Natural Rubber Composites with Nanocellulose: suspension rheology and elastomeric properties

Pieter Samyn, Guy Reggers, Robert Carleer

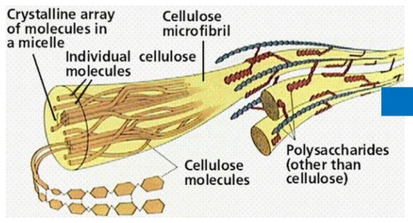
Hasselt University (Belgium), Institute for Materials Research (IMO), Materials Chemistry (MAT-CHEM)

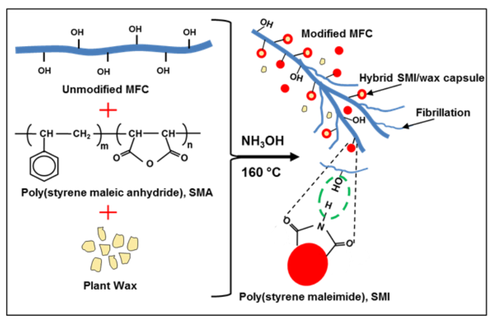
Contact: Pieter.Samyn@uhasselt.be
Agoralaan Gebouw D,
B-3590 Diepenbeek
Tel. +32 11 26 84 95

Introduction

Natural rubbers are ideal candidates for green composites and mechanical properties can be adapted by adding different types of microfibrillated cellulose (MFC), nanofibrillated cellulose (NFC) and microfibrillated cellulose with hydrophobic surface modification (mMFC), in contrast with common cellulose nanowhiskers.[1] The influences of morphology and surface functionality of cellulose on the rheological properties and dynamic mechanical performance of natural rubber composites are evaluated. The shear viscosity of the natural rubber was dominated importantly by adding fibrillated cellulose even in small amounts of 1 to 7 wt.-%, representing more pronounced shear thinning behaviour and hysteresis at high fiber concentrations. The NFC provides lowest viscosity while surface modification of mMFC slightly increases the viscosity due to formation of a network structure. A specific study on the flow properties of natural rubber composites against frequency revealed the development of shear-induced curing properties depending on the compatibility between the cellulose fillers and the rubber (i.e. immobilization mechanism). In parallel, an increase in crosslinking density was highest for the NFC, while intermediate for the MFC and lowest for the mMFC. The latter was confirmed by thermal analysis considering variations in glass transition temperatures and modelling the curing kinetics at different temperatures and times. The dynamic mechanical analysis on uncured and cured films confirmed a shift in loss modulus and broadening of tan delta peak depending on the filler concentration and restriction of chain mobility and the fiber/matrix interface. The mechanical response under creep, frequency and temperature testing inferred that the reinforcing capacity and elastomeric properties depends on the fiber dispersion and phase interaction.

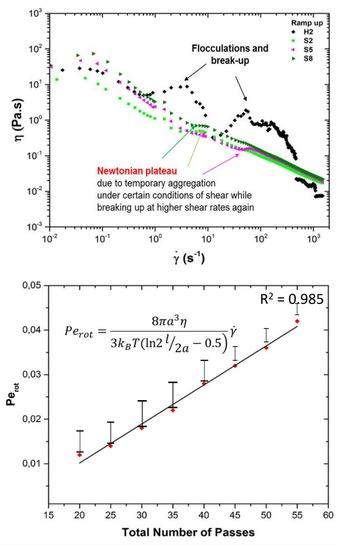
Nanocellulose types





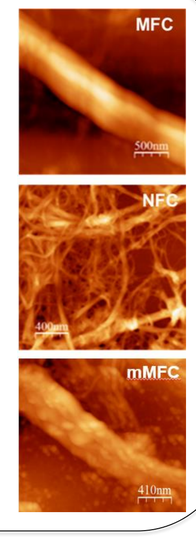
Production and morphology of cellulose nanofibers as 'green' filling agent

Hydrophobic surface modification by nanoparticle deposition

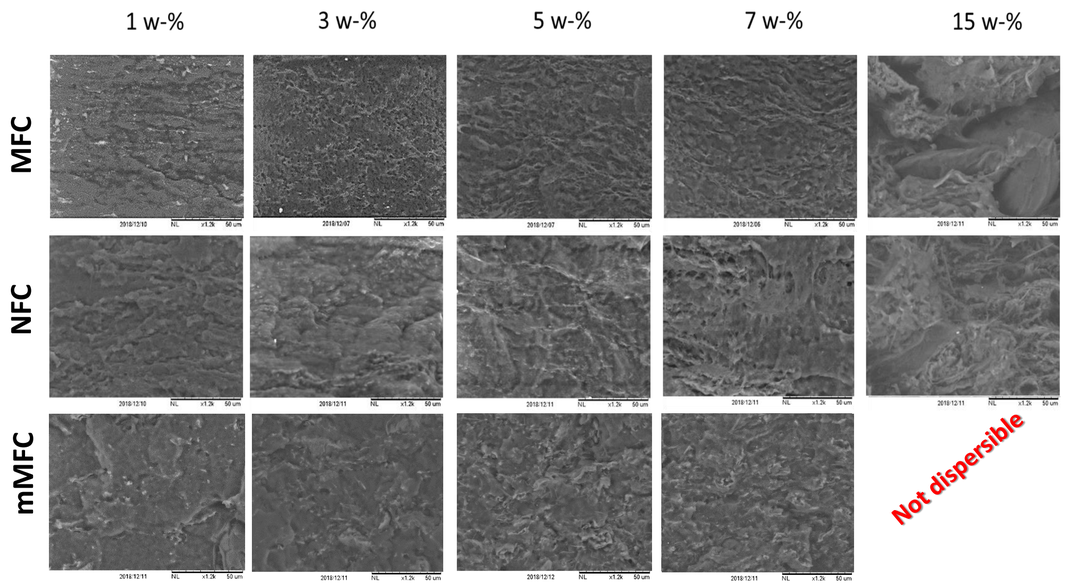


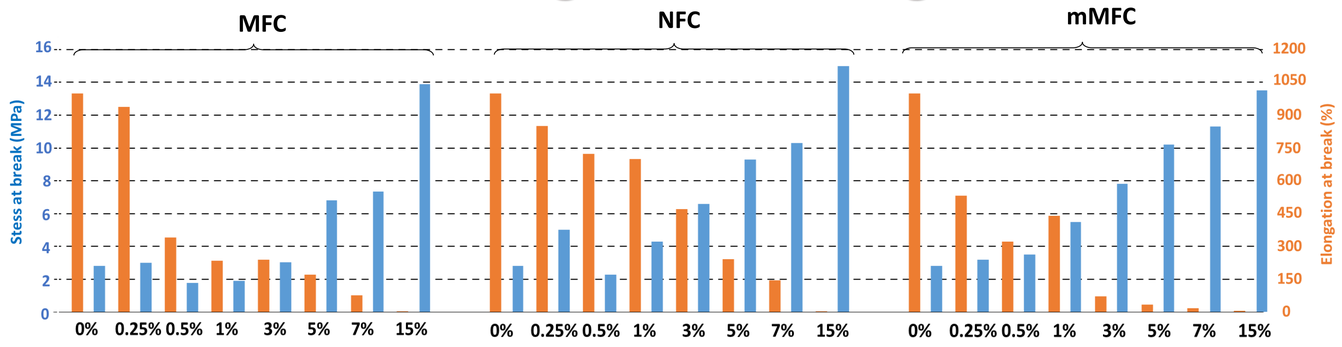
The quality of the fiber suspensions are evaluated by rheological testing. The optimum processing conditions of the MFC/NFC suspensions should provide an optimum fiber network morphology with smooth rheological characteristics. An increment of the number of passes results in a higher rotational Péclet number, which can interestingly serve as a unique parameter that directly relates the morphology and rheological behavior of MFC/NFC suspensions at low shear rate / shear stress. Based on this value, the processing parameters for MFC/NFC suspensions can be adapted towards specifically required rheological properties.[2]

The surface modification is done in aqueous conditions by imidization of SMA precursors in presence of ammonium hydroxide. No chemical degradation of the cellulose main chain (e.g. chain scission) is observed, while physical interactions among cellulose and SMI through the formation of hydrogen bonding. The degree of imidization of the nanoparticles is qualitatively lower for modified MFC than for pure SMI due to surface interactions. The fiber crystallinity increases from 76 % (MFC) to 82 % (mMFC) likely due to the protective action of the SMI/wax against fiber degradation.[3]



Bio-elastomeric Composites of Natural Rubber through Latex Mixing

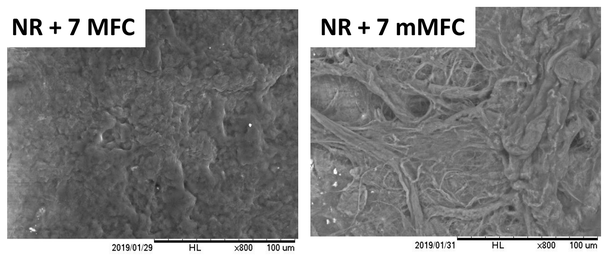




The MFC/NFC can be homogeneously dispersed within a natural rubber matrix up to concentrations of 15 wt.-%. The fracture morphology is ductile for unfilled rubbers, the MFC forms an extensive separated network with fiber tear out at high concentration, while NFC seems to be more mingled in the matrix, showing ductile tearing effects. The NFC provides systematically higher strength and elongation than MFC, while mMFC provides highest strength but almost no elongation.

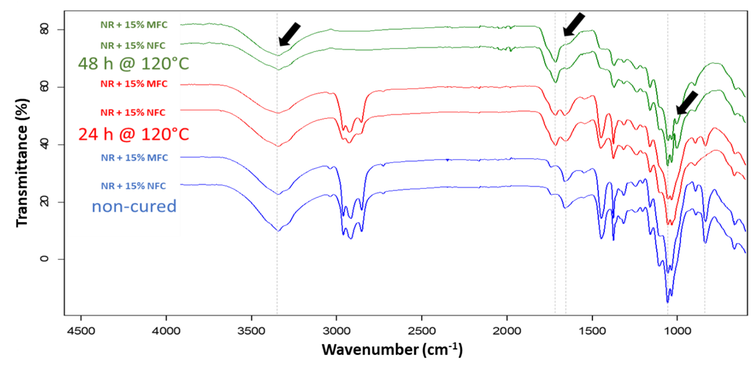
Paper Coating Application

The favourable exposure of mMFC fibers in the coating provides better hydrophobicity and gas barrier properties compared to MFC.

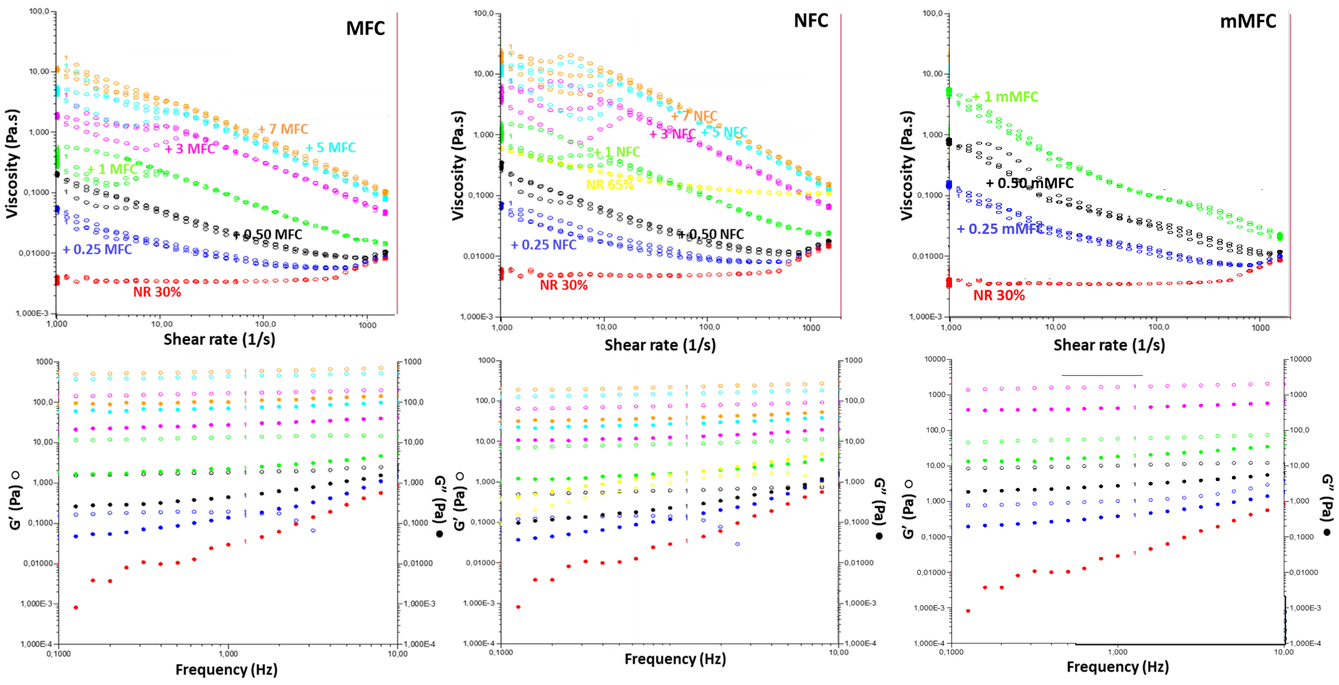


Fibrillated cellulose enhances network formation during curing, with reduction in the band associated with double carbon bonds (–C=C–) located at 1660 - 1640 cm^{-1} and increase in carbonyl band, in parallel with decrease in –OH functionality of the cellulose at 3200 cm^{-1}. This is explained by hydration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

Based on FTIR, cross-linking by NFC was highest and lower for MFC due to surface effects and exposure of hydroxyl groups, while cross-linking was not efficient for mMFC where hydroxyl groups are occupied by SMI.

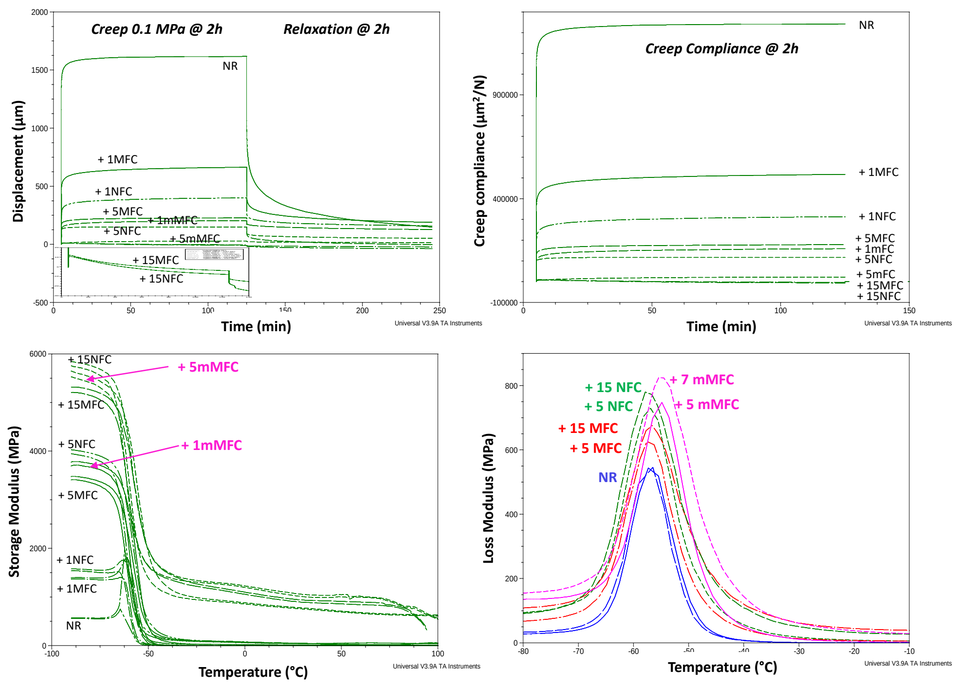


Latex Suspension Rheology



The viscosity is dominated by the shear thinning effect of the fibrillated fibers, indicating the formation of a penetrating fiber network. The viscosity of NFC is slightly higher than MFC due to more intense network formation, while mMFC causes hydrophobic/hydrophilic phase separation. 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.

Elastomeric creep and stiffness



The fibrillated cellulose provides better mechanical properties to the natural rubber, with superior performance for the surface modified mMFC providing lower creep and higher storage modulus at lower fiber concentrations compared to the MFC and NFC. The improved interface properties can be inferred from the high loss modulus related to energy dissipation at the fiber/matrix interface.

Conclusion

Good compatibility between fibrillated cellulose and natural rubber matrix

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

Highest mechanical strength/stiffness and somewhat lower viscosity with nanofibrillated fibers, superior properties for surface-modified MFC

References

[1] P. Dittanet et al., Natural rubber reinforced by nanocellulose extracted from dried rubber leaves, AIP Conf. Proc. 2083 (2019), 030008
[2] H. Taheri, P. Samyn, "Effect of homogenization (microfluidization) process parameters in mechanical production of micro- and nanofibrillated cellulose on its rheological and morphological properties", Cellulose 23 (2016), 1221
[3] V. Rastogi, P. Samyn, "Reaction efficiency and retention of poly(styrene-*co*-maleimide) nanoparticles deposited on fibrillated cellulose surfaces", Carbohydr. Polym. 14 (2016), 244.