Influence of cellulose nanocrystals on the rheological behaviour of Portland cement and pure limestone suspensions

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ABSTRACT

This paper evaluates the effects of CNC on Brazilian Portland cement and pure limestone pastes and mortars. Dry CNC was characterized by SEM and dispersion in water was monitored using optical microscopy. Mini-slump and rotational rheometry were employed to evaluate the effects of CNC in water and in suspensions. Flow table was used to assess flow behaviour of mortars containing these pastes. Unlike some results reported in literature, there was no indication of dispersing effects on cement suspensions. In fact, the opposite was observed. Conversely, pure limestone suspensions showed significant increase of fluidity due to addition of CNC.

INTRODUCTION

Cellulose nanocrystals (CNCs) are a new type of bio-based nanoparticles that are whisker-shaped with few nm wide and high aspect ratio (10-100) [1]. They can be used, amongst other applications, for reinforcement of materials' microstructure and for modification of rheological behaviour of suspensions and emulsions [1-4]. Cementitious materials are essential for modern society since they are widely employed for housing and infrastructure [5]. Cement technology is mainly based on the capacity of anhydrous phases to react with water and form hydrated binding phases that can provide the development of important properties to mixtures of granular materials (i.e. mortar, concrete, fibre-cement) such as mechanical strength, reduced permeability, chemical resistance, etc.

In this sense, CNC appears as a potential additive to cement formulations because its effects on both fresh (rheology, robustness, hydration mechanisms) and hardened properties (mechanical strength and rigidity, mass transport, etc) may provide beneficial changes regarding the performance of cementitious materials for specific applications and types of processing.

Furthermore, its renewable, health and environmentally friendly features are welcome for the cementitious materials industry, which has one of the highest CO_2 emissions of the planet (10% of total) [5]. This paper explores the effects of CNC on the rheological behaviour of a Brazilian Portland cement suspension, as well as, on calcium carbonate (limestone) suspension, since this mineral is one of the main supplementary cementitious materials as part of the strategy to reduce the environmental impact of this industry [5].

EXPERIMENTAL

Materials

Ordinary Portland cement: cement with high content of clinker (> 90%), Brazilian type CPV (high early strength). Specific gravity = ρ = 3.1g/cm^3; Mean particle size = D_{50} = 15µm; Volumetric surface area = VSA = 5.1m^2/cm^3.

Limestone filler: ≈ 90% $CaCO_3$ with similar particle size distribution of the cement. Commonly employed to partially substitute cement to reduce cost and environmental impact. ρ = 2.7g/cm^3; D_{50} = 11μm; VSA = 3.2m^2/cm^3.

CNC: Commercial cellulose nanocrystals (CelluForce), dry powder form of cellulose sulphate sodium salt produced by sulfuric acid hydrolysis. ρ = 1.6g/cm^3; D_{50}=71μm; VSA = 1.0m^2/cm^3. Fig. 1 shows a SEM image of dry particles of CNC and EDS analysis (not shown) indicated the elements carbon, oxygen, sodium and sulphur. Before mixing with cement, CNC was dispersed in deionized water for 15min using a high shear mixer (10rpm) either with 0.1%vol or 1%vol. The efficiency of the mechanical dispersion can be seen in Fig. 2.

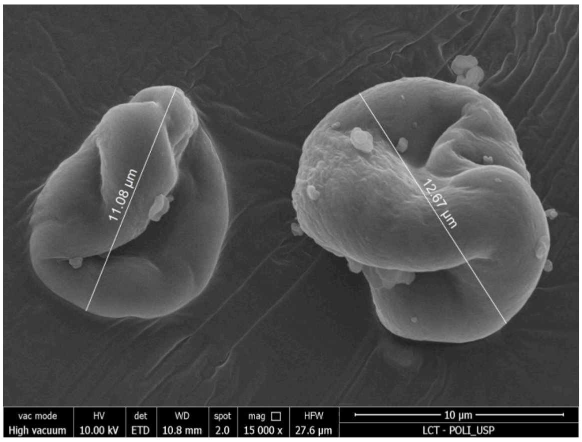

Figure 1. SEM image of dry CNC particles.

Suspensions

Cement and limestone suspensions were prepared with 35%vol of solids in a high shear mixer for 3min. When CNC was added in 0.1 and 1%vol in relation to the powder content, the deionized water used for CNC dispersion was discounted, thus, maintaining solid concentration practically constant (CNC amount was not considered).

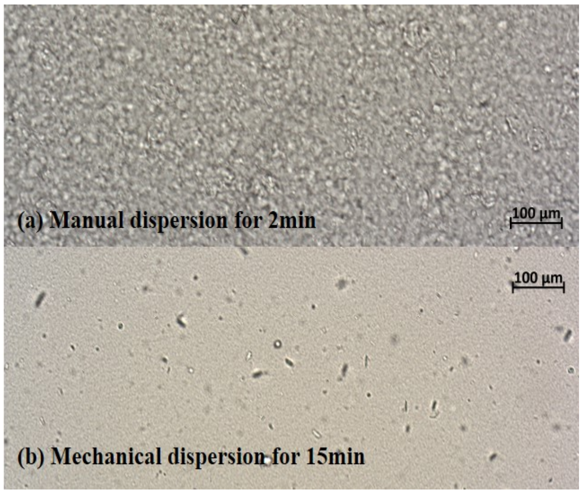

Figure 2. Optical microscopy images of CNC dispersion in water: (a) manual dispersion for 2min; (b) mechanical dispersion for 15min.

Mortars

In addition to the pastes, mortar formulations (75%vol sand + 25%vol fine particles) with OPC and Limestone were also prepared to evaluate the CNC influence. The sand used was a normalized material (IPT – Brazil) with maximum particle size of 2.4mm that is employed for standard determination of cement mechanical strength. The solid content of the mortars was 71%vol.

Testing

Rotational rheometry (AR550, TA Instruments) was employed to evaluate the suspensions (Vane geometry with 1mm gap) as well as the effects of CNC solely in water (rough concentric cylinder with 1mm gap). For the suspensions, two consecutive shear cycles (continuous ramp from 0-50-0 s^{-1}) were applied, with total time of 200s. While for water measurements, a fixed shear rate of 10 s^{-1} was employed for 30s. Tests were performed immediately after mixing.

In addition to rotational rheometry, a simple and common test for cement suspensions was also used: the mini-slump [6]. A conic sample (top diameter = 39mm; bottom = 38mm; height = 57mm) of the suspension is subjected to flow on its own weight; hence, cessation of flow relates to the material's yield stress.

The fresh mortars were evaluated by flow-table test for determination of the consistence index; i.e. final spread diameter after the conic mortar sample is subjected to 30 strokes of the table according to standard ABNT NBR 13276:2016.

RESULTS

CNC in water

Fig. 3 shows the effect of CNC on water viscosity. The addition of 0.1% of CNC increased water viscosity in 40%, while 1% of CNC shifted water viscosity 6 to 8 times higher than pure water, owing for the whisker-like particle colliding and perturbing the flow fields as well as their capacity to absorb water (≈ 40% of its volume).

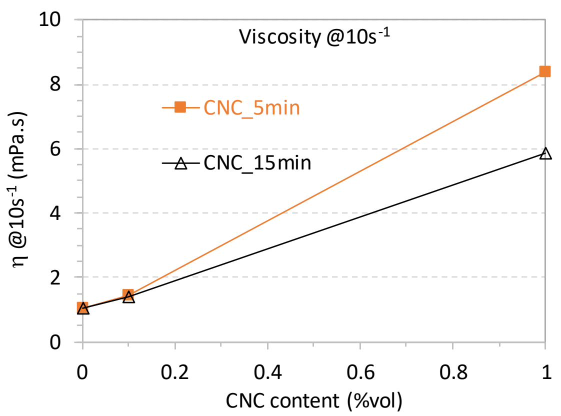

Figure 3. Influence of CNC content on viscosity of water as measured at $10s^{-1}$ for different mechanical dispersion times.

CNC in particle suspensions

Fig. 4 presents images of the final spread in the mini-slump test of the cement (OPC) and limestone suspensions. For OPC, CNC progressively reduced the final spread of the samples indicating an increase of yield stress. For the limestone suspension the same trend is observed at a dosage of 0.1% CNC, however, at 1%, the opposite behaviour occurred as the final spread diameter was significantly higher.

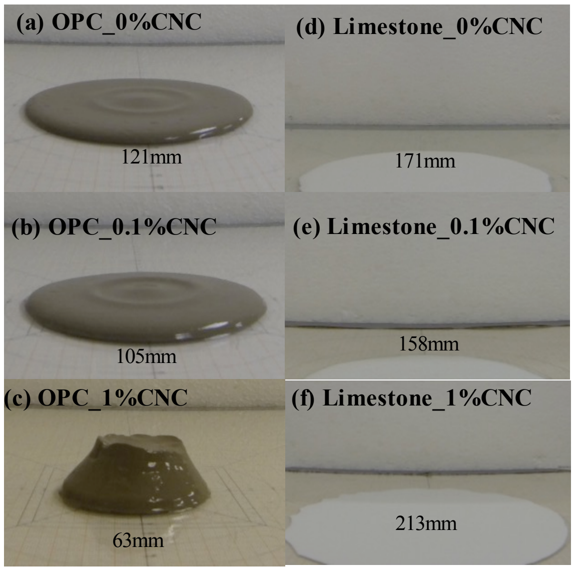

Figure 4. Mini-slump images and results of OPC and limestone suspensions in function of CNC content.

Rheometry results displayed in Fig. 5 are from the first acceleration curve since there was no significant hysteresis during the cycles. However, the data considered for fitting the rheological models was only up to $10s^{-1}$ because after this shear rate there was a punctual and systematic change of slope for all curves, possibly indicating slip on the outer cylinder or disruption of the samples.

Nevertheless, when comparing the yield stress results between the compositions, they qualitatively agree fairly with the trends pointed out by the mini-slump. For limestone (graphic a), 0.1% of CNC slightly decreased yield stress and increased plastic viscosity when compared to pure limestone; whereas at a dosage of 1%, a highly non-linear behaviour (shear thinning) took place with very low yield stress, but with higher values of apparent viscosity at faster shear rates than those observed for the other limestone suspensions. This indicate possible particle dispersion effect caused by CNC whiskers.

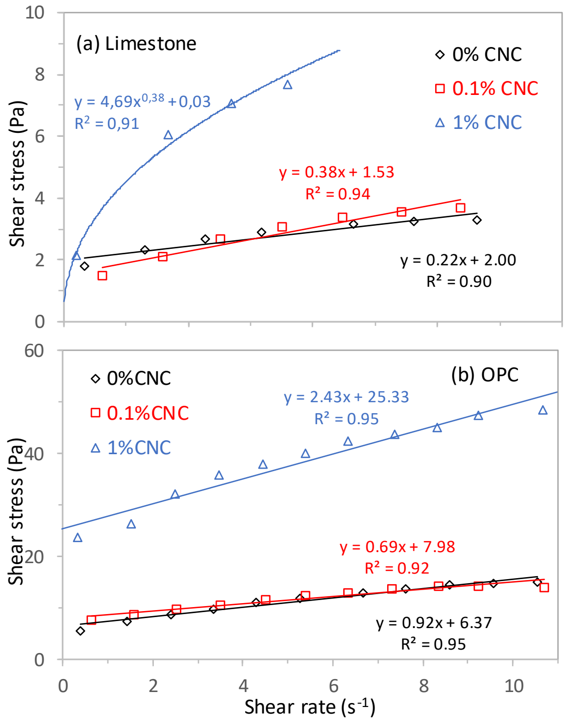

Figure 5. Rotational rheometry results of (a) Limestone and (b) OPC suspensions in function of CNC content.

Fig. 5 (b) shows linear stress vs. rate behaviour of the cement suspensions within the analysed rate range. Results also agree with mini-slump: increase of yield stress with CNC content. With 1% of CNC both yield stress and plastic viscosity increased significantly and, unlike for limestone, no dispersing effects can be considered. This must be related with the much more complex multiphase chemistry surface of clinker grains, the high ionic force inherent to cement suspensions as the hydration mechanism is based on dissolution of ions and precipitation of hydrated phases when saturation occurs. It is worth mentioning that an interesting published work [2] has reported a decrease of yield stress for dosages below 0.2%vol of CNC and even a significant increase on hydration degree, however the cement employed was a very particular one, and did not have the cementitious phase C_3A ($3CaO.Al_2O_3$). This is a highly reactive phase, sometimes associated to flash setting of cement, and therefore calcium sulphate ($CaSO_4$) is normally added to the clinker to control the hydration kinetics of the aluminate compound. The Brazilian cement tested in the present study has common content of C_3A (6-8%), which has a chemical affinity with sulphate ions that are also present on the surface of CNC whiskers produced by sulphuric acid hydrolysis. Results suggest that chemical composition of the cement plays an important role on the dispersion/agglomeration effect of CNC on cement suspensions and thus on their rheological behaviour. In addition to the cement type, the raw material source and processing techniques used to produce the CNC change surface charges of the whiskers and also affect their interaction with the diverse cement types [3].

In Fig. 6 a direct comparison between yield stress measured by rheometry and the final spread diameter obtained in the mini-slump test is performed. A good correlation can be observed between the techniques indicating that the trends regarding the CNC effects observed are consistent, and corroborating that, even though limited, the mini-slump test can be useful.

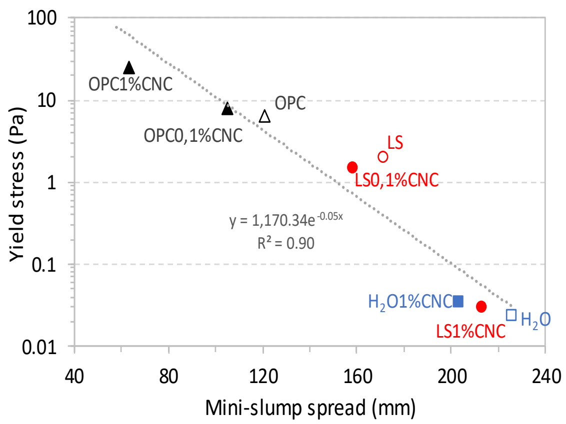

Figure 6. Yield stress as determined by rotational rheometry vs. spread diameter obtained in the mini-slump test. LS = Limestone; OPC = Cement; H_2O = water.

<u>CNC in mortars</u>

Images and results of the flow-table tests with the mortar compositions are detailed in

Fig. 7, Fig. 8 and Fig.9. Generally, the same trends, regarding the effects of CNC, observed in the mini-slump tests occurred also in the mortars subjected to the flow-table: CNC increased flowability of limestone compositions, whereas it reduced the flowability of cementitious compositions. The only difference is that for 0.1% of CNC, the OPC mortar flowed more than the one with no CNC (Fig. 7). This might be caused by the interaction of the paste with the sand, since a more viscous paste maybe able to carry sand particles more effectively (to a certain point) when flowing radially, thus improving the system homogeneity and resulting in larger spread diameter. This type of effect – enhancing viscosity – is useful in some situations, specially when liquid-solid phase separation and/or particle segregation must be avoided (self-levelling compositions, transportation by pumping and application by spraying).

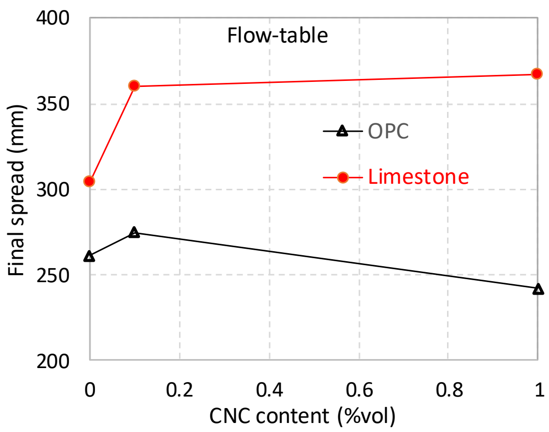

Figure 7. Flow-table results of mortars prepared with Limestone and OPC as a function of CNC content.

The visual effect of the higher flowability of the limestone mortar with 1%CNC is quite clear, since, even before the strokes, the geometry of the mortar indicates that it has flowed due to the reduction of yield stress caused by fine particles dispersion.

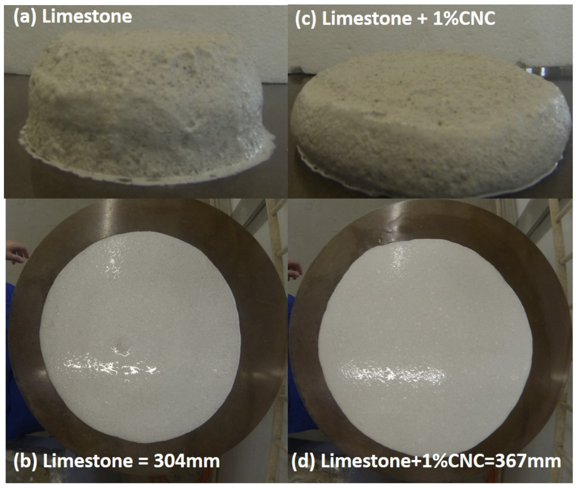

Figure 8. Flow-table images of mortar prepared with Limestone. (a), (b) 0%CNC; (c), (d) 1%CNC. (a), (c) before the test; (b), (d) after the test.

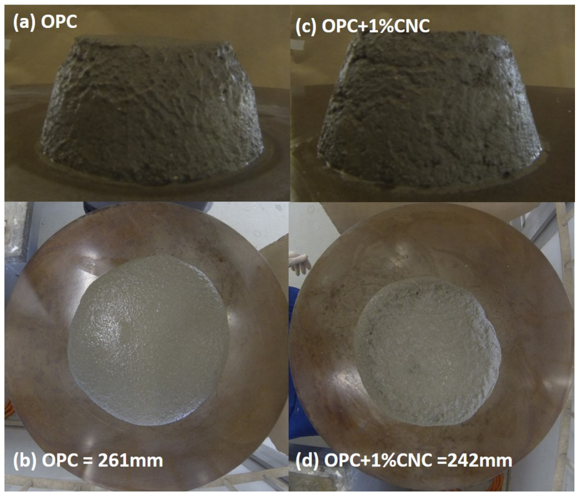

Figure 9. Flow-table images of mortar prepared with OPC. (a), (b) 0%CNC; (c), (d) 1%CNC. (a), (c) before the test; (b), (d) after the test.

CONCLUSION

Cellulose nanocrystals (CNC) were added into limestone and cement pastes and mortars affecting their rheological behaviour in a different fashion. In the inert limestone suspension, CNC increased flowability most probably due to dispersion of $CaCO_3$ particles and consequent reduction of yield stress. Direct measurements of the dispersion effect (Zeta potential for instance) and identification of the mechanism (electrostatic and/or steric) has still to be addressed. On the other material, the multiphase reactive cement grains (Brazilian Portland high early strength cement), CNC caused a decrease of flowability, as it increased both yield stress and plastic viscosity when employed at a dosage of 1%vol. Based also on previous literature, it seems that CNC - Portland cement interactions are quite complex and depend on the chemical features of both materials. Further research is required to understand these interactions, their effects and explore potential technological applications of CNC in cementitious materials.

ACKNOWLEDGMENTS

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REFERENCES

1. Robert Moon, Stephanie Beck, Alan Rudie. “Cellulose Nanocrystals - A Material with Unique Properties and Many Potential Applications.” In Production and Applications of Cellulose Nanomaterials, Chapter 1 - Cellulose Nanocrystals, 9–12. Peachtree Corners, USA: Tappi Press, 2013.

2. Yizheng Cao, Pablo Zavaterri, Jeff Youngblood, Robert Moon, Jason Weiss. “The Influence of Cellulose Nanocrystal Additions on the Performance of Cement Paste.” Cement and Concrete Composites 56 (2015): 73–83.

3. Tengfei Fu, Francisco Montes, Prannoy Suraneni, Jeffrey Youngblood, Jason Weiss. “The Influence of Cellulose Nanocrystals on the Hydration and Flexural Strength of Portland Cement Pastes.” Polymers 9, (2017): 424.

4. Yizheng Cao, Nannan Tian, David Bahr, Pablo D. Zavattieri, Jeffrey Youngblood, Robert J. Moon, and Jason Weiss. “The Influence of Cellulose Nanocrystals on the Microstructure of Cement Paste.” Cement and Concrete Composites 74 (2016): 164–73.

5. Karen L. Scrivener, Vanderley M. John, Elis M. Gartner, “Eco-efficient cements: potential, economically viable solutions for a low-CO2, cement-based materials industry”, UNEP (2016).

6. D.L. Kantro. “Influence of Water-Reducing Admixtures on Properties of Cement Paste - a Miniature Slump Test.” Cement, Concrete and Aggregates 2, no. 2 (1980): 95–102.