



From colloidal spheres to nanofibrils: Extensional flow properties of mineral pigment and mixtures with micro and nanofibrils under progressive double layer suppression



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ABSTRACT

Suspensions of mineral pigment and cellulose fibrillar derivatives are materials regularly found in the forest products industries, particularly in paper and board production. Many manufacturing processes, including forming and coating employ flow geometries incorporating extensional flow. Traditionally, colloidal mineral pigment suspensions have been considered to show little to no non-linear behaviour in extensional viscosity. Additionally, recently, nanofibrillar materials, such as microfibrillar (MFC) and nanofibrillar cellulose (NFC), collectively termed MNFC, have been confirmed by their failure to follow the Cox-Merz rule to behave more as particulate material rather than showing polymeric rheological properties when dispersed in water. Such suspensions and their mixtures are currently intensively investigated to enable them to generate likely enhanced composite material properties. The processes frequently involve exposure to increasing levels of ionic strength, coming either from the weak solubility of pigments, such as calcium carbonate, or retained salts arising from the feed fibre source processing. By taking the simple case of polyacrylate stabilised calcium carbonate suspension and comparing the extensional viscosity as a function of post extension capillary-induced Hencky strain on a CaBER extensional rheometer over a range of increasing salt concentration, it has been shown that the regime of constriction changes as the classic DLVO double layer is progressively suppressed. This change is seen to lead to a characteristic double (bimodal) measured viscosity response for flocculated systems. With this novel characteristic established, more complex mixed suspensions of calcium carbonate, clay and MNFC have been studied, and the effects of fibrils versus flocculation identified and where possible separated. This technique is suggested to enable a better understanding of the origin of viscoelasticity in these important emerging water-based suspensions.

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1. Introduction

There is an increased interest concerning the production of cellulosic materials with characteristic size on the nanometre scale [1,2], which bear great potential to contribute to the development of novel “green” bio-based materials being a major aspect of the future development of the forest products industry. Microfibrillated (MFC) and nanofibrillated (NFC) cellulose possess distinctly different properties compared to standard macroscopic fibres, which depend on the origin of the cellulosic raw materials [3–5]. Some of these properties are very high mechanical strength and elastic

modulus and low thermal expansion, and are related to their partially crystalline nature and high surface area [6]. MNFC can be obtained with both mechanical and/or chemical procedures [7–9]. Chemical pathways include enzymatic hydrolysis with cellulases leading to micro and nanofibrils 4, or selective oxidation of primary hydroxyl groups into carboxylate groups (TEMPO) [10], resulting in high aspect ratio fibrils in the product with a diameter varying between 5 and 100 nm. The size of NFC is smaller, and its surface charge much higher compared to MFC [11,12] and therefore capable of binding more water to its surface [13,14], which results in the observed differences in the rheological and dewatering behaviour between MFC and NFC [15–21].

Microfibrillar (MFC) and nanofibrillar (NFC) cellulose, collectively termed here as MNFC, are currently under intense investiga-

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tion in respect to their potential for advanced material properties ranging from use in paper and board to sophisticated nanocomposites [22,23]. Extensive rheological studies have also been made on the component interactional and dewatering characteristics of suspensions of mineral pigment and MNFC as might be used in enhanced strength paper and board furnish or in novel design coating colours [24,25]. Defining and evaluating the rheological properties of these materials, such as shear viscosity, elongational viscosity, and elasticity recovery (e.g. flow under the metering blade and the recovery stage after metering) is playing an important role in developing MNFC-containing formulations for coating processes [23–26].

MNFC reduced to the polymeric bundle-like strands of cellulose [1,4,10], does not behave as a conventional flexible polymer chain, in that the viscosity fails to follow the Cox-Merz rule [22], but behaves rather as a particulate of high aspect ratio (shape factor) having strongly adsorbed water and a high specific anionic charge [14,18,19,27]. MNFC suspensions are usually found to form a gel network at rest with the rheological response of the suspension being predominantly elastic ($G' \gg G''$) and largely independent of the angular frequency of oscillation (ω) [15,28,29]. Under steady state conditions MNFC suspensions are both shear thinning and thixotropic [30–32] due to the prevailing fibril–fibril packing organisation and subsequent break-down of the gel network upon shearing. The flow curves of MNFC suspensions at low shear rates exhibit constant shear stress, but after reaching a certain threshold, the shear stress rises as a function of shear rate, due to spatial organisation of flowing agglomerates at higher shear [15,28,29,33]. It is to be expected, therefore, that, given the lack of direct absorptive interaction between the highly anionic nanofibrillar component and highly anionically dispersed pigment(s), the flow independence of mixed particle systems should be maintained unless the stabilising double layer depicted by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory is suppressed [34]. The addition of salt to a suspension reduces the Debye length of the surface charge potential in solution which is in turn inversely related to ionic strength [35] leading to a decrease in the zeta potential of the particles [36]. Thus, under the influence of salts, the particle–particle interactions shift from repulsive to attractive, resulting in flocculation and ultimately leading to irreversible aggregation [37–39].

In spite of a good understanding of the importance of elongational flow in the application of coating colours and emulsions [40,41] there is little to no research done regarding the elongational flow of salt flocculated particulate systems. Given the likely elevated salt concentrations in typical manufacturing processes, not least from the source material production [42,43] but also from the extensive use of closed water circuits for environmental reasons, the behaviour of the colour constituent materials is likely to become more complex [44–48] leading to further, difficult to deconvolute mechanisms for inducing elastic structure behaviour. Hence, as we discuss in this paper, direct analysis of MNFC-containing coating colours is too complex to interpret without breaking the problem down first into the case of simple pigment particle flocculation and then extending to the superposition of the nanofibrillar material response.

The addition of salts in electrostatically dispersed coating pigment slurries is known to reduce the thickness of the charge double layer resulting in a decrease in the electrostatic repulsion interactions between the polyions [48,49]. Furthermore, increase in apparent viscosity due to addition of salt is also related to the impact of the increase of ion concentration in the suspension system inducing the flocculation deposition of binders on pigment [36,45,46]. In this study we focus on the influence of salt-induced flocculation on the rheology of ground calcium carbonate suspensions in order first to reduce the complexity of the mixed MNFC-containing system problem to that of the more simple case of a

distribution of approximately spherical particles undergoing progressive colloidal destabilisation [48]. This approach provides complementary and differentiating rheological analysis of the effect on shear flow and extensional parameters obtained by the addition of a simple monovalent electrolyte (NaCl). Secondly, for the more complex mixed systems of pigment and MNFC we newly compare extensional geometry with previous results for vane-bucket and parallel plate analyses including those for coating colours which have salt-containing MNFC and polyelectrolyte soluble polymers (CMC) as co-binders [24]. Here, we use the capillary breakup elongational rheometer (CaBER) technique to characterise the elongational capillary filament surface energy constriction behaviour of the MNFC-containing coating colours and calcium carbonate-salt dispersions.

In CaBER experiments the sample is placed between two coaxial parallel plates creating a fluid connection between them, which are rapidly moved apart [50,51]. This motion corresponds to a steep strain deformation. Under the action of viscoelastic and capillary forces, liquid between the plates contracts into a filament. Once the physical separation of the plates is completed, the filament undergoes constriction as the surface tension acts to reduce interface surface area between liquid and air, and finally breaks [52–54]. Thus, the instrument enables the assessment of the longer relaxation times and extensional stresses of viscoelastic fluids through monitoring the nature of the capillary thinning and breakup dynamics of the sample filament thread connecting the two circular end plates.

Our findings illustrate an identifiable difference between stable and flocculated systems under capillary constriction extension, such that the stress–time relation develops a bimodality for simple particulate salt-flocculated suspensions containing fine particles, more particularly nanoparticles in the range <100 nm, suggesting a columnar geometry of the filament as the elastic energy stored initially during physically-driven extension (plate separation) limits the formation of the usual concave “pinching” constriction geometry adopted by a pure viscous system. Isolating this bimodality in the data first of a mixed system of pigment, binder and polymer thickener is necessary, as thickening polymer, such as carboxymethyl cellulose (CMC), is known also to flocculate pigment and binder particles, to enable analysis of the pigment and latex binder flocculation in isolation from any later added MNFC [26,55]. The nanofibrillated MNFC material will then expose its rheological properties when dispersed by CMC as a separable function independent of the flocculation-induced bimodality. In this way, the analysis can be applied to the complex mixtures of pigment, binder, thickener and MNFC to assist in identifying the origin of viscoelasticity, i.e. gelation of the nanofibrillar content versus ion-induced flocculation.

2. Materials and methods

As reported earlier, two types of MNFC materials are used, [18,19,31,34,25,55] with MFC being produced by grinding birch kraft pulp with an ultra-fine friction grinder (Masuko Supermasscolloider, MKZA 10–15 J) and NFC produced in a pilot process by oxidising the birch kraft pulp using TEMPO catalyst to induce fibrillation 20. Detailed specifications of MNFC materials have been presented earlier [18,19,31,34,24,25].

2.1. Coating formulations

To help characterise the constituents of the coatings, the charge of the pigments (zeta potential (ζ)) was determined by a Zeta-sizer (Malvern Instruments Ltd.). The particle size of the pigments, MNFC and flocculated pigment agglomerates was measured with

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