Microfibrillated cellulose as reinforcing fillers in elastomeric composites: control on degree of fibrillation

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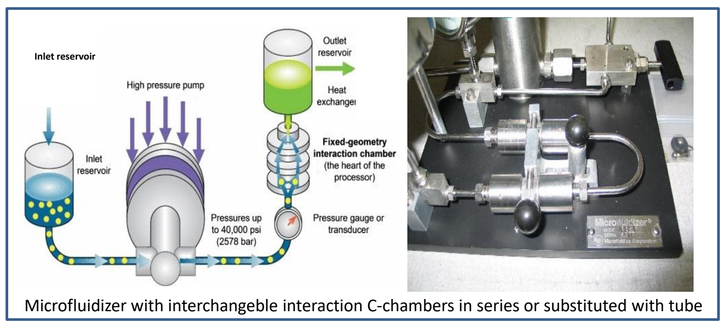
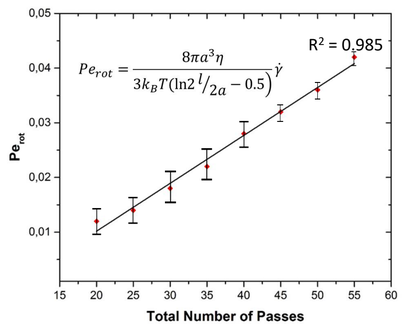
Introduction

Due to a high aspect ratio and thin fiber network, fibrillated cellulose provides excellent opportunities as mechanical reinforcement in composites. The fibrillated structures can be obtained from various natural resources and/or processed from side-stream products of pulp- and paper industries, but their effective use in industrial applications has to be further implemented. The morphology of fibrillated cellulose is often very heterogeneous depending on processing conditions (grinding, homogenizing, microfluidizing) and needs to be efficiently quantified. Therefore, different fiber fractions are collected separately depending on the number of processing steps during microfluidization , providing fibers with progressively increasing degree of fibrillation. The properties of the different fractions are quantified by variations in the rheology of the fiber suspensions, indicating variations in gel properties. The micro- and nanofibrillated cellulose is added by latex mixing into a natural rubber matrix and subsequent **efficiency on the curing process** is illustrated. The good distributive and dispersive mixing within the matrix are controlled by the rheological parameters. The changes in fiber morphology with gradually **increasing degree of fibrillation indicate better interactions with the natural rubber matrix** and more homogeneous mixing. This is evidenced with results from thermo-analytical testing and spectroscopy to identify changes in the elastomeric structure and interfacial interactions. The mechanical properties of the **elastomers with nanofibrillated cellulose are superior to those with microfibrillated cellulose**.

Micro- to Nanofibrillated cellulose

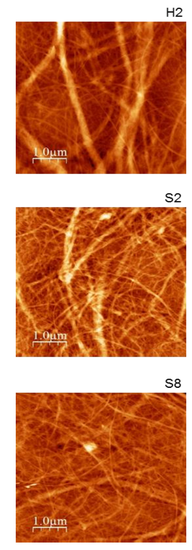


Microfluidizer with interchangeble interaction C-chambers in series or substituted with tube

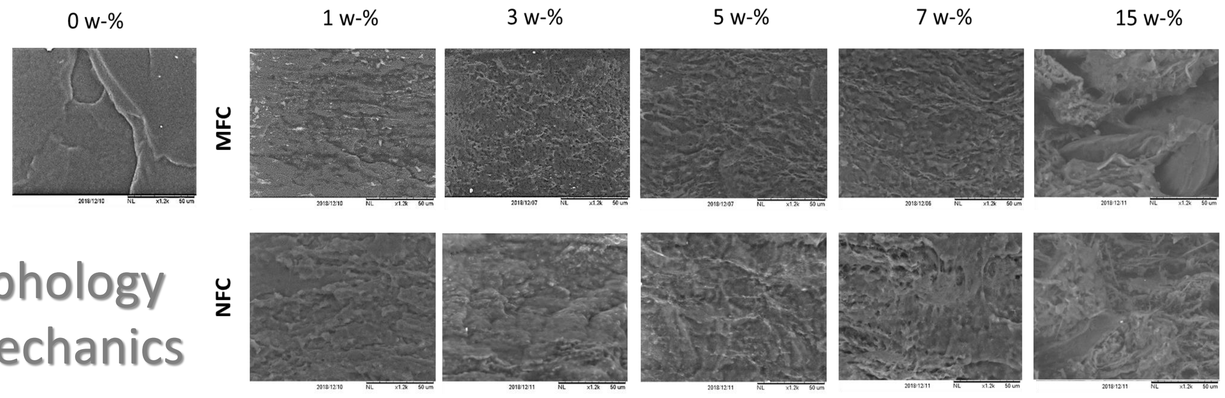


Relating processing conditions in Microfluizer EH-110EH to morphology and rheology: An increment of the number of passes results in a higher rotational Péclet number, which interestingly serves as a unique parameter that directly relates the morphology and rheological behavior of MFC/NFC suspensions. From this value, the processing parameters for MFC/NFC suspensions can be adapted towards specifically required rheological properties.

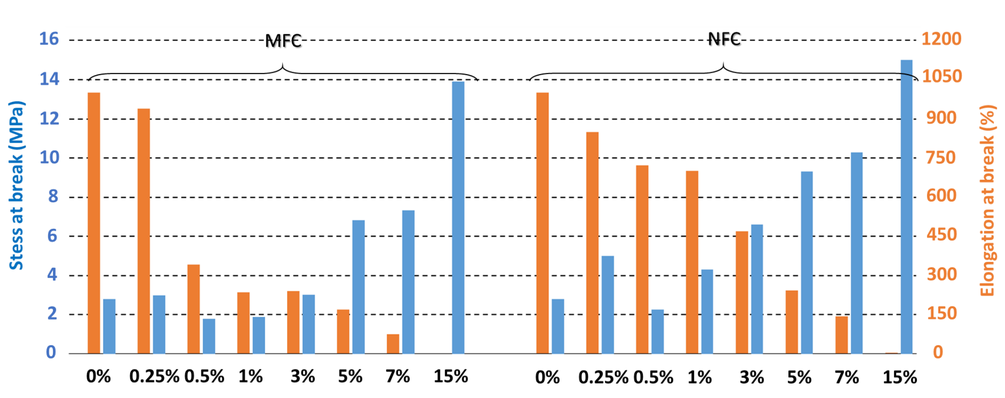
	Sample Name	Number of passes			Zetapotential	Fiber diameter		
		homogenizer	200 µm	87 µm		Minimum diameter from AFM	Maximum diameter from SEM or AFM*	
1	H1	20	-	-	-39.3 ± 1.25 mV	45 nm	45 µm	Cryst
	H2	25	-	-	-48.8 ± 0.81 mV	45 nm	25 µm	72 %
	H3	30		-	-45.7 ± 1.14 mV	45 nm	20 µm	
2	S1	20	10	-	-50.1 ± 1.13 mV	20 nm	15 µm	
	S2	25	10	-	-63.2 ± 1.34 mV	20 nm	9 µm	66 %
	S3	30	10	-	-52.3 ± 1.97 mV	20 nm	7 µm	
3	S4	25	5	-	-61.3 ± 1.51 mV	20 nm	10 µm	
	S5	25	15	-	-66.7 ± 1.62 mV	20 nm	5 µm	69 %
	S6	25	20	-	-53.7 ± 1.64 mV	20 nm	3 µm	
4	S7	25	15	5	-62.2 ± 0.49 mV	15 nm	60 nm*	
	S8	25	15	10	-67.0 ± 1.02 mV	15 nm	50 nm*	60 %
	S9	25	15	15	-53.5 ± 1.18 mV	15 nm	35 nm*	



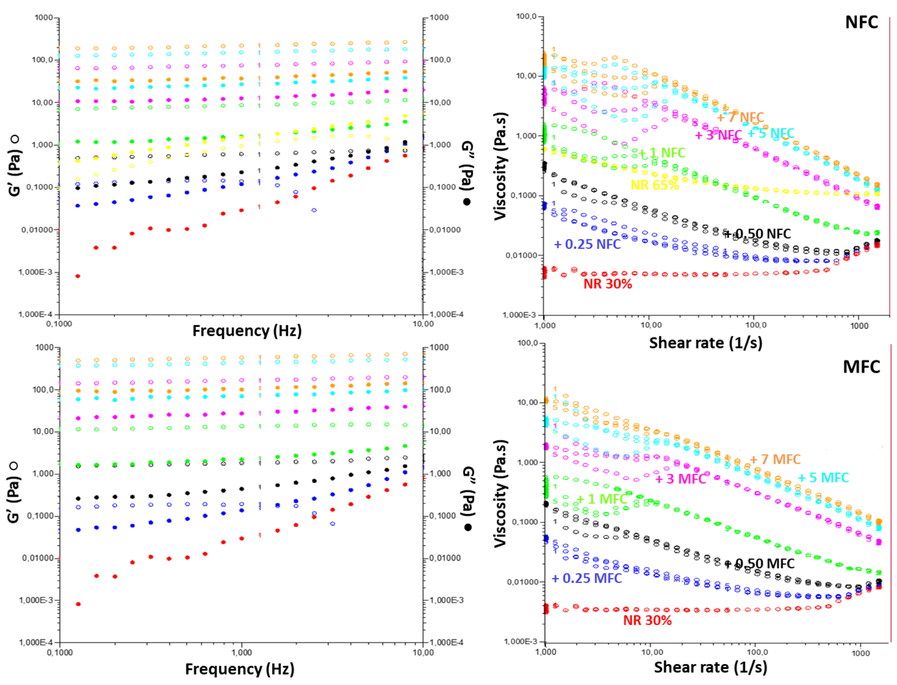
Bio-elastomeric Composites of Natural Rubber



Morphology & Mechanics



The MFC/NFC can be homogeneously dispersed within a natural rubber matrix up to concentrations of 15 wt.-%. The fracture morphology is ductile for unfilled rubbers, the MFC forms an extensive separated network with fiber tear out at high concentrations , while NFC seems to be more mingled in the matrix, showing ductile tearing effects. The NFC fibers provide systematically higher strength and elongation than MFC fibers.

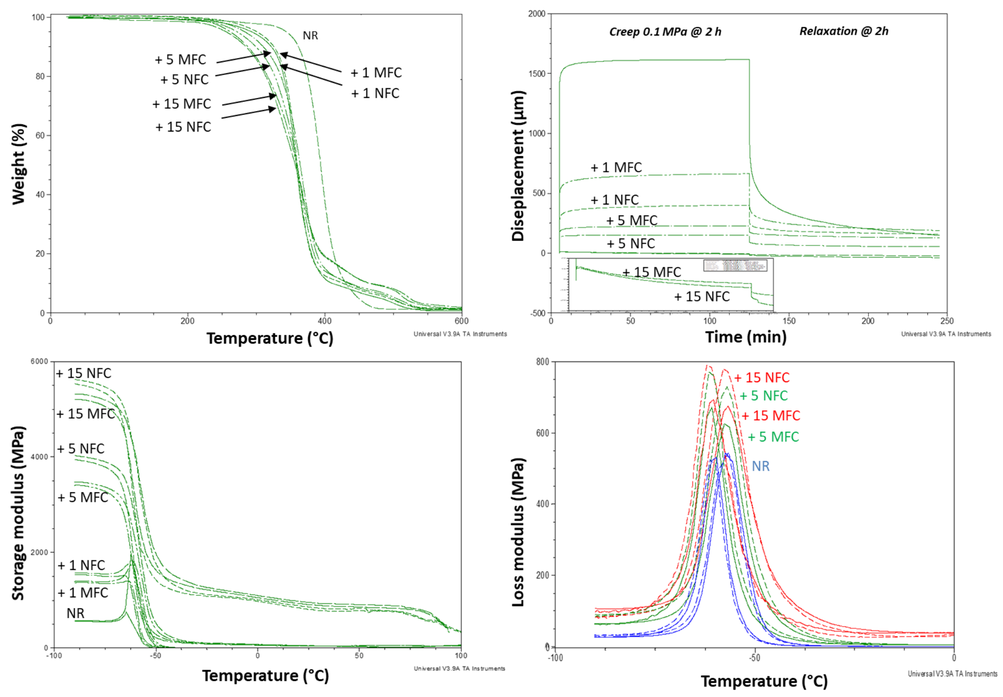


Processing conditions

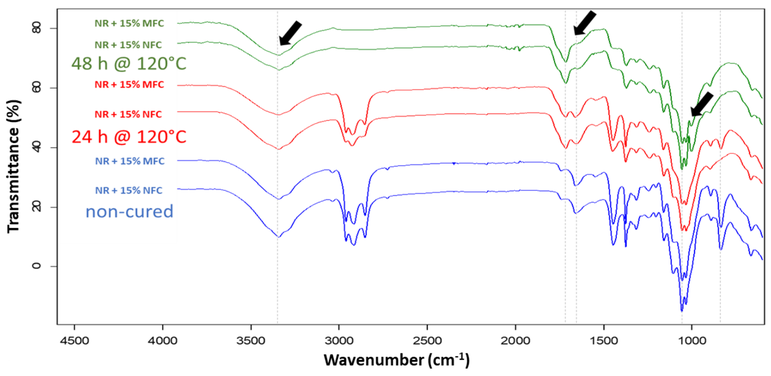
The G' and G" moduli of suspensions show different behaviour with cross-over point G" > G' (liquid-like) at lower concentrations and fully G' > G" (solid-like) at higher concentrations.

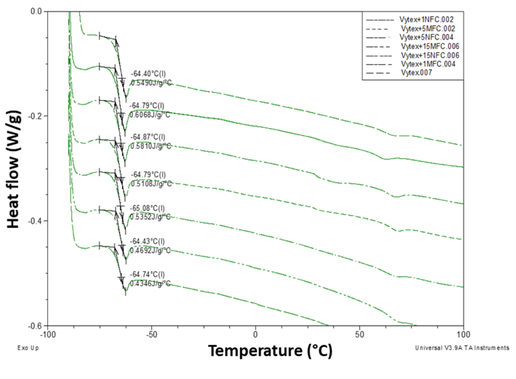
The viscosity is dominated by the shear thinning effect of the NFC and MFC fibers, indicating the formation of a penetrating fiber network. This is more prevalent for NFC than for MFC.

The thermal stability of biocomposites can be attributed to the oxidative character of the cellulose, depending on the surface area. The NFC provides better creep stability and shows higher storage and loss modulus owing to good interface compatilibty.



Fibrillated cellulose enhances network formation during curing, with reduction in the band associated with double carbon bonds (–C=C–) located at 1660 - 1640 cm^{-1} and increase in carbonyl band, in parallel with decrease in –OH functionality of the cellulose at 3200 cm^{-1}. This is explained by hydration of double bonds and hydrogen bridging by cellulose.





Curing conditions

Natural rubbers are characterized by low T_g, where heat capacity change in the amorphous state reduces after addition of fibrillated cellulose, and is smallest in presence of NFC due to strong network formation.

The Tg value is almost independent of the morphology and content of cellulose fibers.

Conclusion

Highest mechanical strength/stiffness and somewhat lower viscosity with nanofibrillated fibers

Good compatibility between fibrillated cellulose and natural rubber matrix, even without need for surface modification

Mechanism for enhancing vulcanization process most efficient for nanofibrillated fibers, due to hydrogen bonding and surface area effects

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