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Effect of CMC and Surfactant on the Physical Properties of Micro Nanofibrillated Cellulose Coating Colors

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Abstract: Rheological characteristics and physical properties of the micro nano fibrillated cellulose suspensions play an important role in curtain coating of paper. In curtain coating layer, curtain stability remains an issue to control the coating operation. The curtain stability is associated with rheological characteristics and physical properties of the micro nanofibrillated cellulose (MNFC) suspensions such as the viscosity and dynamic surface tension. Thickeners are used to control the viscoelasticity of the MNFC suspensions. Use of surfactant has been recognized as useful approach to increase the curtain stability because low dynamic surface tension is desirable to get a stable liquid flow. Effect of carboxymethyl cellulose (CMC) and anionic surfactant (Niaproof4) on viscoelasticity and dynamic surface tension was examined and compared. The change of air bubble content brought was also investigated. Our study showed that CMC didn’t influence the dynamic surface tension of MNFC suspensions. Conversely, viscoelasticity decreases with increasing the amount of CMC in the MNFC suspensions. Furthermore, surfactant didn’t have effect on viscoelasticity of MNFC suspensions but decreases significantly dynamic surface tension. In addition, we have observed that the use of CMC increases air content, but surfactant was more effective. The use of both at once generates more air bubbles in the MNFC suspensions.

Key words: micro nano fibrillated cellulose, viscosity, dynamic surface tension, elastic modulus, content of air bubbles, curtain coating

1. Introduction

Nanocellulose is a cellulosic material composed of fibrils and/or nano-sized cellulose crystals (as far as diameter or width is concerned). As cellulose is a naturel abundant organic compound originating from biomass, nanocellulose is also considered as renewable natural forest product. Micro Nanofibrillated Cellulose (MNFC), a cellulose filament with micro dimension in length and nano dimension fibrils in width, has become relatively straightforward to produce both in the laboratory and pilot scale.

Being a type of nanocellulose or “cellulose filaments”, the micro-nano-fibrillated cellulose (MNFC) has a good potential for application in papermaking. Today, the use of MNFC in papermaking processes is becoming a renewed research topic [1]. As it has been shown that micro-fibrillated cellulose may well succeed in improving the mechanical and barrier properties of paper [2]. The integration of MNFC in paper products attracts more interest. The MNFC can be added with two methods. The first aim is to mix the MNFC with the pulp before forming the paper [3, 4], which leads to a significant increase in the mechanical properties of the sheet (up to 21% for the tensile index for an MNFC amount of 4%). In the second method, the MNFC is applied to the surface of a wet paper sheet [5], which increases the barrier properties, such as the very significant drop in paper air permeability (from 6.5×10^4 nm $Pa^{-1}.s^{-1}$ to 360 nm.$Pa^{-1}.s^{-1}$ with a 8 g.m^{-2} MNFC coating).

The general approach of our project is to incorporate a layer of MNFC into the paper structure. To do this, it is necessary to intervene before the end of the formation of the paper so in wet part on the formation

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table of the paper machine. It's proposed to apply MNFC during papermaking as a structuring layer within a Thermomechanical Pulp (TMP) sheet to improve the mechanical and barrier properties of TMP sheet. It can be done commercially through the use of a Hydra-Sizer^{TM}, a curtain coating equipment to be integrated at the wet-end of a paper machine, provided by the GL&V Group. To maintain the properties of MNFC in order to improve the mechanical properties and barriers, the fibrils must preserve their micro-nano dimension: they must not agglomerate and must then be well dispersed. For this reason, we thought to use Carboxy Methyl Cellulose (CMC) as dispersing agent. The effect of CMC on fiber dispersion at the micro level has been the subject of several studies [6-8]. The adsorption of CMC on cellulose nanofibrils was investigated by S. Ahola et al. [7], who demonstrates that the adsorption of CMC is reversible on the nano-fibrils film surface and that CMC adsorption results in dispersion effects. Another study by P. Myllytie et al. [6] shows the effect of CMC on the surface of fibrils using light microscopy to see the fibrils in water. The results show that when the fibers treated with CMC, the fibrillar structure on the surface of the fiber becomes very extensive and finely dispersed. On the other hand, understanding the rheology of MNFC is important to ensure a stable MNFC curtain. Regardless of how the suspension is obtained and its source, Micro Fibrillated Cellulose (MFC) in an aqueous environment reveals shear thinning behavior, i.e., as the shear rate increases, the viscosity of the suspension decreases [9, 10]. Independently of the concentration (between 0.125 and 5.9 wt %), MFC suspensions show gel-like behavior and values of storage modulus are rather high. These results show that at the lowest concentration of 0.125 wt%, MFC suspensions will form a rather strong network [9]. Other studies stated that higher concentrations result in increased yield stress and higher viscosities [11]. Furthermore, the effect of the CMC on the rheology of MFC was shown in the study of A. H. Vesterinen et al. [12]. For the (MFC+CMC) solution, the strongly shear thinning behavior of MFC disappear. The authors predict that CMC have a dispersing effect in the MFC, and that it probably decreases the amount of free water in the suspension. The rheological analyses presented, are still insufficient to formulate a proper explanation of the peculiar behavior of MFC. In this study, CMC is used to extend the dispersion of MNFCs observed at the micro level to the nano level.

The MNFC coating mixtures for curtain coating need to have curtain stability and extensional property that withstand the change in surface area and stretching in machine direction. Curtain stability is associated with the increase in surface area of the free falling curtain layer. The dynamic surface tension of the coating color is often used to see the curtain stability. To control this property diverse chemical approaches may be used which include the use of surfactants. Use of surfactants has been recognized as an easy and useful approach to increase the curtain stability since low surface tension is highly desirable to get a stable extensional curtain flow. To understand the effect of CMC and surfactant addition, the dispersing effects of CMC and surfactant effect on MNFC is researched. In other words, the effect of CMC and surfactant on viscoelasticity and surface tension of MNFC mixtures will be studied. Moreover, use of surfactants, however, tends to increase the foaming tendency of coating mixtures. Addition of surfactant to MNFC coating mixtures can generates more air bubbles that cause coating defects. The surfactant may cause rapid absorption that's why it's important to select a surfactant that increases curtain stability and at the same time causes less foaming and printing problems. The effect of surfactant and CMC on the air bubble content of MNFC coating mixtures was studied.

2. Material and Methods

2.1 Micro Nanofibrillated Cellulose

The MNFC was produced by Omya International

AG with the Masuko grinding equipment. Bleached Eucalyptus fibers are co-processed with ground calcium carbonate (Hydrocarb 50–GU, Omya) in the ratio of 80% cellulose and 20% filler to improve the fibrillation of the cellulosic fibers. The obtained MNFC has a diameter varied from 20 nm (nano-part) to 15 µm (micro-part) and a length of up to 1 mm, hence the MNFC name. For our work, the MNFC suspension was diluted to a concentration of 0.5 (wt %) fibrils. The characteristics of MNFC are presented in Table 1.

2.2 Carboxymethylcellulose

In our experiments, carboxymethylcellulose (CMC) as dispersant is the Finnfix 10 from CP Kelco. It is a commercial product of minimum 98% purify grade with small amounts of sodium chloride and sodium glycolate. Its degree of substitution (DS) is 0.8, molecular weight is about 60 g/mol. The calcium carbonate used to prepare the (CMC+$CaCO_3$) solution is provided by OMYA International AG. It's the same calcium carbonate used in the grinding process of OMYA International AG to manufacture the MNFC.

2.3 Surfactant

The surfactant proposed is NIAPROOF 4 of anionic nature, i.e., with a hydrophilic part negatively charged. The critical micellar concentration is 2.1 mM and a molecular weight of 316.4 g.mol^{-1}. NIAPROOF 4 is a good wetting agent. For effective wetting, the concentrations considered of NIAPROOF4 are 0.01; 0.03 and 0.05%. Many types of MNFC coatings colors were prepared to examine the effect of CMC, surfactant and combined effect of these two modifiers on the physical properties of MNFC coatings colors. The MNFC 0.5%+CMC 0; 2; 4; 6% and MNFC 0.5%+NIA 0; 0.01; 0.03; 0.05% are simply referred as M-CMC 0; 2; 4; 6 and M-N 0; 0.01; 0.03; 0.05 respectively. Similarly, the $CaCO_3$ 0.125% + CMC 0; 8; 16; 24% solutions are referred to as C-CMC 0; 8; 16; 24 respectively. The different colors are presented in Tables 2-4.

Table 1 Characteristics of MNFC.

	Solid content (%)	Fillers Ratio (%)	Fibrils Ratio (%)
MNFC	3.52	0.71	2.82

Table 2 MNFC suspensions preparation to test CMC addition effect.

	M-CMC0	M-CMC2	M-CMC4	M-CMC6
Fibrils (g/g $_{MNFC}$)	0.5			
$CaCO_3$ (g/g $_{MNFC}$)	0.125			
CMC (g/g $_{MNFC}$)	0	1E-4	2E-4	3E-4

Table 3 MNFC Suspensions preparation to test surfactant addition effect.

	M-NIA 0	M-NIA 0.01	M-NIA 0.03	M-NIA 0.05
Fibrils (g/g $_{MNFC}$)	0.5			
N (g/g $_{MNFC}$)	0	5E-7	15E-7	25E-7

Table 4 MNFC Suspensions preparation to test CMC and surfactant effect.

	M-CMC 2-NIA0.01	M-CMC 6-NIA0.05
Fibril (g/g $_{MNFC}$)	0.5	
$CaCO_3$ (g/g $_{MNFC}$)	0.125	

2.4 Viscoelasticity and Dynamic Surface Tension

Viscosity and dynamic modulus were determined using Rheologica rheometer Stresstech from ATS Rheo-System. For all the rheology measurements, parallel plates P20 is used and the gap is set as 1mm. Before each rheology measurement, 0.2 ml sample is deposited on the plate by using the syringe and is allowed to rest for 10 minutes. During measurement, the temperature is controlled to be constant at 21°C. We have implemented the following procedure to fully describe the rheological behavior of MNFC coating colors under moderate shear stresses:

- The MNFC coating colors were prepared and allowed moderate agitation during all tests.
- A conditioning step (21°C, shear rate 10 s^{-1} followed by an equilibrium step 21°C).
- A continuous shear ramp (21°C, 1 s^{-1} to 100 s^{-1}).

The MNFC coating colors were centrifuged and dynamic surface tension of the supernatants was measured with a bubble pressure tensiometer. During measurements, the temperature is controlled to be constant at 25°C. Surface tension is a very important factor in curtain coatings because curtains can be stably formed if the interface expands rapidly. Surface age is the time required for the curtain to eject and escape onto the substrate. Therefore, the surface age depends on the height of the curtain, and the surface tension at each height is different. The bubble pressure tensiometer adjusts the surface age by varying the air injection rate in the capillary. For example, if the air is injected quickly and the bubble formation cycle is short, the surface age is low. In the process of forming the curtain, the lower the surface tension, the better it is.

2.5 Measurement of Bubble Content

To measure the bubble content in MNFC suspensions, the entrained gas tester (EGT) is used. The EGT uses Boyles Law for gases to determine the amount of air in a sample. One atmosphere of pressure is applied to the sample in the EGT by turning a Knob. A trapped air bubble in the Pressure Indicator indicates the pressure and one atmosphere is reached when the bubble is reduced in size by one half. At this time, it is compressing the volume of all the air in the sample by one half. Since the total volume of the sample chamber is a known constant, there is just a simple percentage of air constant factor for each full revolution of the Knob. Simply stated, after the one atmosphere is reached, all one has to do is count the number of revolutions it takes to get the Knob all the way back out. Then subtract the correction factor and multiply by the percentage of air factor to get the final answer in percentage of air.

3. Results and Discussion

3.1 Effect of CMC

The content of CMC didn’t have effect on the dynamic surface tension of MNFC suspensions (Fig. 1). Low surface age gave higher surface tension. The dynamic surface tension for all suspensions (M-CMC0; M-CMC2; M-CMC4 and M-CMC6) at a low surface age (order of 1s) is close to the surface tension of the water (≈ 72 Nm/m at 25°C). Indeed, as the content of the CMC in the MNFC coating colors increases, the phenomenon of thickening of the coating liquid does not intensify and the pressure at the time of formation of the bubble remains almost constant. On the other term, intermolecular forces between CMC, MNFC and water are low. The interaction potential generated by these intermolecular forces contributes to reducing the energy of the fluids, and to stabilizing them. In general, the dynamic surface tension of the MNFC suspensions decreases with the age of the surface. This leads to say that the dynamic surface tension decreases with higher curtain height since a higher curtain height increases curtain velocity and available surface age.

In Fig. 2, All the MNFC suspensions present shear thinning behaviour (viscosity decreases as shear rate increases). Without CMC, MNFC suspension presents the highest viscosity value. Moreover, MNFC suspensions show some slight disturbances at high shear rate (between 10 and 100 s^{-1}).

As the addition of CMC is from 2 to 6%, the increased proportion of CMC contributes to the decrease of the low shear rate viscosity but the slight instabilities at high shear rate remain. Furthermore, when the addition of CMC is increased to 6%, the behavior of the viscosity remains the same at low shear rate, but at high shear rates (between 50 and 100 s^{-1}), the viscosity of the MNFC suspension becomes almost

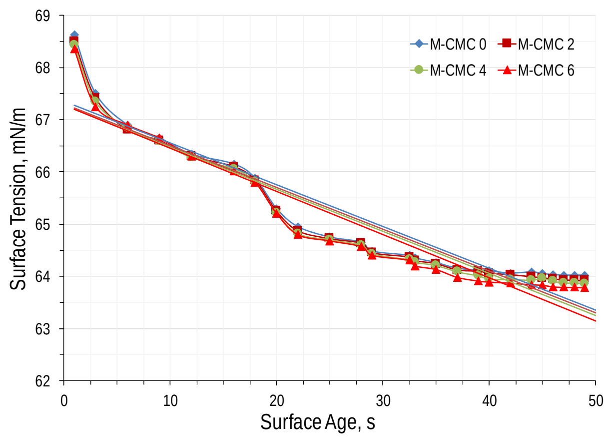

Fig. 1 Effect of CMC on MNFC suspensions surface tension.

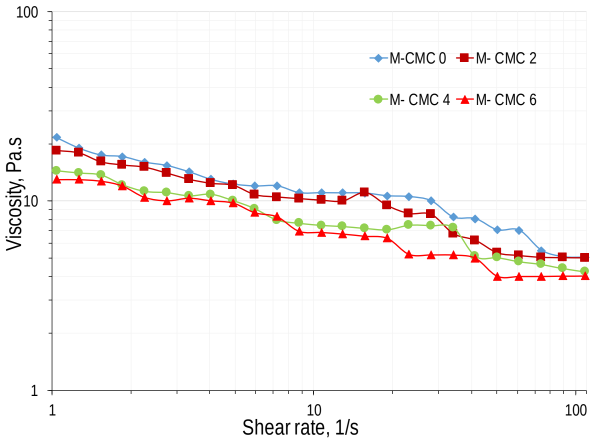

Fig. 2 Effect of CMC on MNFC suspensions viscosity.

constant. The action of the CMC is a little visible from 2% but is clear with 6% of CMC. The CMC makes it possible to have a more homogeneous suspension with smoother rheology curves. Rheological tests are here used to explore the influences of CMC on the rheological characteristics and the intern structure of MNFC suspensions as an indication to fibril-fibril interactions. We interpret the rheological results obtained by the ability of CMC to prevent fibril-fibril interactions within the internal structure of the MNFC.

Elastic modulus shows almost similar tendency with viscosity. MNFC suspensions with low CMC content (2%) showed lower elastic modulus than suspension without CMC (Fig. 3). This can be explained by the fact that the CMC disperses the MNFC and prevents it to forming flocks. This means also that the CMC decreases the rigidity of the MNFC and prevents it from behaving as a gel.

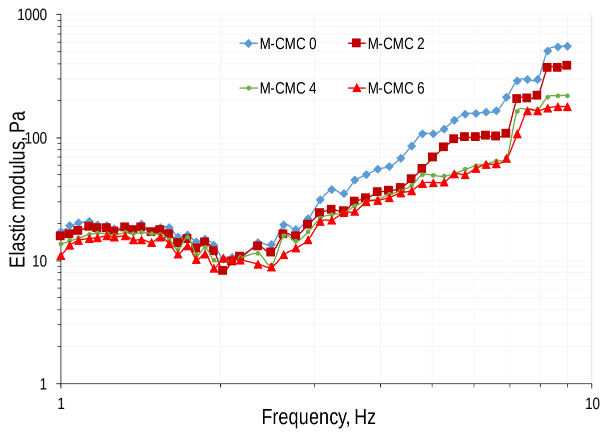

Fig. 3 Elastic modulus of MNFC suspensions with CMC.

3.2 Effect of Surfactant

The content of surfactant (Niaproof4) has significant influence on the dynamic surface tension of MNFC suspensions unlike the CMC (Fig. 4).

Even a small amount of surfactant decreases surface tension significantly. The maximum bubble drop measurements showed the surface tension of all MNFC suspensions to decrease with low surface age, although by varying degree. This can be explained by the activity of the surfactant that reduces the surface tension of the MNFC suspensions due to adsorption at the surface (Van Der Waals interactions with the fibrils of the MNFC). At high surface ages, the surface tension remains almost constant. This can be explained by the fact that the effective surface tension of the MNFC coating colors tends towards the surface tension of the anionic surfactant at high surface ages.

The effect of the anionic surfactant (Niaproof4) on the viscosity of the MNFC coating colors is presented on the Fig. 5. We observe that the amount of the surfactant does not visibly influence the viscosity of the MNFC coating colors. The rheological behavior of the suspensions is always shear-thinning behavior. As the addition of surfactant is from 0.01% to 0.05%, the increased amount of surfactant contributes very slightly to the decrease of the viscosity with the appearance of some slight instabilities at high shear rate. This can be interpreted by the low interaction between the surfactant and the MNFC fibrils.

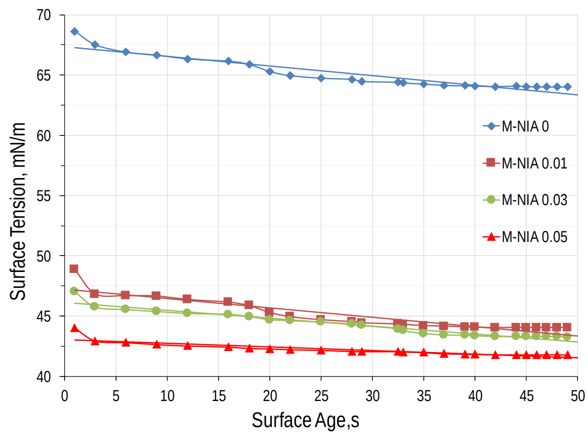

Fig. 4 Effect of surfactant on MNFC suspensions surface tension.

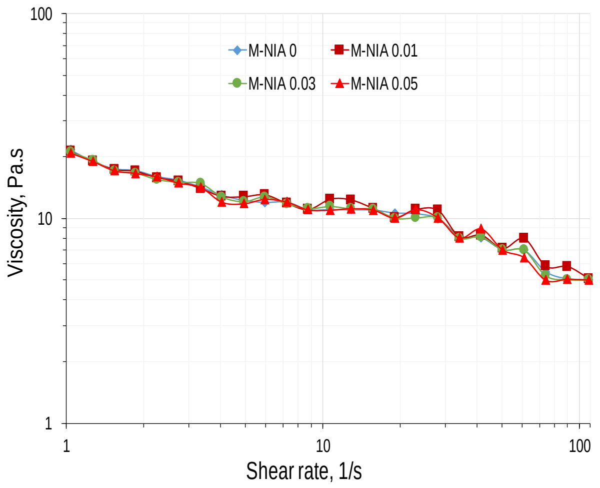

Fig. 5 Effect of surfactant on MNFC suspensions viscosity.

Elastic modulus shows similar tendency with viscosity. MNFC coating colors with low surfactant content (0.01%; 0.03% and 0.05%) showed a slight decrease of elastic modulus than suspension without surfactant (Fig. 6). This can be explained by the fact that the surfactant disperses the MNFC but with a less degree than the CMC and prevents suspensions to forming flocks. This means also that the surfactant decreases the rigidity of the MNFC and prevents it from behaving as a gel.

3.3 Combined Effect of CMC and Surfactant

The content of CMC and surfactant has significant influence on the dynamic surface tension of MNFC suspensions (Fig. 7). The surface tension of the both MNFC suspensions decreases as the concentration of the two constituents (surfactant and CMC) increases. The action of the surfactant remains visible even in a mixture with the CMC. The maximum bubble drop measurements showed the surface tension of both MNFC suspensions to decrease with low surface age. Surfactant activity is evident even in the presence of CMC. At high surface ages, the surface tension remains almost constant and tends towards the surface tension of the anionic surfactant. We can deduce that even in a tertiary mixture (MNFC, CMC and surfactant), the action of the surfactant on the surface tension is clear but it decreases with a degree less than in the case of a binary mixture (MNFC and surfactant). The result can be interpreted that in the presence of CMC with the surfactant in a MNFC suspension, the hydrogen interactions of water on the surface are more than in the case where the surfactant is alone.

In the case of combined effect of surfactant and CMC, the both MNFC suspensions have a shear thinning character: The viscosity decreases as a function of the shear rate. The action of the CMC remains visible even in a mixture with the surfactant As the addition of CMC and surfactant (2 and 6% for CMC; 0.01% and 0.05% for surfactant), the increased proportion of CMC and surfactant contributes to the decrease of the low shear rate viscosity but always the slight instabilities at high shear rate remain. This confirms the absence of action of the surfactant on the viscosity of the MNFC suspensions shown in the dedicated part to the effect of the surfactant (Fig. 8).

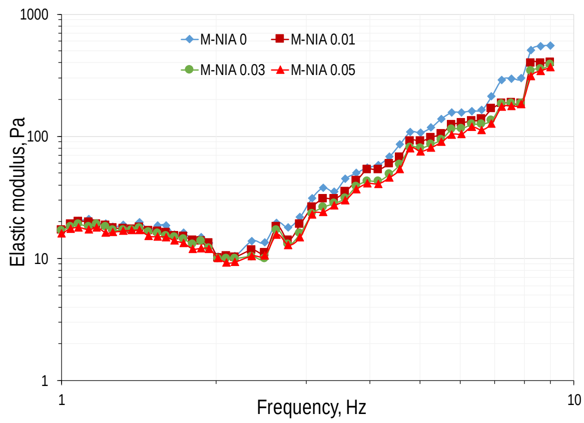

Fig. 6 Elastic modulus of MNFC suspensions containing surfactant.

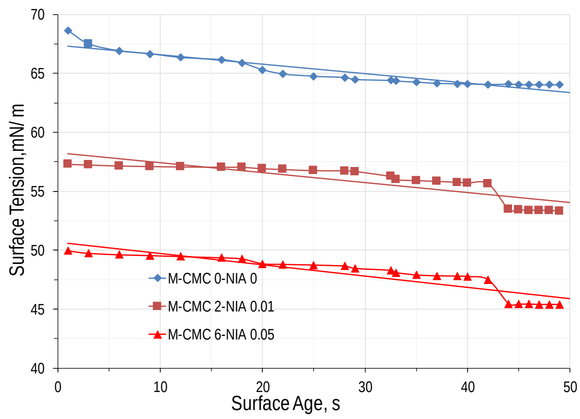

Fig. 7 Combined effect of CMC and surfactant on surface tension of MNFC suspensions.

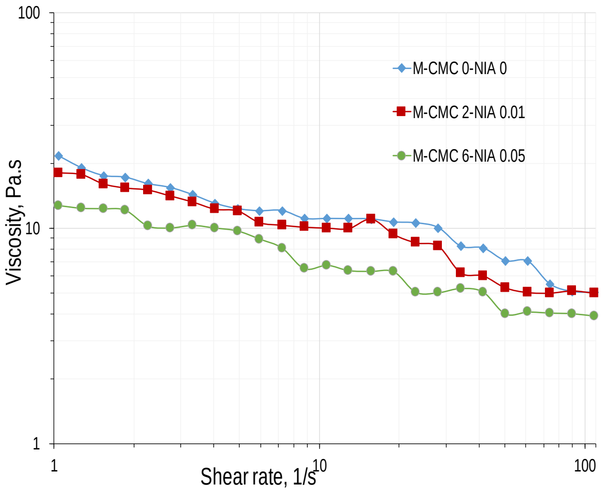

Fig. 8 Combined effect of CMC and surfactant on viscosity of MNFC suspensions.

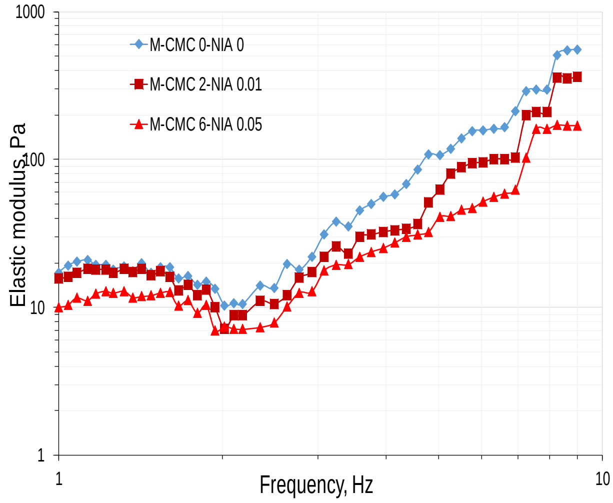

Fig. 9 Elastic modulus of MNFC suspensions containing CMC and surfactant.

Elastic modulus shows similar tendency with viscosity. MNFC suspensions with low CMC and surfactant content (2% and 0.01%) showed lower elastic modulus than pure suspension of MNFC (Fig. 9). The same trend is observed with the amounts 0.05% of the surfactant and 6% of the CMC with an obvious decrease of the elastic modulus. This can be explained by the fact that the CMC disperses the MNFC in the presence of the surfactant and prevents it to forming flocks.

3.4 Results of the Content of Air Bubbles

The pure suspension of MNFC contains a low air content (less than 1%). the addition of CMC from 2% to 6% increases slightly the air content. On the other hand, the addition of the surfactant increases significantly the air content in the MNFC suspensions (almost 3% for 0.05% of the niaproof4 and 6% for 0.05%). When CMC was used as a rheology modifier, air bubbles were generated in MNFC suspensions (Fig. 10). With an increase of CMC addition rate, the amount of Bubble increase. The surfactant generates more air bubbles in the MNFC suspensions than the CMC. The use of both modifiers generates even more air bubbles. This can be explained by the fact that the surfactant is positioned at the water-air interface, its hydrophilic part in the water, and the other part in the air. Therefore, increasing the amount of surfactant increases the air

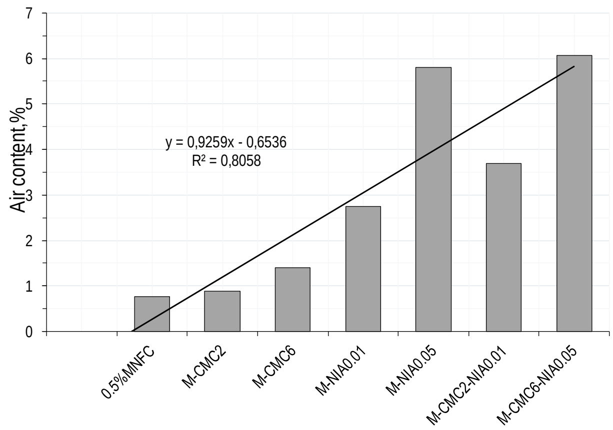

Fig. 10 Bubble content of MNFC suspensions with CMC and surfactant.

bubbles in the MNFC suspensions. We have seen that the CMC has a slight influence on the surface tension of the MNFC suspensions that is clear in this part, which reflects the slight amount of air bubbles in the MNFC suspensions in the presence of the CMC.

4. Conclusion

In this study, the effects of CMC and surfactant addition on rheological properties, dynamic surface tension and content of air bubbles of the MNFC suspensions were investigated. When CMC is added, the dispersibility of the MNFC suspensions is improved: The viscosity and the elastic modulus decrease when the amount of CMC increases, which shows that the CMC has a good ability to prevent fibril-fibril interactions within the internal structure of the MNFC. In addition, CMC didn't influence the dynamic surface tension of MNFC suspensions. On the contrary, surfactant didn't have effect on viscoelasticity (viscosity and elastic modulus) of MNFC suspensions but it significantly reduces the dynamic surface tension of MNFC suspensions. The addition of the CMC and the surfacant at the same time does not bring new results, the conclusions drawn previously remain valid for the combined effect. On the other side, we found that the surfactant generates more air bubbles in the MNFC suspensions than CMC, which can cause defects on the final paper.

It appears that it is better to use the CMC and the surfactant to control the viscoelasticity and the surface tension of the MNFC suspensions. The disadvantage is that the use of these two modifiers increases the content of air bubbles.

References

[1] F. W. Brodin, O. W. Gregersen and K. Syverud, Cellulose nanofibrils: Challenges and possibilities as a paper additive or coating material — A review, *Nord. Pulp. Pap. Res. J*. 29 (2014) 156-166.

[2] N. Lavoine, I. Desloges, A. Dufresne and J. Bras, Microfibrillated cellulose — Its barrier properties and applications in cellulosic materials: A review, *Carbohydrate Polymers* 90 (2012) 735-764.

[3] I. González, S. Boufi, M. A. Pèlach, M. Alcalà, F. Vilaseca and P. Mutjé, Nanofibrillated cellulose as paper additive in eucalyptus pulps, *BioResources* 7 (2012) 5167-5180.

[4] O. Eriksen, K. Syverud and O. Gregersen, The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper, *Nordic Pulp & Paper Research Journal* 23 (2008) 299-304.

[5] K. Syverud and P. Stenius, Strength and barrier properties of MFC films, *Cellulose* 16 (2009) 75.

[6] P. Myllytie, S. Holappa, J. Paltakari and J. Laine, Effect of polymers on aggregation of cellulose fibrils and its implication on strength development in wet paper web, *Nord. Pulp. Pap. Res. J.* 24 (2009) 125-134.

[7] S. Ahola, P. Myllytie, M. Österberg, T. Teerinen and J. Laine, Effect of polymer adsorption on cellulose nanofibril water binding capacity and aggregation, *BioResources* 3 (2008) 1315-1328.

[8] K. Oksman, Y. Aitomäki, A. P. Mathew, G. Siqueira, Q. Zhou, S. Butylina, S. Tanpichai, X. Zhou and S. Hooshmand, Review of the recent developments in cellulose nanocomposite processing, *Composites Part A: Applied Science and Manufacturing* 83 (2016) 2-18.

[9] M. Pääkkö, M. Ankerfors, H. Kosonen, A. Nykänen, S. Ahola, M. Österberg, J. Ruokolainen, J. Laine, P.T. Larsson and O. Ikkala, Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels, *Biomacromolecules* 8 (2007) 1934-1941.

[10] F. W. Herrick, R. L. Casebier, J. K. Hamilton and K. R. Sandberg, Microfibrillated cellulose: morphology and accessibility, *J. Appl. Polym. Sci.: Appl. Polym. Symp.*, United States, ITT Rayonier Inc., Shelton, WA, 1983.

[11] M. Iotti, Ø. W. Gregersen, S. Moe and M. Lenes, Rheological studies of microfibrillar cellulose water dispersions, *Journal of Polymers and the Environment* 19 (2011) 137-145.

[12] A. H. Vesterinen, P. Myllytie, J. Laine and J. Seppälä, The effect of water-soluble polymers on rheology of microfibrillar cellulose suspension and dynamic mechanical properties of paper sheet, *Journal of Applied Polymer Science* 116 (2010) 2990-2997.