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Effect of rheological properties of dissolved cellulose/microfibrillated cellulose blend suspensions on film forming

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ABSTRACT

Enzymatically treated cellulose was dissolved in a NaOH/ZnO solvent system and mixed together with microfibrillated cellulose (MFC) in order to find the threshold in which MFC fibers form a percolation network within the dissolved cellulose solution and in order to improve the properties of regenerated cellulose films. In the aqueous state, correlations between the rheological properties of dissolved cellulose/MFC blend suspensions and MFC fiber concentrations were investigated and rationalized. In addition, rheological properties of diluted MFC suspensions were characterized and a correlation with NaOH concentration was found, thus partly explaining the flow properties of dissolved cellulose/MFC blend suspensions. Finally, based on results from Dynamic Mechanical Analysis (DMA), MFC addition had strengthening/plasticizing effect on regenerated cellulose films if low concentrations of MFC, below the percolation threshold (5.5–6 wt%, corresponding to 0.16–0.18 wt% of MFC in the blend suspensions), were used.

1. Introduction

Due to growing environmental concerns, the interest of using natural polymers as replacements for synthetic polymers in certain product areas, such as packaging applications has increased during recent years. In this context, cellulose, being the most abundant natural polymer, has an important role. During the last two decades new ways to utilize cellulose have emerged and re-discovered types of cellulose such as micro- and nano-fibrillated cellulose and regenerated cellulose have been the subject of several research studies.

Cellulose can be dissolved in aqueous solvents such as NaOH in water under specific conditions. The first dissolutions of cellulose in a NaOH/water system were reported by Davidson (1934). However, Sobue, Kiessig, and Hess (1939) are often regarded as the invertors of this system, since they developed the fundamentals for the cellulose–NaOH–water ternary phase diagram (Sobue et al., 1939). According to the NaOH/water phase diagram, cellulose can be dissolved in a narrow range of temperatures and concentrations. However through recently developed solvent systems with additives such as urea (Cai & Zhang, 2005; Qi, Chang, & Zhang, 2008; Qi, Yang, Zhang, Liebert, & Heinze, 2011; Zhou & Zhang, 2001), thiourea (Qi et al., 2008, 2011; Ruan, Zhang, Zhou, Jin, & Chen, 2004) or ZnO (Liu, Budtova, & Navard, 2011; Vehviläinen et al., 2008) the dissolution range of cellulose in NaOH/water based solvents has become wider. With these newly developed systems, additives such as zinc oxide or urea are used to promote the cellulose dissolution process since they work as solution stabilizers against gelation. Through these solvent systems cellulose can be dissolved with NaOH concentrations ranging from 6 to 18 wt% at a temperature of +1 to −8 °C (Egal, Budtova, & Navard, 2007; Isogai & Atalla, 1998; Moigne & Navard, 2010; Qi et al., 2011; Roy, Budtova, Navard, & Bedue, 2001; Roy, Budtova, & Navard, 2003) or through a freeze-melting procedure (Isogai & Atalla, 1998; Vehviläinen et al., 2008).

Microfibrillated cellulose (MFC) is produced from pulp by mechanical disintegration processes (grinding or fluidization), sometimes combined with chemical or enzymatic pre-treatments. The MFC fibers are up to several micrometers long and have nanoscale diameters (Vartiainen et al., 2011). A characteristic feature of MFC is its tendency to form continuous, web-like, flocculated, entangled network structures (Karppinen et al., 2012; Saarikoski, Saarinen, Salmela, & Seppälä, 2012; Siró & Plackett, 2010) in water suspensions down to very low (~0.1 wt%) concentrations (Pääkkö et al., 2007). Because of this property, MFC is obtained as a dilute water suspension usually below 2 wt% solid content.

Due to its particular microstructure, MFC has specific rheological properties in aqueous environments. Under steady shear conditions, MFC suspensions are reported to be both shear thinning and

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thixotropic (Agoda-Tandjawa et al., 2010; Goussé, Chanzy, Cerrada, & Fleury, 2004; Lasseuguette, Roux, & Nishiyama, 2008; Pääkkö et al., 2007; Turbak, Snyder, & Sandberg, 1983) and dependent on shearing history (Saarikoski, Saarinen, et al., 2012). As a thixotropic material, the shear viscosity profile of MFC suspensions is strongly dependent on time. If the flocculated network structure of MFC is broken down by shearing, it takes time for it to reach an equilibrium at any given shear rate (Karppinen et al., 2012; Saarikoski, Saarinen, et al., 2012). In general, the rheological behavior of MFC suspensions is very sensitive to measuring conditions. Therefore it is also important to take into account that when measuring the rheological properties of MFC, the geometry itself and the gap size used for the measurements could also have an impact on the results (Saarikoski, Saarinen, et al., 2012; Saarinen, Lille, & Seppala, 2009; Saarinen, Haavisto, Sorvari, Salmela, & Seppälä, 2014).

During recent years, growing interest in sustainable material concepts has led to the development of biocomposite materials. Within this field, all-cellulose composites (ACC) have emerged as new interesting materials. In order to overcome the comb ability problems related to conventional composites, the basic idea behind ACCs is to remove the chemical incompatibilities between reinforcement and matrix phases by utilizing cellulose as both components. Consequently there would be no need for use of coupling agents or fiber treatments in order to improve chemical bonding at the reinforcement–matrix interface. Thus ACCs can be considered as bio-derived monocomponent composites. (Gindl & Keckes, 2005; Huber et al., 2012) Cellulose materials offer several advantages due to their high modulus, stiffness and high strength. In all-cellulose blends/composites hydrogen bonding between —OH groups is an important factor by providing driving forces for the attainment of miscibility between polymer phases. Basically two different techniques have been utilized to prepare all-cellulose composite films. First method is to use partial dissolution technique (partially dissolved cellulose is regenerated in the presence of undissolved cellulose) by using for example ionic liquids (Duchemin, Mathew, & Oksman, 2009). Second method is to regenerate a fully dissolved component in the presence of fibers (Gindl & Keckes, 2005).

In addition to rheological properties, interest in microfibrillated cellulose has been raised due to its mechanical properties in the dry state. The mechanical strength of an individual cellulose microfibril is very high, which together with its high surface area makes MFC a potential reinforcement material for composites (Miao & Hamad, 2013). In the area of all-cellulose composites, MFC has been used as reinforcement material for high strength paper sheets with different pulp types such as unbleached eucalyptus pulp (Alcalá, González, Boufi, Vilaseca, & Mutjé, 2013) or bleached sulfite softwood pulp from spruce (Sehaqui, Allais, Zhou, & Berglund, 2011) or for example as a reinforcement in composites with filter paper (Duchemin et al., 2009). In addition, in the area of biocomposites, MFC/polylactic acid (PLA) composites have been produced (Boissard, Bourban, Plummer, Neagu, & Månson, 2012; Iwatake, Nogi, & Yano, 2008). Regenerated cellulose fibers can also be used as reinforcement material, although their mechanical properties are not as good compared with other fiber types (Adusumali et al., 2006). In addition, natural fibers usually show a large scatter of properties compared to industrially made fibers.

Polymer blending is an important procedure to improve and modify the physical properties of polymers and in order to prepare new functional materials with properties that are unattainable by using only single components. The properties of dissolved cellulose can be modified by blending with synthetic polymers, such as poly(vinylpyrrolidone) in dimethyl sulfoxide-paraformaldehyde (DMSO-PF) solvent (Masson & Manley, 1991). In aqueous environments, dissolved cellulose can be blended with acrylic acid copolymers to enhance the mechanical strength of precipitated cellulose films (Lipponen, Saarikoski, Rissanen, & Seppälä, 2012; Saarikoski, Lipponen, Rissanen, & Seppälä, 2012; Saarikoski, Rautkoski, Rissanen, Hartman, & Seppälä, 2014). Also natural polymers can be blended with dissolved cellulose. For instance, Twu, Huang, Chang, and Wang (2003) prepared cellulose/chitosan blends via homogeneous dissolution of chitosan and cellulose in N-methylmorpholine N-oxide (NMMO) (Twu et al., 2003). Furthermore, Wu, Wang, Li, Li, and Wang (2009) prepared cellulose/starch/lignin composite films, showing that the content of cellulose and lignin significantly affects the mechanical properties of the composite films, while starch brings flexibility to the films (Wu et al., 2009).

In this paper, blend suspensions of dissolved cellulose and microfibrillated cellulose (MFC) were prepared using a solution mixing method. To characterize the rheological properties, studies were carried out by rotational rheometry. By providing information about the mixing of the polymer phases, rheological behavior is one of the key properties to be measured when preparing new types of blends. The aim of this study was to investigate the threshold at which MFC fibers are able to build a network structure within the dissolved cellulose solution. This feature can be useful in, for instance, paper coating applications where the stability of the coating plays an important role. Generally, MFC-suspensions have been under rheological investigation due to their potential as rheological modifiers for coating applications (Grüneberger, Künniger, Zimmermann, & Arnold, 2014). Microfibrillated cellulose suspensions are known to have stable network structures over time in storage by preventing the sedimentation of the coating fillers. It is known from literature that 0.1% MFC concentration in water is close to the lowest network forming concentration of MFC suspensions (Karppinen et al., 2012; Pääkkö et al., 2007), meaning that only small additions of MFC could be sufficient for coating or paint, in order to prevent sedimentation.

Rheological properties may reflect and have a very significant impact on the final dry product. Mechanical properties of all-cellulose composites after precipitation are often reported in the literature, but solution state and rheological properties prior to the precipitation has received only limited attention. However, rheological properties are one of the key properties when identifying the single aspects that might be responsible for mechanical properties. For instance small deformation oscillatory rheology has been used to evaluate the roles of cellulose and xyloglucan in determining the mechanical properties of primary plant cell walls (Yi & Puri, 2014). Therefore systematic analysis and close inspection of rheological properties is needed to provide essential background information and knowledge if for instance direct preparation of ACC materials is planned.

After the mixing steps and rheological characterization, all-cellulose composite films were prepared by co-precipitating the blend suspensions, whereafter the final dry blend films were characterized by Dynamic Mechanical Analysis (DMA) and Scanning Electron Microscopy (SEM). It is known that mechanical properties of anisotropic composites depend on dissolution and regeneration conditions (Huber et al., 2012). Secondly, it is known that fiber concentrations have significant effects on precipitated films. In this study, we wanted to determine how rheological properties, especially close to the percolation threshold, are reflected in the blend films prepared by co-precipitation in acidic medium.

2. Experimental

2.1. Materials

Cellulose water solution (3 wt% cellulose, 6.5 wt% NaOH, 1.3 wt% ZnO, pH 13) was provided by Tampere University

Table 1
Compositions of the suspensions and solutions.

ID	Dissolved cellulose/MFC ratio	Cellulose concentration (wt%)	MFC concentration of the suspension (wt%)	NaOH concentration (wt%)	ZnO concentration (wt%)
Cell/MFC (96/4)	24/1	2.86	0.114	6.0	1.2
Cell/MFC (95/5)	19/1	2.86	0.143	6.0	1.2
Cell/MFC (94.5/5.5)	17/1	2.86	0.157	6.0	1.2
Cell/MFC (94/6)	15/1	2.86	0.179	6.0	1.2
Cell/MFC (93/7)	12/1	2.86	0.205	6.0	1.2
Cell/MFC (91/9)	10/1	2.86	0.258	6.0	1.2
Cell 100 (3%)	–	3.00	0	6.5	1.3
Cell 100 (2.75%)	–	2.75	0	6.0	1.2
MFC (3%)	–	3.00	3.00	0	0
MFC (1.39%)	–	1.39	1.39	0	0

of Technology. Softwood (spruce-pine) sulfite cellulose pulp from Domsjö Fabriker AB (intrinsic viscosity 520 ml/g, 96.2 wt% cellulose, 1.4 wt% xylan, 2.1 wt% glucomannan, 0.3 wt% monosaccharides) was shredded mechanically and treated with commercial enzyme preparation (dosage 250 nkat/g). The enzyme-treated pulp was dissolved in NaOH/ZnO through a freeze–thaw procedure as published previously by (Vehviläinen et al., 2008). After the dissolution, the cellulose solution was stored in a freezer (−20 °C).

Microfibrillated cellulose was provided by VTT Technical Research Centre of Finland. The suspension was prepared by mechanical disintegration of bleached birch pulp. First, the pulp was ground once in a supermasscolloider (Masuko Sangyo, Japan) and then fluidized by five passes through an M110Y Microfluidizer (Microfluidics International Corporation, USA). The solids content of the prepared water suspension was 1.39 wt %. The pH of the MFC suspension was ~6. The fiber diameters of almost similarly prepared MFC suspension have been reported to be between 5 and 30 nm (with some larger fibril bundles/aggregates) and having an average floc size of approximately between 0.01 and 0.04 mm^2 (Pääkkö et al., 2007; Saarikoski, Saarinen, et al., 2012). Dilution of the MFC suspensions was made with Milli-Q water at room temperature (~23 °C) by mixing with a magnetic stirrer for the same amount of time as the blend suspensions were mixed.

Both solutions and suspensions were allowed to warm up to room temperature prior to use and all of the preparation steps were made at 23 °C unless otherwise mentioned. The abovementioned solutions and suspensions were mixed vigorously in a 50 or 100 ml glass vessel with a magnetic stirrer (cellulose batch ~30–80 ml). Dosing of the MFC suspension was done with a metal spoon by feeding it slowly into the vortex of the cellulose solution. The formed suspension was then mixed directly for 24 h with vigorous stirring. In order to find out the effect of increasing the MFC concentration on the blend suspensions, polymer content and water content of the suspensions were kept constant and only the ratio between dissolved cellulose and MFC was changed. The polymer/water ratio of the suspensions was kept the same for every sample. As a baseline, a blend suspension with 24/1 cellulose/MFC ratio was used, and the water content of the blends was adjusted accordingly, by adding water or removing water by evaporating during the mixing. The pH of the blend suspensions and neat cellulose solution was approximately 13. Polymer compositions of the blend suspensions are presented in Table 1. Photographs of the final blend suspensions and neat cellulose solution are shown in Fig. 1.

After mixing, precipitated blend film samples (for DMA and SEM) were prepared as follows: 2 ml of the blend suspension was pressed between two glass plates, and then immersed in an sulfuric acid solution (20 wt% H_2SO_4), wherein it regenerated slowly as the acid absorbed to the layer. After complete regeneration (~24 h), the glass plates came loose and the sample was washed carefully with water until neutral. The wet film samples were placed between two polyimide films attached to metal plates and were dried slowly at room temperature for one month and finally in an oven at 50 °C overnight. The thicknesses of the final films were between ~20–100 μm.

2.2. Characterization

The rheological characterization were performed using a Physica MCR 301 rotational rheometer (Anton Paar GmbH, Austria) equipped with a standard concentric cylinders geometry (CC 27) with a bob (Ø 26.67) and a stainless steel cup (Ø 28.92 mm). A series of measurements were performed. First, a rotational steady shear flow measurement from 0.01 s^{-1} to 1000 s^{-1} and from 1000 s^{-1} to 0.01 s^{-1} was performed. After this, an amplitude sweep measurement was performed in order to determine the linear-viscoelastic region of the suspensions. Finally a frequency sweep measurement with frequency ranging from 0.01 to 100 Hz at strain of 0.25 or 1% (depending on results from the amplitude sweeps) in the linear-viscoelastic region was performed. The same procedure was applied to all of the suspensions and solutions.

The mechanical properties of the film samples were analyzed with DMA (TA instruments Q800) at 28 °C (room relative humidity ~25%) using a film/tension measuring head. Oscillating stress sweep measurements for the samples were made with 1 Hz frequency (amplitude 2 μm) from 0 to 12 N or until they failed. Three to five replicate measurements were performed for each sample. All of the tested film samples were kept at the same conditions at RT for over 48 h prior to the testing.

Photomicrographs of solutions and blend suspensions were taken with an Olympus BH-2 optical microscope equipped with a digital camera with 100× magnifications. The morphology of the cross sections of the DMA -characterized precipitated film samples were estimated using a scanning electron microscope (SEM, Zeiss Sigma VP) with an acceleration voltage of 3 kV. The exposed fracture surfaces of the film samples were coated with a thin layer (~1–2 nm) of gold/palladium by sputtering to promote conductivity before SEM observation.

3. Results and discussion

In order to determine the influence of MFC addition on the rheological properties of dissolved cellulose solution, rheological measurements were performed. First, flow properties of dissolved cellulose/MFC blend suspensions are discussed in a general manner, after which the effect of MFC addition on the flow properties of the blend suspension is evaluated. Following this, the effect of increasing pH on rheological behavior of the blend suspension will be discussed. Finally, rheological properties of the blend suspensions are evaluated by frequency sweep studies. After the rheological part, mechanical properties and morphology of the

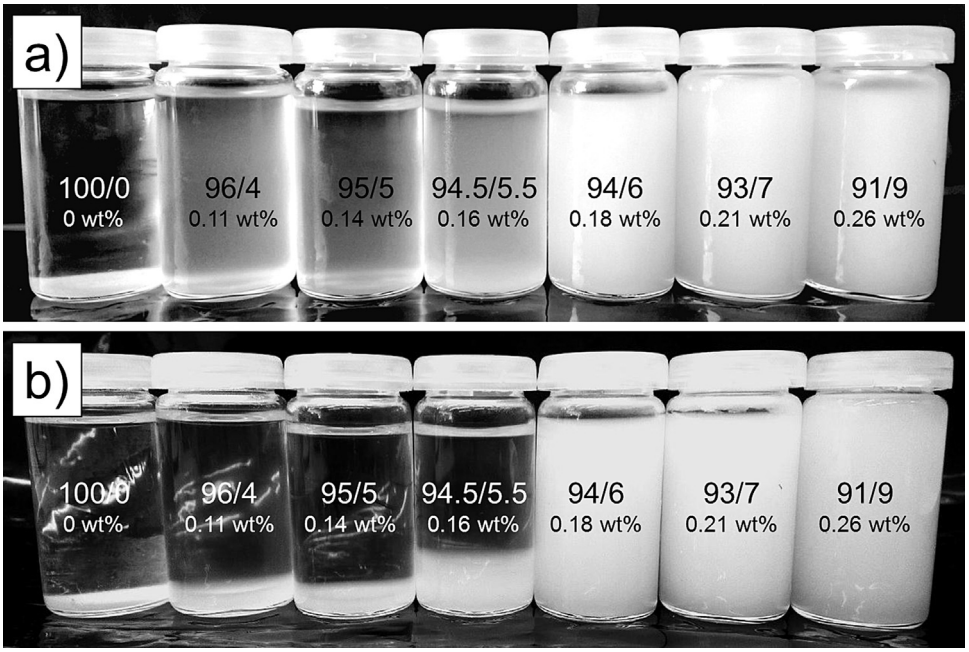

Fig. 1. The blend suspensions Cell/MFC 96/4, 95/5, 94.5/5.5, 94/6, 93/7, 91/9 and neat cellulose solution (100/0) after (a) 24 h of mixing and (b) six months in refrigerator (+ 5 °C). The MFC concentration of the each sample is reported under the suspension ID.

all-cellulose composite films, co-precipitated from the blend suspensions will be deliberated.

3.1. Flow properties

Evaluation of viscosity–shear rate curves of dissolved cellulose/MFC suspensions is complex as the flow properties are affected by e.g. flocculated flow properties of MFC, interaction of the MFC suspensions with the measuring geometry and changes in pH.

Fig. 2 presents the flow curves of dissolved cellulose/MFC blend suspensions with corresponding MFC suspensions and neat dissolved cellulose solutions presented in Fig. 2c. First, shear flow measurements were conducted from low shear rates end to high shear rate end (Fig. 2a) and back (Fig. 2b) in order to test if there was mixing taking place during the first flow measurement and thereby influencing the flow. Comparison of Fig. 2a and b proved that a flow curve measurement conducted either from 1 s^{-1} to 1000 s^{-1} or from 1000 s^{-1} to 1 s^{-1} ends on same curve with no remarkable differences.

Latest studies of MFC suspensions indicate that the viscosity–shear rate profile of MFC suspension, including the shape of the flow curve and the shear thinning characteristics of the MFC result partly from wall depletion ("wall slip") between the MFC suspension and measuring geometry (even with standard measuring geometries used for this study). Due to the wall depletion, the MFC suspensions appear highly shear thinning at low shear rates until a yield stress is reached and the geometry wall obtains proper contact with the suspension. Within the low shear rate range, MFC suspension is not under shear but flows in a plug attached to the inner geometry surface. The rheological properties observed below yielding of the suspension network are mainly related to the formation and properties of depletion layer. (Saarinen et al., 2014; Sorvari et al., 2014). In order to minimize this problem; viscosity data between 0.01 and 1 s^{-1} were excluded from the flow curves (Figs. 2–4). In addition, shear rate and viscosity values can be considered only apparent. The effect of wall depletion can be evaluated in more detail from the shear stress–shear stain curve of the suspension. Comparison of the viscosity–shear stress profiles between neat cellulose solution and the blend suspensions (Fig. 2a) shows that the shear stress profiles are very similar. This is an indication that the flow curves are comparable. Looking at the flow curves of blend suspensions with 0.18–0.26 wt% MFC concentrations in the low shear rate end (1–10 s^{-1}) of the flow curve in Fig. 2a, the shear stress value is not constant, but slowly increases as the shear rate is increased. At this regime, the effect of the wall depletion on the flow properties is minimized but yet could affect the flow (measurements of 0.5 wt% MFC have showed yield stresses of ca. 3 Pa for continuous and steady shear measurement (Saarinen et al., 2014)). At the low shear rate end of the flow curve, the initial viscosity value increases steadily once the MFC concentration is increased. This is presumably from the increase in viscosity of the depleted layer.

Comparison between the flow curves of diluted neat cellulose solution and blend suspensions (Fig. 2) shows the influence of added MFC on the blend suspension. At low MFC concentrations (0.11–0.16 wt%) the viscosity profiles were close to each other, but as the MFC ratio of the suspensions is increased, the viscosity values at low shear rates increased with MFC concentration. A slight change in the slope of the viscosity curve is seen when moving from 0.14 wt% to 0.16 wt%, but the change in slope is more significant between 0.16 wt% and 0.18 wt% concentrations. It appears that the shear thinning characteristics of MFC suspension become dominant between these two concentrations. This finding can be considered as proof that the suspension reached the saturation/percolation threshold somewhere between these two concentrations (0.16 and 0.18 wt%), but needs to be confirmed by frequency sweep studies.

3.2. Effect of MFC addition on the flow properties

The flow curve of the MFC suspension has a characteristic shape (a shoulder in viscosity and shear stress curves) as can be seen from the curve measured for the concentrated MFC suspension in Fig. 2c, arising mainly from the wall depletion phenomenon. However, the typical MFC flow curve shape is not noticed for dissolved cellulose/MFC blend suspensions in Fig. 2a. In addition to wall depletion, there are also different reasons behind the change in flow behavior,

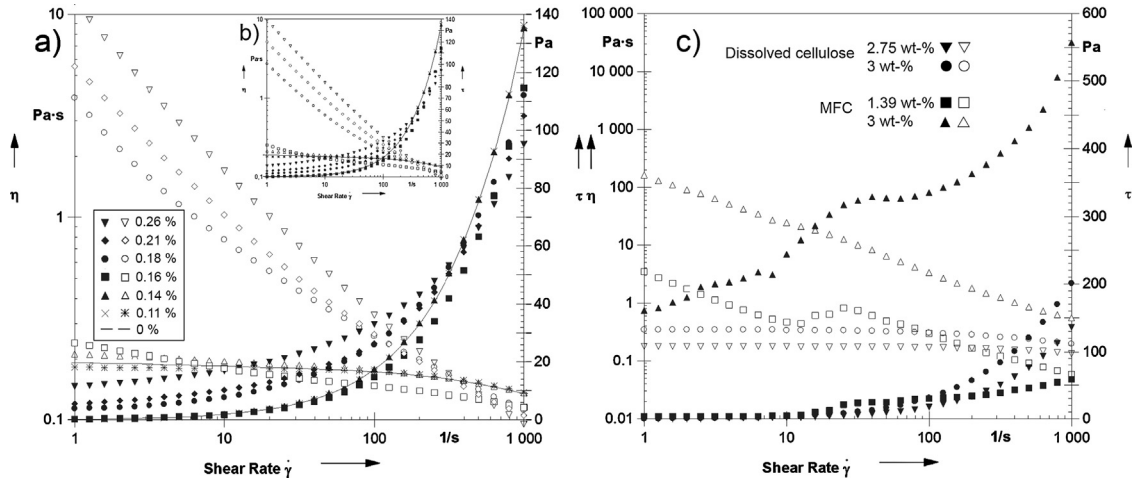

Fig. 2. Viscosity and shear stress as a function of shear rate for Cell/MFC 91/9 (▼,▽), Cell/MFC 93/7 (♦,◊), Cell/MFC 94/6 (●,○), Cell/MFC 94.5/5.5 (■,□), Cell/MFC 95/5 (▲,△), Cell/MFC 96/4 (×,✳) and neat dissolved cellulose (-,-) represented from (a) 1 s^{-1} to 1000 s^{-1} and (b) 1000 s^{-1} to 1 s^{-1}. The MFC concentration of each suspension is marked on the figure. (c) Flow curves of dissolved cellulose Cell 100 solution with added water (2.75 wt%) and without added water (3 wt%) with 1.39 wt% and 3 wt% MFC suspensions represented from 1 s^{-1} to 1000 s^{-1}.

including changes in flocculated network structure and changes in ion concentration (discussed more detail in chapter 3.3). Studies of MFC suspensions have shown that in the transition region of the flow curve (around 1–20 s^{-1}), the rate of recovery of the flocculated MFC network is not sufficient to retain a completely uniform network structure (Karppinen et al., 2012, Saarikoski, Saarinen, et al., 2012, Saarinen et al., 2009). These characteristic flow behaviors of MFC are seen already at low fiber concentrations (0.1–0.25 wt%) (Karppinen et al., 2012).

In order to test the reliability of the viscosity–shear rate curves of the dissolved cellulose/MFC blend suspensions in more detail, measurements with diluted MFC were carried out with a corresponding MFC concentration and the results were compared. Fig. 3 presents the flow curves of diluted MFC suspensions without dissolved cellulose. As might be expected, the flow curves of diluted MFC suspensions were approximately two decades lower than for corresponding dissolved cellulose/MFC blend suspensions with the same MFC concentrations. In addition, diverging from the blend suspensions, slight irregularity in the flow curve was noticed

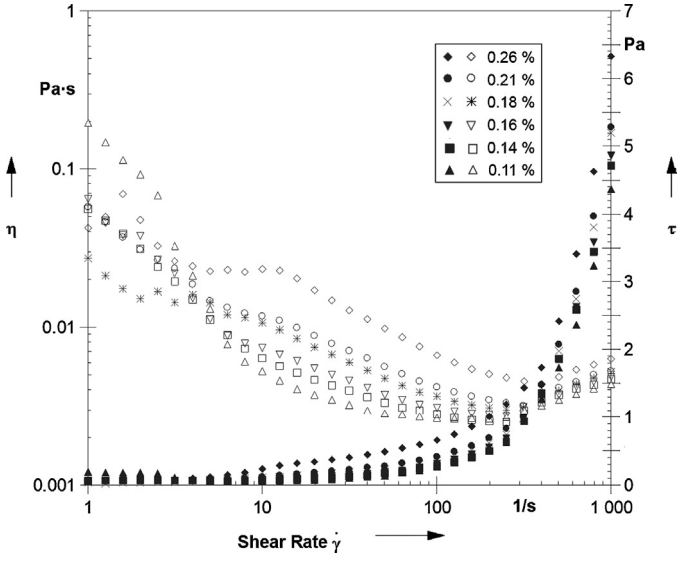

Fig. 3. Viscosity and shear stress as a function of shear rate for diluted MFC suspensions.

since the concentration of the suspensions were near to the gel forming concentration of MFC (Karppinen et al., 2012). Additionally, increased viscosity at high shear rates was seen at the end of the flow curves due to turbulent eddies (Karppinen et al., 2012). When these flow curve results were compared to the results from dissolved cellulose/MFC blend suspensions in Fig. 2, the effect of MFC on the flow properties of blend suspensions was distinguished in more detail. As mentioned, with the blend suspensions there was a clear increase in the slope of the viscosity curve as the MFC concentration was shifted from 0.16 wt% to 0.18 wt%. However, with the diluted MFC no such shift in viscosity profile was seen. Instead, with the diluted MFC suspensions, the viscosity values increased constantly as the MFC concentration was increased. In the blend suspensions, the formation of a MFC network structure was inhibited by the presence of dissolved cellulose. The network structure of MFC within the dissolved cellulose was not formed until the saturation/percolation threshold was reached. However as the percolation threshold was achieved, the viscosity increased.

3.3. *Effect of increased pH*

Ionic strength and pH are among the most important factors affecting the rheological properties of MFC suspensions. The gel strength and network formation of MFC is dependent on the strength and number of the fiber–fiber contact points in a certain volume. This is also the reason why the flow properties of MFC suspensions are highly dependent on the ion concentration of the suspension. If the MFC suspension is washed to sodium form, the result is seen directly in the shape of the flow curve (Saarinen, Karppinen, & Seppälä, 2012). The pH of the dissolved cellulose/MFC blend suspension was ~13 as the pH of the MFC suspension was ~6. It is known that at high pH values the MFC fibers present a lower degree of interaction in the suspension. High pH may result in the energy barrier collapse and aggregation of the MFC fibers (Ono, Shimaya, Sato, & Hongo, 2004; Saarikoski, Saarinen, et al., 2012). This could also be the case with dissolved cellulose/MFC blend suspensions. Increased pH may affect the interaction between MFC fibers within the dissolved cellulose solution and hence the viscosity profile. A recent study by Sorvari et al. (2014) has shown that addition of carboxymethylcellulose (CMC) addition can prevent shear-induced flocculation of MFC suspensions, leading to a clearly better dispersion. Based on findings by Sorvari et al. (2014), Karppinen, Vesterinen, Saarinen, Pietikäinen, and Seppälä (2011),

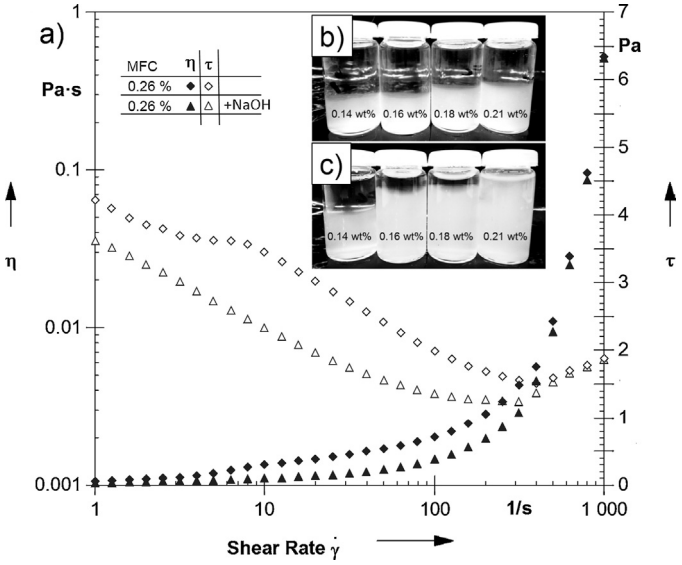

Fig. 4. (a)Viscosity as a function of shear rate (open symbols) and shear stress as a function of shear rate (filled symbols) for diluted MFC suspensions with and without NaOH addition represented from 1 s^{-1} to 1000 s^{-1}. Diluted MFC suspensions with (b), and without NaOH addition (c), after 24 h in refrigerator (+ 5 °C).

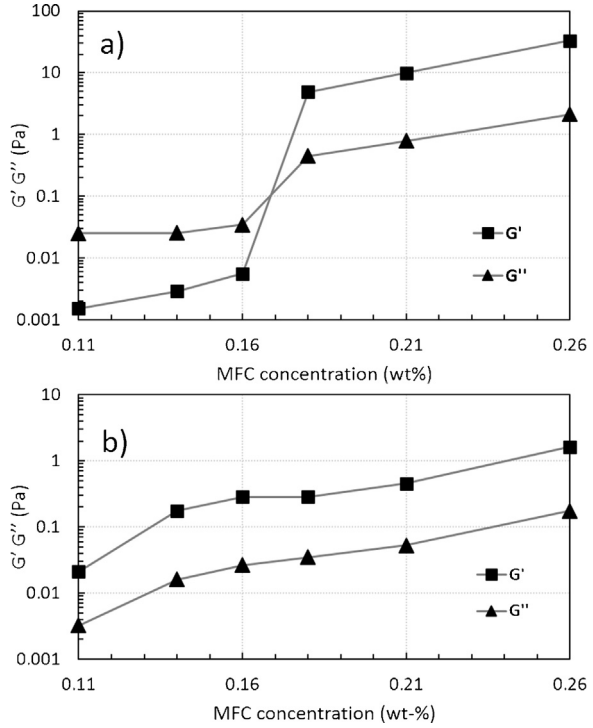

Fig. 5. Storage modulus (G′) and loss modulus (G″) for (a) dissolved cellulose/MFC suspensions (b) diluted MFC suspensions. Measured at 0.25% strain and 0.02 Hz frequency.

Saarikoski, Saarinen, et al. (2012) and Ono et al. (2004), increase in pH may reduce shear-induced flocculation of diluted MFC suspensions, leading to enhanced dispersion and lower modulus levels. Thus in dissolved cellulose/MFC blend suspensions the dispersing mechanism would be a combination of the increased viscosity of the suspending medium and the steric hindrance effects, preventing collisions/contacts between fibers/flocs. Furthermore, reducing the pH by adding MFC suspension to the dissolved cellulose solution may cause some coagulation of the cellulose.

To test the influence of increased pH on the diluted MFC suspensions, corresponding amounts of NaOH were added to the diluted MFC suspensions as in the dissolved cellulose/MFC blend suspensions and the rheological properties were compared. Fig. 4a presents the flow curves of diluted MFC suspension with 0.26 wt% MFC concentration with and without NaOH addition. Within Fig. 4a, the influence of added NaOH can be seen immediately as decreased viscosity values. In addition, the shape of the flow curve changed. This is an indication that the increased pH may have affected the flocculated flow properties of MFC fibers. Lowered and changed viscosity profile would be seen as weakened interactions between MFC flocs. If the interactions between the flocs are weakened, the network structure of MFC may disintegrate more easily. This result proves that the changes in viscosity profile seen for the dissolved cellulose/MFC blend suspensions may be related partly to changes in pH. However, it is also important to keep in mind that the increase of the viscosity curves of diluted cellulose/MFC blend suspensions compared to diluted MFC suspension comes mainly from diluted cellulose which acts as a medium for the MFC fibers. In addition to rheological studies, the weakened interactions between MFC fibers in NaOH concentrated suspensions could be verified from the stability test performed for the diluted MFC suspensions with (Fig. 4b) and without NaOH addition (Fig. 4c). These tests showed that after 24 h, MFC suspensions with added NaOH were more phase-separated than the corresponding diluted suspensions.

3.4. Frequency sweep studies

In order to study the rheological behavior of the dissolved cellulose/MFC blend suspensions in more detail, frequency sweep studies were conducted. Fig. 5 shows a comparison between storage modulus (G′) and loss modulus (G″) as function of MFC concentration for the blend suspensions and diluted MFC suspensions at 0.02 Hz frequency. Fig. 5a shows how the storage modulus of the blend suspension increases progressively with MFC concentration, as expected. When the MFC concentration of the blend suspension was increased from 0.16 wt% to 0.18 wt% the storage modulus increased above the loss modulus and started to be the dominating component of the suspension. This was a sign that the suspension reached the saturation/percolation threshold somewhere between these two concentrations (0.16 and 0.18 wt%) by forming a continuous MFC network within the dissolved cellulose. As the MFC content of the blend suspension reached the percolation threshold, typical characteristics of MFC suspensions became more dominant, leading finally to a gel-type of rheological behavior. Mechanical spectra of the blends at MFC concentrations of 0.16 wt% or lower have solution-like characteristics ($G' \ll G''$; large increase in moduli with increasing frequency), but the spectra obtained for the blends at higher concentrations of MFC, and for MFC alone (Fig. 5b) at all concentrations studied, show gel-like response ($G' > G''$; little frequency-dependence of either modulus).

Finally, the effect of added water on the properties of the dissolved cellulose solution was tested. Fig. 6 shows a frequency sweep measurement for 3 wt% dissolved cellulose solution and diluted (2.75 wt%) dissolved cellulose solution having the added water amount corresponding to a blend suspension with 24/1 cellulose/MFC ratio (Cell/MFC 96/4) that worked as a baseline for the blend suspensions. This evaluation together with OM-photomicrographs taken from 2.75 wt% dissolved cellulose solution showed that the added water did not cause gelation within the dissolved cellulose solution, even though some coagulation may occur due to the changes in pH. Thus, the increase in storage modulus of the blend suspensions parallel to the increased MFC concentration can be said to be due to the MFC addition.

Finally, the network formation of MFC within the dissolved cellulose was confirmed by stability tests of the blend suspensions.

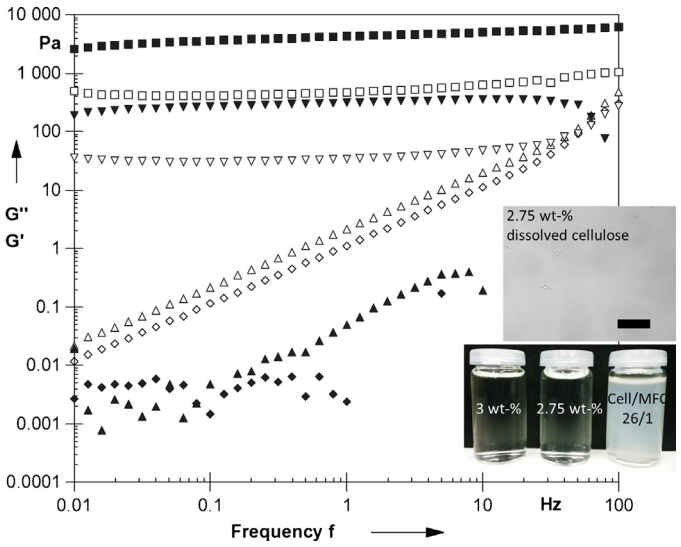

Fig. 6. Storage modulus (filled symbols) and loss modulus (open symbols) of dissolved cellulose Cell 100 with and without added water. 2.75 wt% (♦,◊), 3 wt% (▲,△). MFC suspensions with 1.39 wt% (▼,▽) and 3 wt% (■,□) concentrations. Samples of dissolved cellulose with 3 wt-%, 2.75 wt-% concentrations with dissolved cellulose/MFC suspensions Cell/MFC 96/4 and OM-photomicrograph of 2.75 wt% cellulose solution (scale bar 100 μm).

From the Fig. 1b it can be seen that at 0.18 wt% MFC concentration there was no phase separation after six months of refrigeration, confirming that the network structure of MFC was formed within the dissolved cellulose solution.

3.5. Precipitated films

Regenerated cellulose/MFC films were prepared via co-precipitation of the dissolved cellulose/MFC blend suspensions. In order to get a more comprehensive understanding of the effects of MFC addition, two more sets of samples were produced with two different MFC concentrations, 2.4 wt% and 3.2 wt% in addition to those listed in Table 1. Thus the MFC amounts in the blend films were 2.4 wt%, 3.2 wt%, 4 wt%, 5 wt%, 5.5 wt%, 6 wt%, 7 wt% and 9 wt%.

Fig. 7a–c shows a comparison of film transparency. The transparency can be also used as a criterion for the miscibility between constituents used for composites. As can be seen from Fig. 7a, transparency decreases steadily as the MFC concentration in the film is increased. From the comparison between neat cellulose film and the film with 3.2 wt% MFC concentration in Fig. 7a–c, it can be stated that MFC is evenly dispersed throughout the film. The films with small MFC addition were smoother and noticeably less brittle than neat cellulose film, indicating that addition of MFC has a plasticizing effect on the films. In order to study morphology of the films in more detail, the precipitated blend films were observed using scanning electron microscopy (SEM). SEM-micrographs of the cross sections of the neat cellulose and precipitated blend films are presented in Fig. 7d–g. The cross section surface of neat cellulose film is rigid and porous as seen from the Fig. 7d, but as MFC content in the films is increased, smoother areas in the cross section surface can be seen. Finally, as the MFC concentration in the blend is increased over the percolation threshold, a predominantly smooth surface is seen in the cross section (Fig. 7e–f), indicating network formation.

Mechanical properties of the co-precipitated blend films were characterized using oscillating stress sweep measurements by DMA. The mechanical properties of the precipitated films are summarized in Fig. 8. Due to the variances between some of the film samples the results can be considered only indicative. Film properties showed increase in tensile strength and slight increase in Young's modulus and strain at break values with the lowest tested MFC amounts (2.4 wt%, 3.2 wt%, 4 wt% in the precipitated blend, corresponding to 0.07, 0.09 and 0.11 wt% in the suspensions), compared to neat regenerated cellulose film. This result indicated an increase in the elastic component of the blend, giving improvements to regenerated cellulose film, even though with substantial variation.

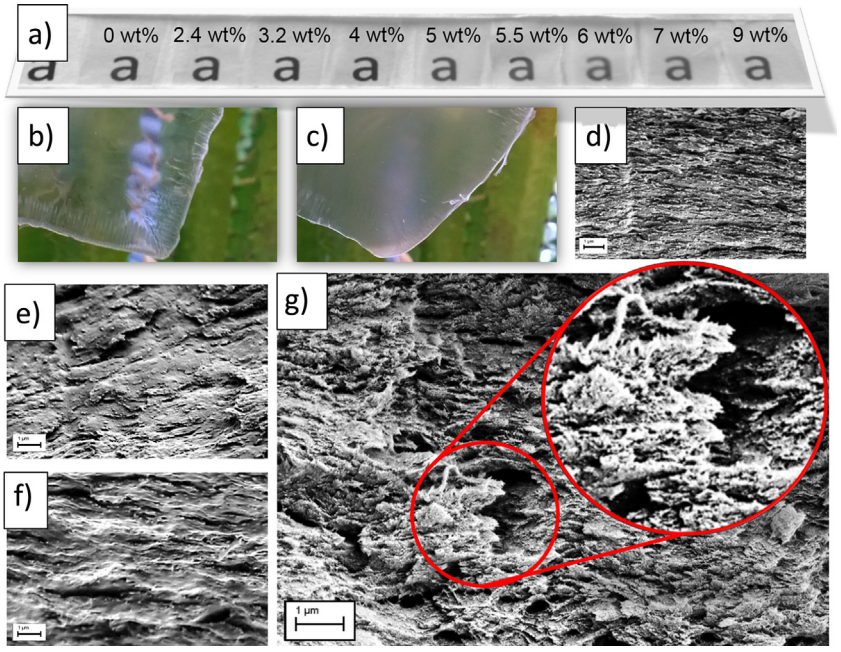

Fig. 7. (a) Comparison of the transparency of the co-precipitated blend films with MFC concentrations marked on the picture (row of äš are to provide background comparison of transparency of the different films) (b) neat regenerated cellulose film (c) co-precipitated blend film with 3.2 wt% of MFC (note the twined strands to differentiate the differences in transparency). SEM-micrographs of the cross sections of (d) neat regenerated cellulose and regenerated cellulose/MFC films with (e) 5 wt% (f) 6 wt%, and (g) 5.5 wt% of MFC (with a magnification circle showing MFC fibrils separating from the surface), photographed from the fracture points of the DMA measured film. Scale bars 1 μm.

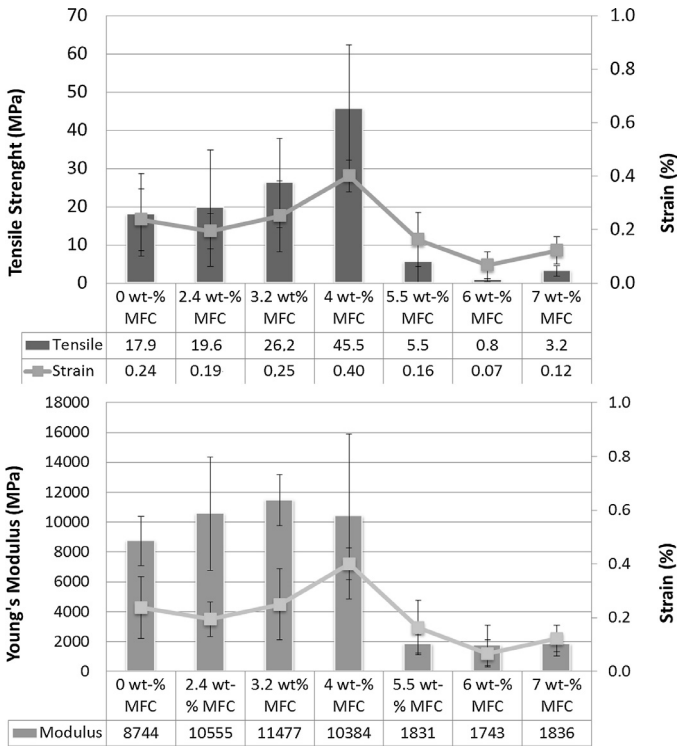

Fig. 8. Tensile strengths and Young's modulus of precipitated dissolved cellulose/MFC blend films and neat regenerated cellulose reference film sample measured with DMA. The MFC concentration of each sample is marked on the figure.

In our previous study by Saarikoski et al. (2014), similar observations regarding small additions of polymers (5–10 wt% in the blend) giving improvements to regenerated cellulose films were reported. Furthermore, small additions of MFC have been reported to improve the mechanical properties of MFC/polyvinyl alcohol composites (Panaitescu et al., 2011). With 4 wt% or lower MFC concentrations, the continuous phase of the blend is a dense crystalline network of regenerated cellulose II held together by strong inter-fibrillar hydrogen bonds and van der Waals interactions, with only some MFC fibers giving reinforcement/elasticity to the film. Based on SEM observations (Fig. 7g), it seemed that the MFC fibers had good contact with regenerated cellulose. This could be due to the surface absorption phenomena. Since MFC has a higher surface energy than regenerated cellulose, it is possible that the regenerated cellulose is absorbed on to the surfaces of MFC fibers (Aulin et al., 2009; Gardner, Oporto, Mills, & Samir, 2008), thus giving improvements to the regenerated cellulose film when sufficiently low MFC concentrations are used. This phenomenon is similar to those observed between MFC and carboxymethyl cellulose (CMC) or regenerated cellulose and CMC (Filpponen et al., 2012; Liu, Choi, Gatenholm, & Esker, 2011) as CMC has a natural tendency to physically adsorb onto cellulose in aqueous medium, thus modifying the properties of MFC or regenerated cellulose.

Comparisons of unidirectional, all-cellulose composites do not reveal dramatic differences in Young's modulus (Huber et al., 2012) and this was also the case with regenerated cellulose/MFC films. Young's modulus values between 4 and 6 GPa have been reported for regenerated cellulose films reinforced with cellulose nanowhiskers, cast from NaOH/urea solution (Qi, Cai, Zhang, & Kuga, 2009). Considering these results, the rigidity of regenerated cellulose/MFC films is high. Improvement of mechanical properties in regenerated cellulose films precipitated from NaOH/urea/ZnO system compared to films precipitated from NaOH/urea have been attributed to the improved dispersion of cellulose molecules in the solution containing ZnO (Yang, Qin, & Zhang, 2011). Literature reports also indicate that addition of nano size cellulosic fibers to regenerated cellulose leads to a decrease in strain at break, but strong increase in stiffness (Gindl & Keckes, 2005). This would also explain why elongation at break of regenerated cellulose/MFC films is low.

As mentioned in the introduction, mechanical properties of anisotropic composites are also known to depend on dissolution and regeneration conditions (Huber et al., 2012). Regeneration is influenced by the diffusion speed of the non-solvent. Due to low viscosity levels, cellulose solution and its blends with MFC were very fluid, resulting in the solution/blend flowing out from between the glass plates during the precipitation process when the acid concentration was too low, resulting in very thin (~10 μm) films. To prevent this outcome, precipitation was performed in 20 wt% H_2SO_4. It is reported in the literature that long immersion times lead to reduced tensile strength values and this was also the case for regenerated cellulose/MFC films.

When the polymer concentration in the blend suspension is increased near the percolating threshold/gel-forming concentration in solution/suspension stage, it is also reflected in the film properties and the strengthening/plasticizing effect of the added polymer is removed. This observation is in line with our earlier findings for co-precipitated blend films (Saarikoski et al., 2014). Above the 4 wt% MFC concentration in the blend, the films were extremely brittle (5 wt% blend films were even too brittle to be measured). Film casting proved troublesome near and above the percolation threshold. Since the films were prepared via acidic treatment, based on simultaneous precipitation of high pH suspensions, bringing neutral pH water to the system was a problem. As a result, the blend suspensions above 7 wt% MFC concentration (corresponding to 0.21 wt% in the suspension) could not be precipitated properly. It is also noteworthy that the final drying of the films was conducted in an oven adjusted to 50 °C. It is reported that at increased temperatures the rate of solvent removal from cellulose is higher, resulting in imperfect regeneration of the precipitated film (Li, Zhang, & Xu, 2012). Therefore, oven-drying, even after a long drying period at room temperature, could have affected the film properties.

4. Conclusions

Dissolved cellulose/microfibrillated cellulose blend suspensions were prepared via a solution mixing method and a variety of rheological analyses were conducted in order to determine their properties. Based on the rheological studies together with stabilization tests, the percolation threshold was observed between 0.16 and 0.18 wt% of MFC in the blend suspensions, corresponding to 5.5–6 wt% of MFC in the co-precipitated blends. Above the percolation threshold, MFC addition provided stable dissolved cellulose/MFC blend suspensions without phase separation. By studying diluted MFC suspensions with corresponding amounts of NaOH in the suspensions, it was found that increased pH may partly affect the flow properties of dissolved cellulose/MFC blend suspensions, even though the rheological properties of the blend suspensions originate mainly from the synergy between dissolved cellulose and MFC fibers.

Studies presented in this paper have shown that by blending sufficiently small amounts of microfibrillated cellulose into cellulose solution – dissolved in a NaOH/ZnO solvent system, it is also possible to produce films by co-precipitation in acidic medium. However, based on results from DMA, it appears that in order to improve the properties of acid-regenerated blend films, only MFC amounts small enough and below the percolation threshold can be used. Mechanical properties regenerated cellulose/MFC blend films were highly dependent on precipitation conditions, thus optimization of

the casting method is crucial to further improve the mechanical properties of regenerated cellulose/MFC blend films.

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