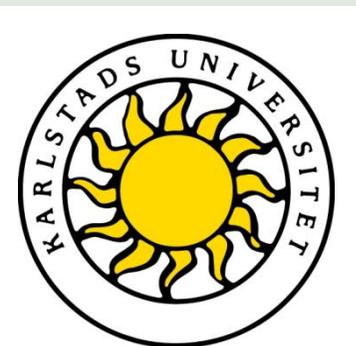




Physical adsorption of PVOH to adjust the rheological profile of NFC

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Outline

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 - Comparison with fully hydrolyzed PVA
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NFC properties

- ❖ High viscosity and gel structure
- ❖ Low solids content
- ❖ Affinity to water

Research objectives:

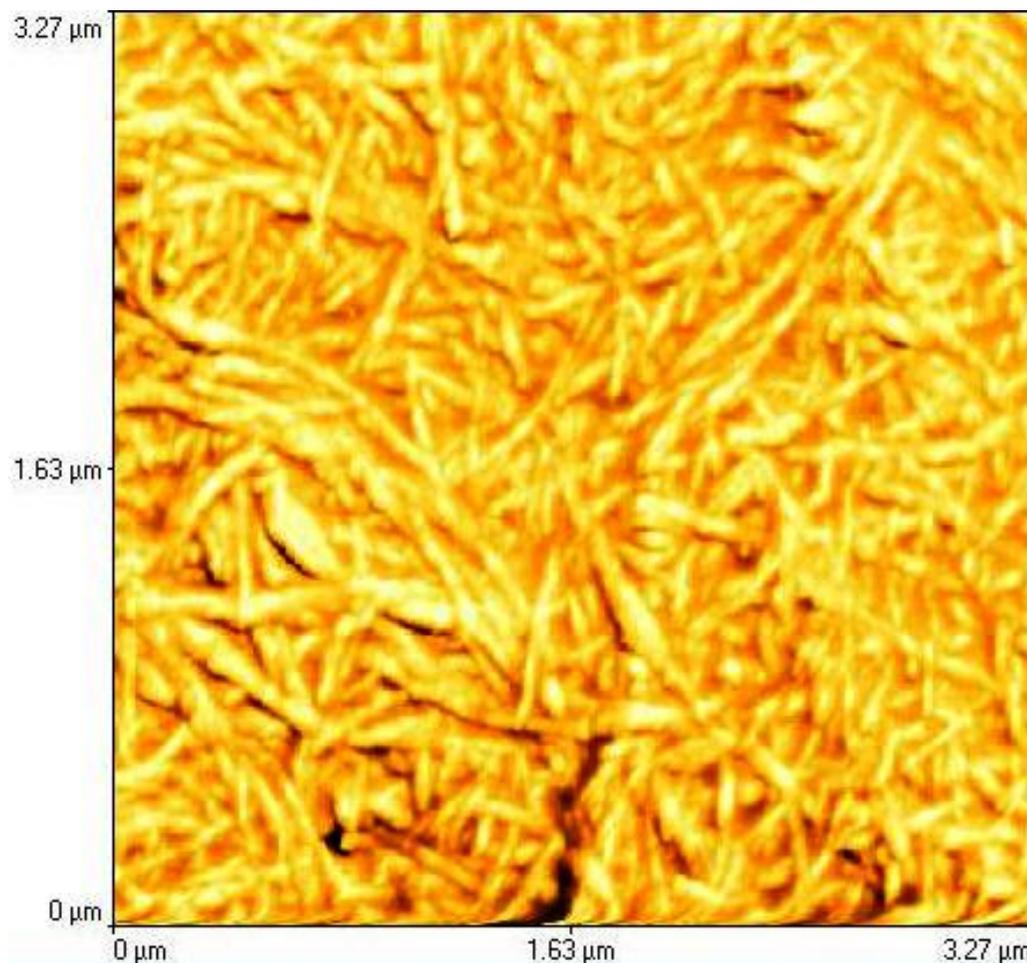
Hydrophobization of NFC surface by physical adsorption of polymers

- viscosity reduction
- solids content increase

Experimental

NFC suspensions were produced by VTT, Finland and CTP, France in cooperation within the framework of SUNPAP. A preservative was added to the suspension at low concentration in order to prevent growth of micro-organisms.

The AFM image shows the as received sample (first generation).



Experimental

The as received NFC suspension diluted with water to 1.5 % (by wt.) solids had a complex viscosity of 72 Pas (frequency 1 Hz) and a steady state shear viscosity of 0.32 Pas (shear rate 100 s^{-1}) as measured after homogenization for 1 day by magnetic stirrer at ca. 500 r.p.m.

Experimental

Random copolymer poly(vinyl alcohol/vinyl acetate) (PVA) were used in physical modification of NFC.

The table shows viscosity of 4% PVA solutions at 20°C and degree of hydrolysis (DH) of the investigated PVA grades.

Trade name	Denoted as	DH (%)	Viscosity (mPas)
Alcotex 72.5	PVA 6-72	72.5	6
Mowiol 4-98	PVA 4-98	98	4
Mowiol 6-98	PVA 6-98	98	6
Mowiol 10-98	PVA 10-98	98	10

Experimental

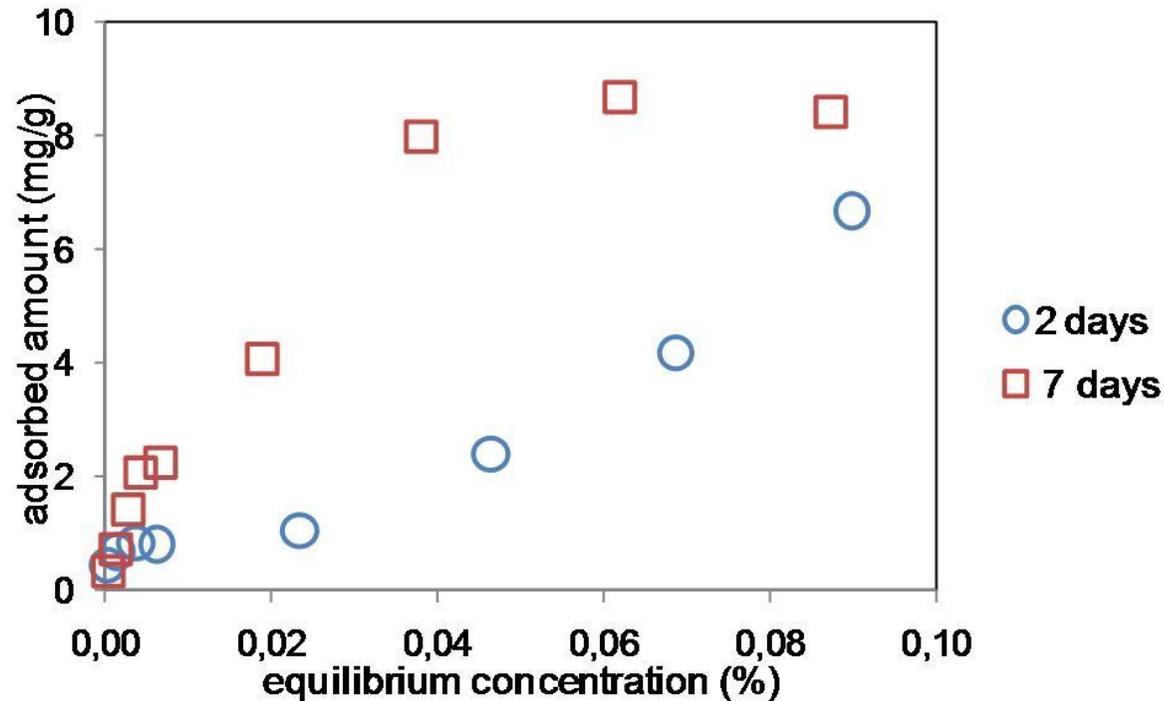
PVA-containing NFC suspensions were prepared by addition of water (or salt solution) and PVA solutions to obtain a final NFC concentration of 1.5 % (by wt.). Several designs of mixing equipments and mixing strategies have been investigated.

The results presented here were obtained by slow mixing of PVA and the NFC suspension, i.e. drop-wise addition of PVA solution under stirring in a magnetic stirrer at ca. 500 r.p.m. to a final volume of 40 ml suspension.

The samples were kept under stirring for whole duration of experiment.

Results - Adsorption isotherms

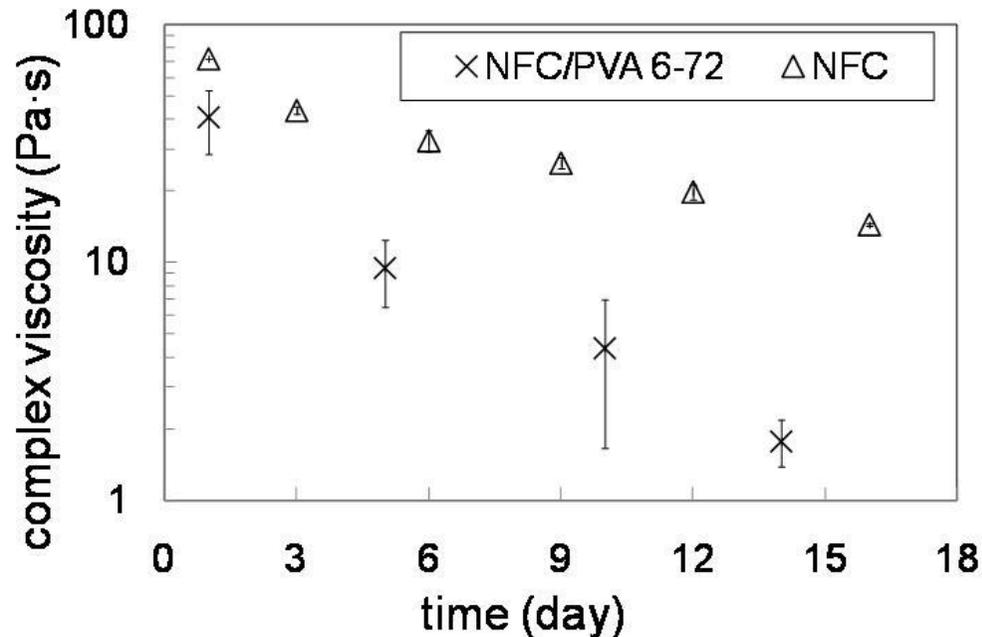
Adsorption of PVA 6-72 on NFC from aqueous solution, pH 7-8 and 23°C at two different equilibrium times. The plateau-value for the sample equilibrated during 7 days corresponded to 8 mg PVA/g NFC.



Results - Rheology

Complex viscosity of pure aqueous NFC suspension and aqueous NFC/PVA suspension (0.06 % PVA) at 1.5 % NFC, 20°C, pH 7-8 and 1 Hz vs. time of stirring at 500 r.p.m.

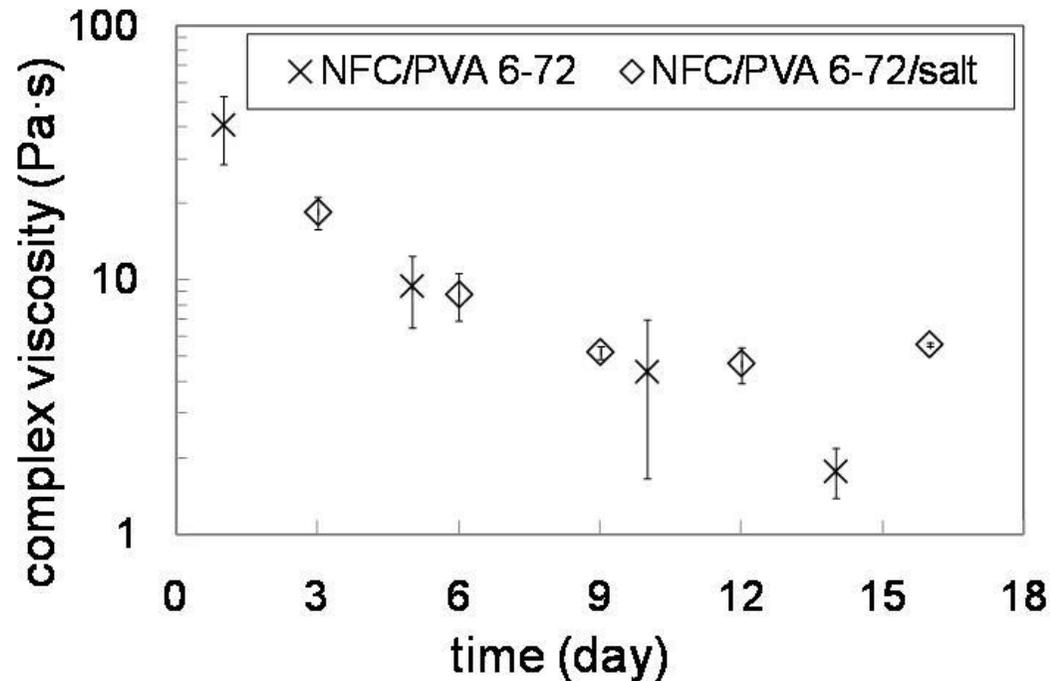
The observed reduction in viscosity caused by PVA was also observed at other concentrations of PVA and with other grades of PVA.



Results - Rheology

Effects of salt: Complex viscosity aqueous NFC/PVA suspension (0.06 % PVA) with and without Na_2SO_4 (0.1 M) at 1.5 % NFC, 20°C, pH 7-8 and 1 Hz vs. time of stirring at 500 r.p.m.

The complex viscosity of the salt-containing suspension seems to level off at 5 Pas.



Results - Increase in solids content by adsorption

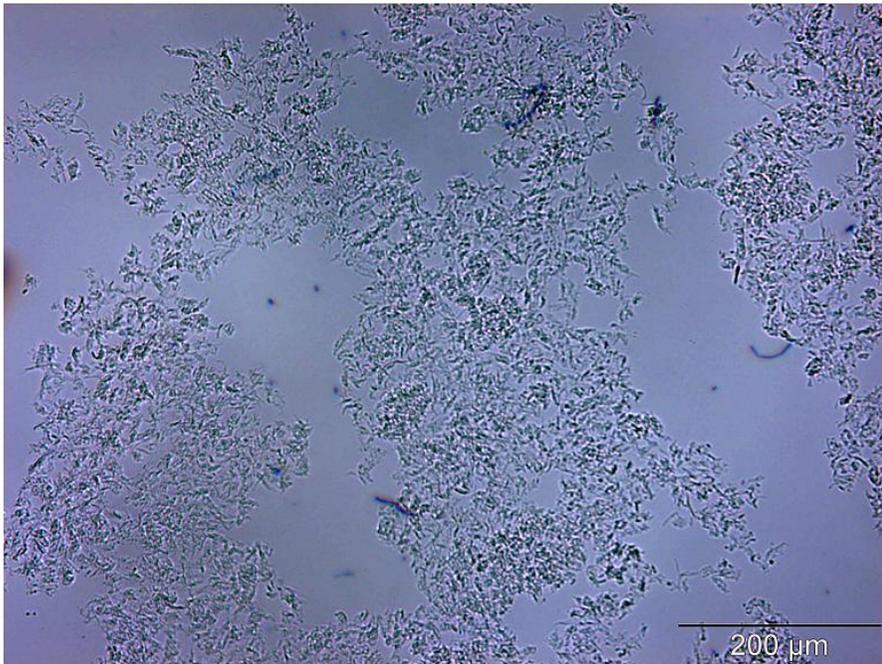
Comparison between shear viscosity at 100 s^{-1} of pure NFC suspensions and a concentrated PVA-containing NFC suspension, prepared by gentle centrifugation of suspensions of NFC (1 %) and PVA (0.15 %) that have been stirred for 13 days on magnetic stirrer.

Sample	Viscosity (Pas)
4% NFC with 0.15 % PVA 6-72	0.20
Pure 1.25 % NFC	0.18
Pure 1.5 % NFC	0.32

The viscosity of the NFC/PVA suspension is approx. the same as for pure 1.3 % NFC (ca. 3 x increase in solids content at constant viscosity).

Results - Suspension structure

Micrograph of as received 1.5 % NFC suspension.



Micrograph of 1.5 % NFC suspension also containing 0.06 % PVA 6-72 at pH 7.5. The PVA-containing suspension was stirred for 41 days after PVA addition.

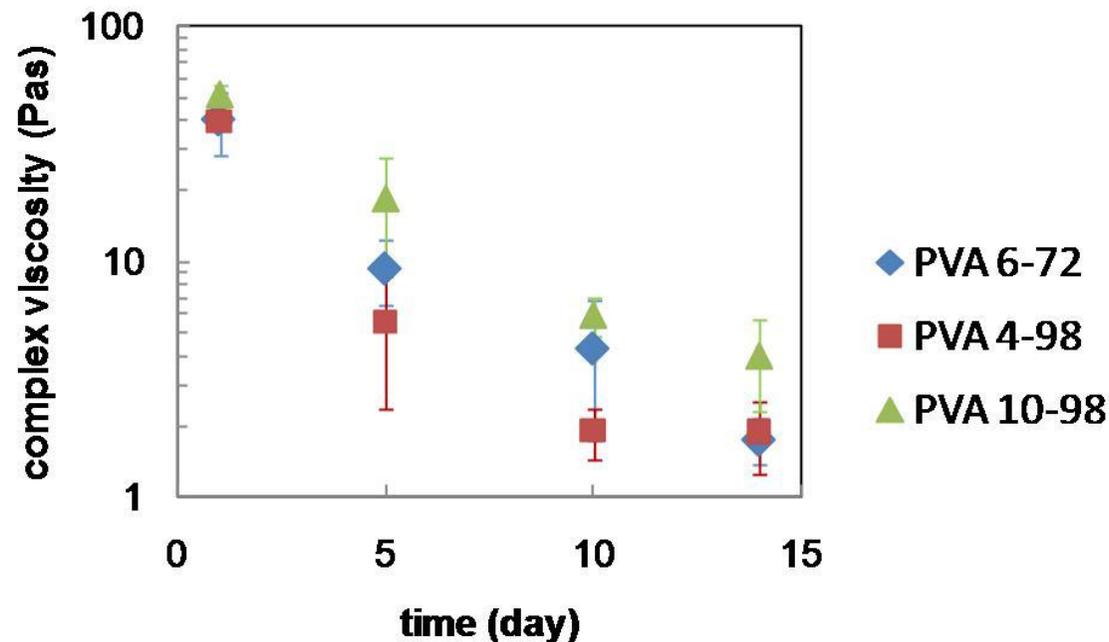


It is likely that the observed viscosity drop in the NFC suspensions during continuous stirring is related to in the structural changes in the suspensions.

Results - Comparison with fully hydrolyzed PVA

Complex viscosity of NFC suspensions at 1.5 % NFC, 0.06 % PVA, 20°C, pH 7-8 and 1 Hz vs. time of stirring at 500 r.p.m.

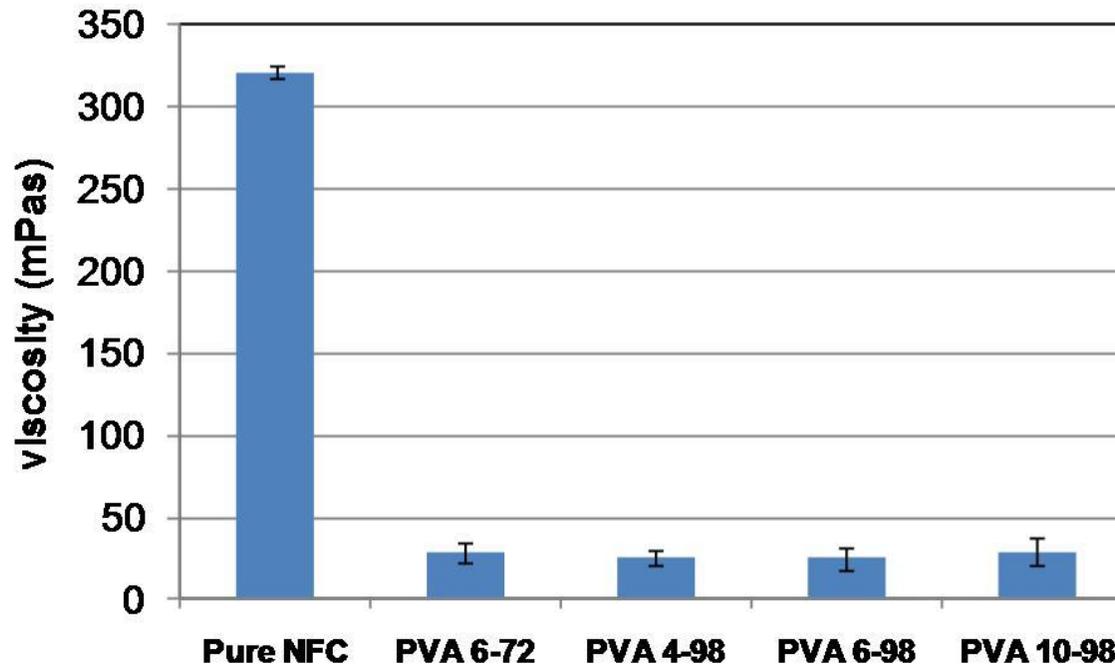
Only small differences in behavior between the different starch grades was observed. The degree of hydrolysis seemed to have no effects.



Results - Comparison with fully hydrolyzed PVA

Shear viscosity at 100 s^{-1} of PVA-containing NFC-suspensions containing 0.06 % PVA stirred 4 days compared with pure NFC suspension stirred one day . Stirring rate 500 r.p.m., 1.5 % NFC, 20°C and pH 7-8.

No significant differences between the PVA grades were observed.



Conclusions

- PVA adsorbs on NFC from aqueous solution and addition of PVA to water-borne NFC suspensions resulted in a decrease in viscosity under continuous mixing.
- The rate of decrease in suspension viscosity were rather slow and it could take several days or weeks for the full effect to be developed.
- Modification of NFC by physical adsorption of PVA is a relatively method simple to reduce viscosity (and PVA is biodegradable).

Acknowledgements

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The received NFC suspensions were produced by VTT, Finland and CTP, France in cooperation.