 6hrs. The actual measurement was started at 0 a_w (water activity, RH 0%), and terminated at 0.95 a_w (RH 95%) with a step increase when the allocated time for the step had been reached. The program was initially set to control the humidity at 0% for 12 h (drying step ~~phase~~). This step allowed the sample water activity to decrease to zero and internally equilibrate. For each step, mass changes (m) and the rate of mass changes (dm/dt) were plotted against time (t). All experiments were run at 20 °C and duplicates tests were carried out for each sample.

The form of the isotherm curves and different hydration stages in current study was described by using Guggenheim, Anderson and De Boer (GAB) model. The GAB model is expressed mathematically in Equation 1:

$$\mathrm{M}=\frac{\mathrm{M_0CKa_w}}{(\mathrm{1\text{-}Ka_w})(\mathrm{1\text{-}Ka_w\text{+}CKa_w})}$$

where *M* is the equilibrium moisture content (in dry basis (db)), M_0 is the water content in the monolayer (g water/100 g dry solids), a_w is the water activity (=RH/100%), The constants *C* and *K* are temperature dependent (Quirijns, van Boxtel, van Loon & van Straten 2005a & 2005b, Kent and Meyer 1984, Yakimets *et al*. 2007), where *C* is a constant related to the monolayer enthalpy of sorption, and *K* is a constant related to the multilayer heat of sorption. The GAB model can be split into contributions from multilayer and monolayer water content, according to the following equations (Kent and Meyer 1984):

$$M_0 = M\,(1 - Ka_w) \qquad \text{(Equation 2)}$$

$$M_{multi} = MKa_w \qquad \text{(Equation 3)}$$

where M_0 and M_{multi} are the equilibrium moisture content in the monolayer and multilayer, respectively. The goodness of fit was evaluated using the maximum degrees of freedom adjusted R-square, R^2_{Adj} ($R^2_{Adj} > 0.98$ is considered here to be a reasonable fit, adapted from Sormoli and Langrish 2015).

$$SSE = \sum_{i=1}^{n} W_i\,(y_i - \widehat{y_\iota})^2 \qquad \text{(Equation 4)}$$

$$R^2_{Adj} = 1 - \frac{SSE\ (n-1)}{SST\ (v)} \qquad \text{(Equation 5)}$$

$$SST = \sum_{i=1}^{n} W_i\,(y_i - \widehat{y_\iota})^2 \qquad \text{(Equation 6)}$$

$$v = n - m \qquad \text{(Equation 7)}$$

where, SSE is minimum sum of squares, SST is the total sum of squares, y_i are the experimental data, $\hat{y}_i$ are the predicted data from the fit, and w_i is the weighting applied to each data point, which was set to unity in these analyses, n is the number of experimental data points, and m is the number of coefficients in each equation.

3. Results and Discussions

3.1. Differential Scanning Calorimetry (DSC):

Figure 1a shows the DSC thermograms of MFC with CMC and LBG added *after homogenisation* followed by drying to low moisture (LM: 2% w/w moisture in solids) and rehydrated to high moisture (HM: 20% w/w) by placing dry samples in an RH93% environment. In the case of CMC15 at low moisture content (2% w/w), 3 endothermic peaks were observed. During the first heating, 2 endothermic peaks between 30-40˚C (P1) and 50-70˚C (P2) were observed, which disappear during the second heating and a new peak between 5-20˚C (P3) was observed. Whereas, in the case of LBG15 at low moisture (2% w/w), the system showed only one peak between 50-70°C during the first heating and which was lost during the second heating, with no peak observed between 5-20°C. Similar thermally induced transitions were observed with MFC/additive when the additives such as LBG and CMC were added *before homogenisation* (Figure 1b). And similar endothermic peaks at 30-40˚C and 50-70˚C were observed with CMC100 and LBG100 during the 1st heating, whereas only LBG100 showed one peak between 5-20°C during 2nd heating (Figure 1c). However, no endothermic peaks were observed with MFC100 during 1st heating, whereas a broad peak was observed between 50-70°C during the 2nd heating (Figure 1c).

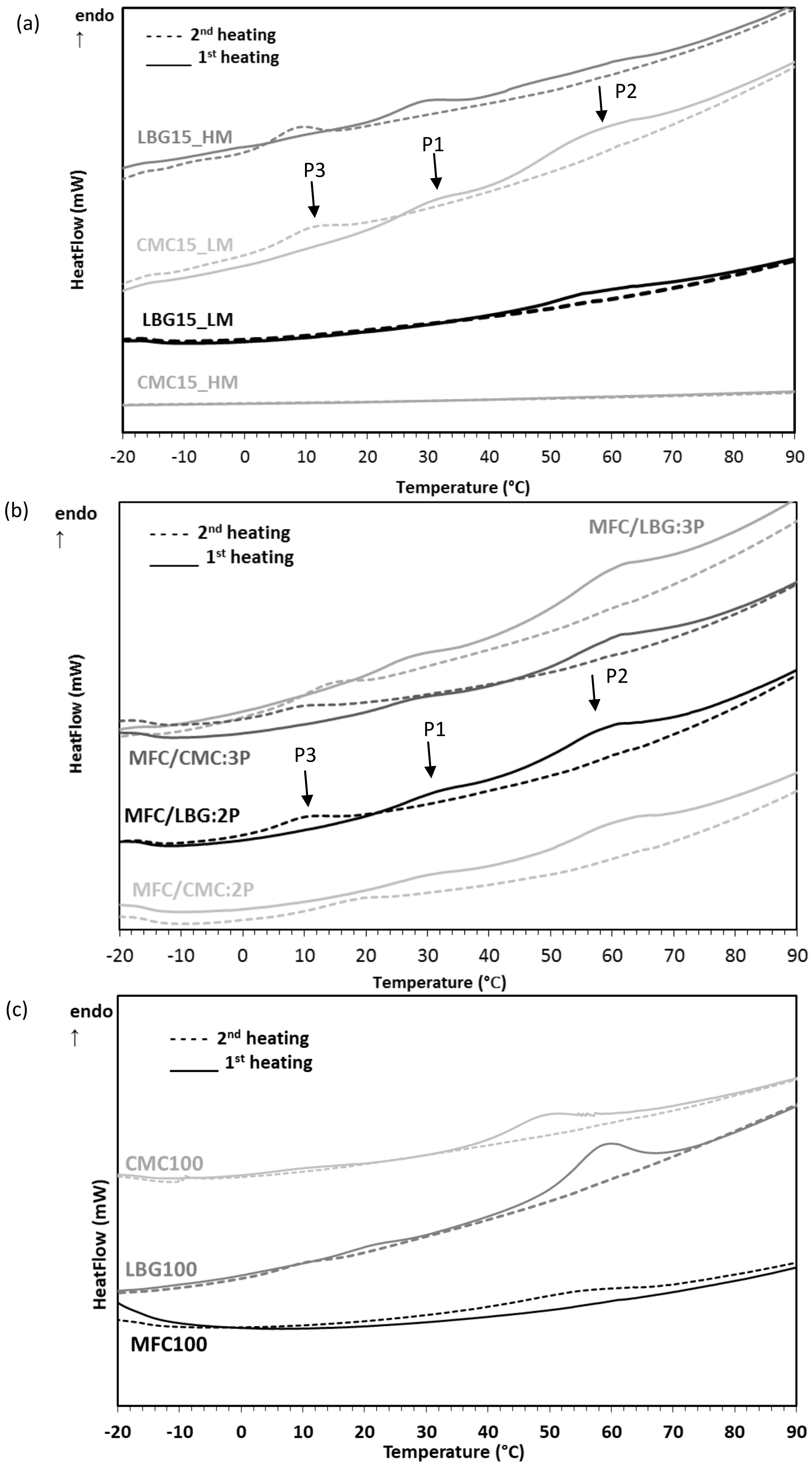
(a)
endo ↑
2nd heading
1st heating
LBG15_HM
CMC15_LM
LBG15_LM
CMC15_HM
P1
P2
P3
HeatFlow (mW)
-20
-10
0
10
20
30
40
50
60
70
80
90
Temperature (°C)
(b)
endo ↑
2nd heating
1st heating
MFC/LBG:3P
MFC/CMC:3P
MFC/LBG:2P
MFC/CMC:2P
P1
P2
P3
HeatFlow (mW)
Temperature (°C)
(c)
endo ↑
2nd heating
1st heating
CMC100
LBG100
MFC100
HeatFlow (mW)
Temperature (°C)

Figure 1: *DSC thermograms of MFC/CMC and MFC/LBG systems at 85:15 ratios, where (a) additive added after homogenisation at low moisture (LM: 2% w/w) and high moisture content (HM: 20% w/w), (b) additive added before homogenisation (at 85:15 ratio) i.e. MFC/CMC and MFC/LBG after 2 passes (2P) and 3 passes (3P) through homogeniser at low moisture content (2% w/w), and (c) CMC100, LBG100 and MFC100 thermograms at low moisture (2% w/w). Black arrows highlight different peaks observed in DSC thermograms.*

During the 1st heating, an endothermic peak between 50-70°C is common for various polysaccharides at low moisture content; this peak is associated with polysaccharide-water interactions and has also been ascribed to polymeric relaxations (Gidley *et al.,* 1990, Abbaszadeh 2014). For MFC without the addition of polymers no peaks were observed in this region during 1st heating, however a peak at 50-70°C was observed during the 2nd heating. This indicates that the addition of CMC and LBG results in temperature-induced structural transitions in the system, *i.e.* associated with hydrogen bonding between MFC-additive and MFC/additive-water. It appears that during the 1st heating the interaction between additives and MFC is driving the polymer relaxations, likely dominated by additives (CMC and LBG). This higher temperature endothermic peak also observed at higher moisture content (approx. 20%) (Figure 1a and supplementary data Figure S1B and S2B), where the moisture content of MFC/additives was manipulated by equilibrating to constant weight under a controlled relative humidity (RH). This behaviour can be explained by the presence of excess bulk water in the system (evident in DTGA data in Figure 2a and 2b by an increase in the moisture loss between 50-150°C and discussed later), similar behaviour was observed with xanthan-water and starch-water systems (Raschip *et al.,* 2008 and Gidley *et al.,* 1991).

The second, lower temperature endothermic transition peak between 30-40°C was observed with MFC/CMC, LBG100 and MFC/LBG:HM. Endothermic peak at 30-40°C was not observed with MFC100, CMC100 and MFC/LBG:LM. The endothermic peak in MFC/CMC systems indicates that the presence of CMC results in thermally induced structural changes which will influence the extent of water interaction with the MFC/additives and cause a re-organisation of hydrogen-bonding. Another explanation for these peaks is that they are associated with backbone interactions between the two polysaccharides *i.e.* cellulose and CMC or LBG. This has been reported previously in mixtures of different polysaccharides *e.g.* xanthan and konjac mannan by Abbaszadeh & Foster (2016). In both cases one of the two polysaccharides is made up of a β-(1-4)-linked backbone, and the other polysaccharides exhibits a thermo-reversible disorder-order transition (coil-helix). The transition at 30-40°C was more pronounced at higher moisture levels (20% w/w) as shown in Figure 1a (LBG15_HM). This highlights the presence of backbone interactions between the cellulose and LBG. Similar 2+1 endothermic peaks were observed with MFC/CMC and MFC/LBG systems when additives were added *before homogenisation* independent of a number of passes through the homogeniser. During the 1st heating, 2 endothermic peaks were observed when MFC is co-processed with LBG indicating the MFC's microfibrillar structure can incorporate LBG as a result of interactions between the two components, allowing more interacting water in the system during the drying process.

Finally, an endothermic peak was observed between 5-15°C during the second heating, at low moisture content for MFC/CMC, CMC100 and LBG100, whereas all MFC/additives systems including MFC/LBG showed this peak at higher moisture content when the polymer was added *after homogenisation*. The peak at 5-15°C can be explained by re-organisation of the liquid-crystalline state with both bulk and associated water with polymers, since all these samples were subjected to cooling up to -30°C before heating up to 120°C. MFC in the presence of additives and varying amounts of water, therefore, undergoes a further structural re-organisation, which may also possibly be due to a combined water MFC-additive liquid-crystalline state. This endothermic peak was observed with all co-processed (*i.e.* polymer added *before homogenisation*) MFC/additives with low and high moisture content.

Interestingly, the presence of endothermic peaks when MFC was co-processed with LBG (which was absent when added *after homogenisation*) at lower moisture content indicates the MFC's microstructure incorporated LBG as a result of interactions between the two components, allowing more interacting water in the system during the drying process. Following DSC thermograms, therefore, supports the theory that the co-processing of cellulose and polymeric additive mixtures has a structural impact.

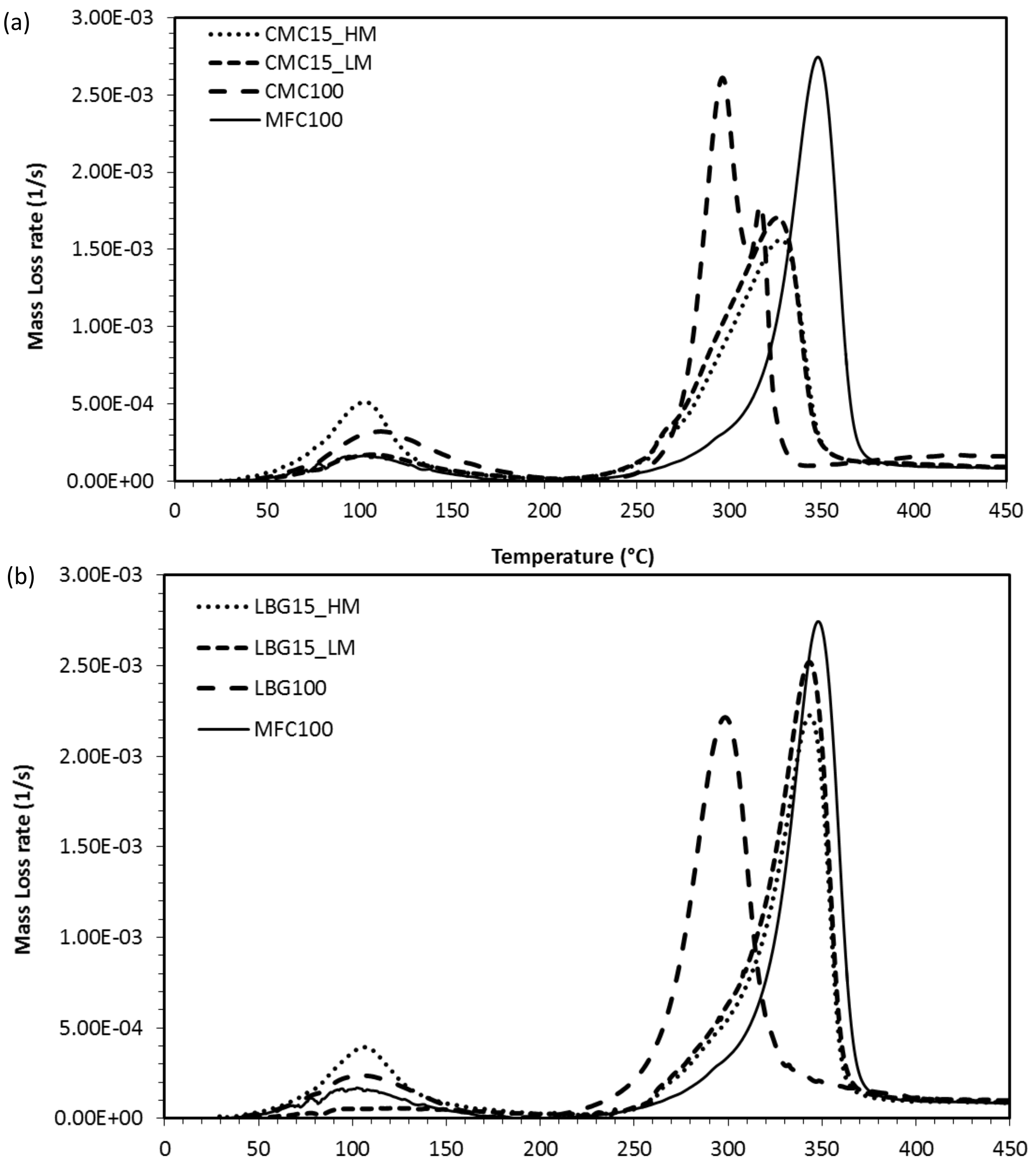

Figure 2: *The thermal degradation (DTGA) under a nitrogen atmosphere of low moisture (LM) and high moisture (HM) MFC/additive formulations, where (a) MFC/CMC and (b) MFC/LBG at 85:15 ratio.*

3.2. Differential Thermo-gravimetric analysis (DTGA):

Under an inert atmosphere of nitrogen, the first stage of weight loss less than a temperature of 180 °C is due to the evaporation of water, whereas the thermal degradation of cellulose/MFC material above 200 °C is characterised by one mass loss step which results in one peak in the DTGA curve (Figure 2a and 2b). The peaks can be loosely characterised according to the degradation of the different components present in the samples. For MFC/additive systems, one peak between 300-350 °C is related to the degradation of cellulose evident from both Figure 2a and 2b and also shown by Barneto *et al.,* (2010) and Moran *et al.,* (2008). It was also evident that the LBG100 and CMC100 degrade earlier as compared to MFC100. A shoulder peak between 250-300 °C which likely belongs to degradation of the additive (*i.e.* CMC and LBG), as the peak size and area of this shoulder increases, as the amount of additive increases in the MFC/additive formulations evident in Figure 3a and 3b.

A comparison of these curves highlights a number of interesting features. One is around the lower temperature shoulder, which is evident in the CMC systems, which also show the main endotherm maximum shifting to lower temperatures. This indicates that the interaction between cellulose and CMC is more susceptible to thermal degradation at lower temperatures. At an equivalent additive content, the LBG system is less susceptible to thermal degradation at lower temperatures than the CMC system. However, the addition of higher amount of LBG to the system (Figure 3b) a pronounced increase in the amount of more thermally sensitive material is seen (an increase in the size of the lower temperature shoulder), with a subsequent decrease in the size of the peak at the original cellulose degradation temperature. These observations support those measured by DSC, in that the

CMC seems to be more effective than LBG in altering the properties of MFC, and either a higher water content and that an increased amount of added LBG are required to have similar effects. Figure 2 demonstrates that CMC has a high level of compatibility with MFC, whereas LBG appears to have limited ~~solubility~~ distribution in the MFC dense microfibrillar network and probably exists as a separate phase when these polymers are added *after homogenisation*.

At levels of 15% CMC, both high and low moisture MFC/CMC have produced a profound change in the shape of the peak, resulting in both a lowering of the peak temperature and a broadening. Figure 3a shows that at a level of 50% CMC, a separate phase is beginning to form as indicated by the low temperature shoulder. This possibly indicates the limit of solubility of the CMC in the MFC when these solutions are mixed. By way of contrast the presence of 15% LBG has produced very little apparent change in the main MFC peak with only a slight increase of intensity in the lower temperature tail of the peak in the region of 300°C consistent with the presence of a relatively unaffected high LBG content phase at a low (15%) level. This is even more apparent in figure 3b where an increasing content of LBG adds in an approximately linear fashion to the MFC, reducing the overall MFC content and increasing the LBG peak intensity with the temperatures on both peaks being relatively unaffected. These materials are mixed intimately as solutions, consequently the possibility of incomplete mixing can be rejected when these polymers are added *after homogenisation*. Therefore the different behaviour of the mixtures represents genuine phase incompatibility. This can also be seen in the water absorption data of figure 4 where over a region of 50 – 70%, the water absorption of a 15% mixture of LBG and MFC appears approximately linear, whereas the effect of CMC appears to be much greater. At one level the TGA effects can be viewed in terms of thermodynamic compatibility between polymers. From a reaction pathway viewpoint it can be proposed that the interaction between CMC and MFC produces a mixture that is more susceptible to chemical degradation, perhaps by the resulting mixture being less dense and having imperfections where the reaction can proceed more rapidly.

Similar results were observed when the polymer was added *before homogenisation* (co-processed MFC/additives at 85:15 ratios) as shown in Figure 3c. The number of passes through the homogeniser when the two components were co-processed also has an impact on the thermal degradation of the system. For instance, it was observed that for the MFC/CMC system, as the number of passes through homogeniser increases, the peak size and area of the shoulder increases (not statistically significantly), but not in the case of MFC/LBG (Figure 3c). This indicates that the interaction between MFC and CMC produced structural changes when co-processed resulting in degradation of the system at lower temperatures compared to MFC alone. Due to inter-molecular cross-linking and strong interactions between MFC and LBG during co-processing, a higher temperature is required by the system to initiate thermal degradation. The DTGA data also supports the DSC data in showing that the interaction and resulting properties of a co-processed MFC/LBG system are different to that when LBG is added post-homogenisation (comparing Figure 3b and Figure 3c). These results correlate well with DVS moisture sorption and desorption isotherms of different MFC/additive formulations (Figure 4a and 4b).

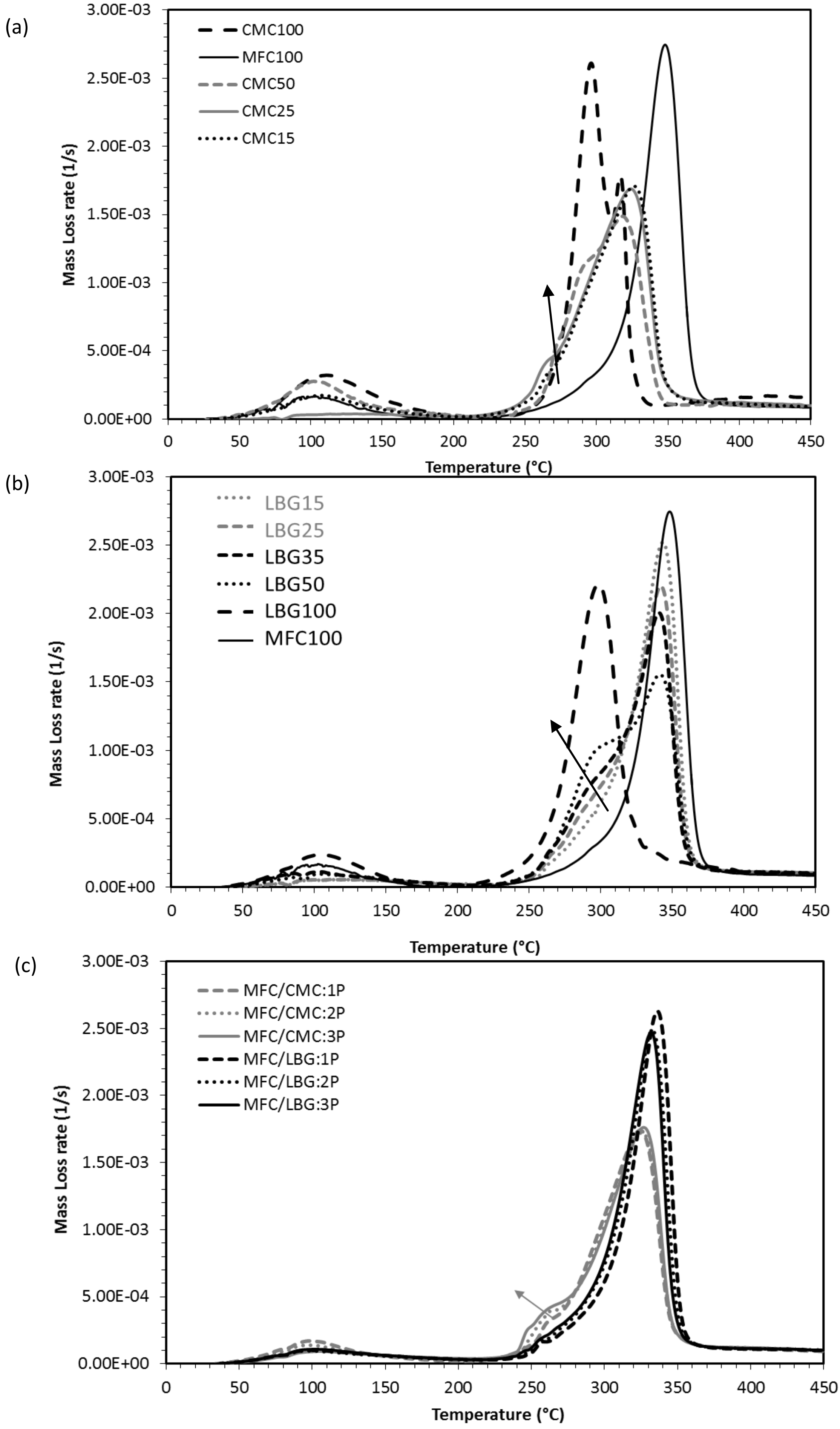
(a)
Mass Loss rate (1/s)
3.00E-03
2.50E-03
2.00E-03
1.50E-03
1.00E-03
5.00E-04
0.00E+00
0
50
100
150
200
250
300
350
400
450
Temperature (°C)
CMC100
MFC100
CMC50
CMC25
CMC15
(b)
Mass Loss rate (1/s)
LBG15
LBG25
LBG35
LBG50
LBG100
MFC100
Temperature (°C)
(c)
Mass Loss rate (1/s)
MFC/CMC:1P
MFC/CMC:2P
MFC/CMC:3P
MFC/LBG:1P
MFC/LBG:2P
MFC/LBG:3P
Temperature (°C)

Figure 3: *The thermal degradation (DTGA) under a nitrogen atmosphere at low moisture (2% w/w) and different MFC/additive ratios, where (a) MFC/CMC, (b) MFC/LBG when polymeric added after homogenisation, and (c) MFC/CMC and MFC/LBG (85:15) systems after 1pass, 2passes and 3passes when polymer added before homogeniser. Arrow near 250°C shows the increasing shoulder peak with increasing amount of additives (in Fig 3a & Fig 3b) in the formulations and number of passes through homogeniser (in Fig 3c).*

3.3. Dynamic Vapour Sorption (DVS)

From the dry state, the moisture uptake of MFC100 was relatively slow as compared to all MFC/additive formulations, due to strong intermolecular hydrogen bonds present between the MFC microfibril forming aggregates with lower diffusivity. After the first cycle of moisture sorption, the microfibril network in MFC100 holds some "associated" moisture evident in desorption isotherm Figure 4b, likely in a form of both monolayer and multilayer. All MFC/additives system showed higher moisture sorption as compared to MFC100 (Figure 4a).

The sorption isotherm for all the samples together with GAB model fit up to an RH of 90% (Equation 1) are shown in supplementary data Figure S3 and the GAB parameters are shown in Table 2 where, the individual contributions of monolayer and multilayer water to the overall isotherms are described by Equation 2 and Equation 3. The constant C and K are temperature dependent factors, where the C values represents the strength of binding for water molecules to the primary binding sites on the product surface (Sormoli *et al.,* 2015, Quirijns *et al.*, 2005a & Quirijns *et al.,* 2005b), higher the value, the stronger the bonds between water molecules to the primary binding sites. The amount of water in the monolayer (M_0) for MFC100 was lowest (similar values were observed with cellulose from parchment paper by Despond *et al.*, 2005), followed by LBG100 and highest with CMC100 (Table 2). Lower M_0 values are not surprising as it is explained earlier, this behaviour is related to hornification of MFC fibres upon drying process, *i.e.*, aggregation of microfibrils due to strong H-bonds, limiting the water mobility and interaction. Similar difference in M_0 values of LBG100 and CMC100 was observed by Torres *et al.*, 2012, authors explained this difference is related to chemical structure and composition of these polymers, the ionic character of CMC due to the substitution of hydroxyl groups by carboxymethyl groups, results in highest monolayer interaction between the CMC100 and water.

MFC/CMC *i.e.* CMC15 (CMC added *after homogenisation*) is able to take up more water (increase in mass) than the other systems, with increasing RH, and is able to retain the highest amount of that water upon drying (desorption, Figure 4b). This behaviour can be explained by higher moisture isotherms observed with CMC100. However, when CMC added *before homogenisation* showed similar moisture sorption up to 80% RH, however lower sorption was observed at 95% RH when comparing CMC15 with MFC/CMC:3P. This behaviour can be explained by structural changes and interactions between cellulose and CMC during homogenisation, which limits the moisture sorption after equilibrium. The LBG containing system is interesting as, at low RH levels, LBG15 showed slightly higher moisture sorption as compared to MFC100, however, at higher RH maps onto the MFC100 and lower than MFC/CMC throughout sorption cycle. This suggests that MFC/LBG requires a higher water content to be effective at changing the MFC properties. Upon submitting the systems to drying (desorption, Figure 4b), there appears to be an ad-desorption hysteresis for all systems. Again, this suggests that the water in the MFC/CMC system is interacting, but can be removed successfully at elevated temperatures (100°C peak in DTGA curves), and that the water taken up by the MFC/LBG system is more tightly “associated” (*e.g.*, lack of a discernible 100°C peak for the low moisture content samples in Figure 2a) and not free for evaporation at elevated temperatures. Interestingly, when LBG is added *before homogenisation*, the MFC/LBG:3P showed similar moisture sorption and desorption to MFC/CMC:3P and CMC15 (up to 80% RH), also reflected on the *K* values, where *K* values of CMC15 is similar to MFC/LBG:3P (K = 0.90, Table 2). These results, correlate with the DTGA and DSC, and suggest that co-processing of the MFC and additives results in closer association of the two polymers enabling a higher amount of tightly associated water.

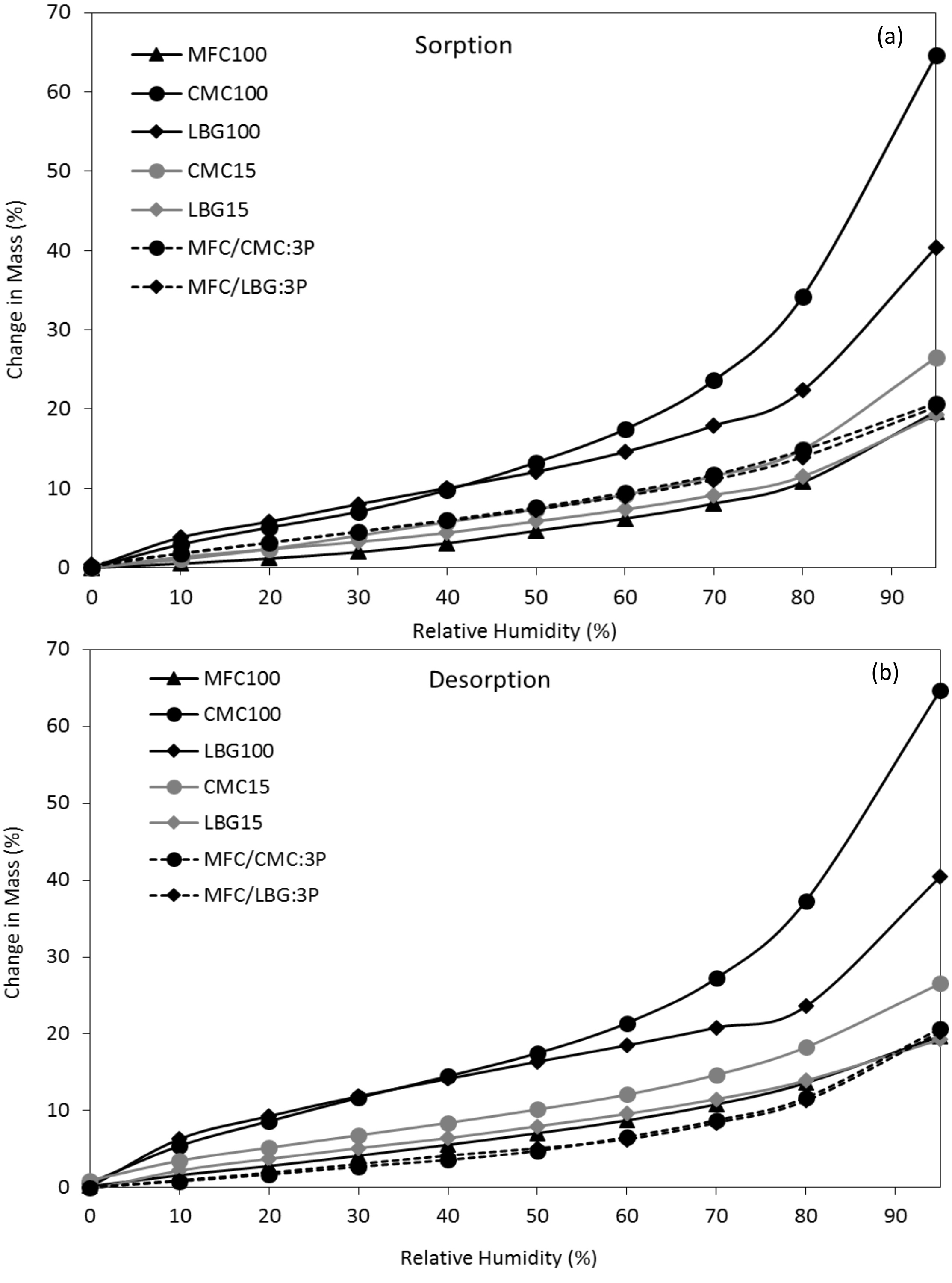

Figure 4: *(a) Sorption isotherm, and (b) Desorption isotherms of different MFC/additives powders, i.e. solid-lines are MFC100, CMC100, LBG100, CMC15 and LBG15, whereas dotted-lines are MFC/CMC:3Pass and MFC/LBG:3Pass, at 20°C temperature.*

Table 2: *GAB model parameters from the fitted sorption isotherms (fitted graphs are present in supplementary data Figure S3).*

	M_0 (g/100 g)	***C***	***K***	***R^2***
MFC100	6.78	23.25	0.84	0.9977
CMC100	12.15	2.14	0.87	0.9994
LBG100	7.58	9.99	0.85	0.9989
CMC15	3.84	28.50	0.90	0.9932
LBG15	5.28	1.84	0.79	0.9984
MFC/CMC:3P	3.28	3.58	0.89	0.9983
MFC/LBG:3P	2.99	6.06	0.90	0.9976

4. Conclusions

This study showed that moisture sorption and thermal induced structural changes in microfibrillar cellulose is a complex process and directly associated with, and controlled by different structural properties of cellulose and can be altered or modified by different polymeric additives and co-processing. Addition of polymeric additives such as carboxymethyl cellulose (CMC) and Locust bean gum (LBG) to microfibrillar cellulose (MFC) results in 2 sets of thermal induced structural changes *i.e.*, associated with polysaccharide-water interactions, and associated with polymer relaxation. The addition of polymeric additives results in the regaining of the structure upon redispersion of the dry material (higher with charged polymer *i.e.*, CMC followed by LBG). Co-processing of MFC and polymeric additives especially LBG results in a highly interconnected network of MFC and LBG which retains a higher amount of moisture influencing the thermally induced structural changes. In conclusions, the interaction between the polymeric additive and microfibrillar cellulose should be thoroughly considered when manufacturing low moisture cellulosic products.

Acknowledgement

This work was supported by the Oslofjordfond, Norway grant (2012-2015). Authors acknowledge the technical support from Val Street for DSC and TGA work.

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