Interfacial Polymerization of Cellulose Nanocrystal Polyamide Janus Nanocomposites with Controlled Architectures

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Abstract

The widespread use of renewable nanomaterials has been limited due to poor integration with conventional polymer matrices. Often, chemical and physical surface modifications are implemented to improve compatibility, however this comes with environmental and economic cost. This work demonstrates that renewable nanomaterials, specifically cellulose nanocrystals (CNCs), can be utilized in their unmodified state and presents a simple and versatile, one-step method to produce polyamide/CNC nanocomposites with unique Janus-like properties. Nanocomposites in the form of films, fibres and capsules are prepared by dispersing as prepared CNCs in the aqueous phase prior to the interfacial polymerization of aromatic diamines and acyl chlorides. The diamines in the aqueous phase not only serve as a monomer for polymerization but, additionally adsorb to, and promote the incorporation of CNCs into the nanocomposite. Regardless of the architecture CNCs are only present along the surface facing the aqueous phase resulting in materials with unique, Janus-like wetting behaviour and potential applications in filtration, separations, drug delivery and advanced fibres.

Main Text

Polymer nanocomposites have become a ubiquitous part of today's society. They have mostly found applications in the automotive and aerospace industries, but additionally in niche markets, such as catalysts, separators and electrolytes.^{1,2} However, as the global demand for sustainable and renewable materials grows, researchers are looking beyond traditional carbon-based nanoparticles (carbon black, carbon nanotubes and graphene) to renewable nanoscale materials such as nanocellulose, lignin and chitin.³

Due to their availability and projected cost, nanocellulose in the form of cellulose nanocrystals (CNC) and cellulose nanofibrils (CNFs) have received the majority of attention.⁴ Sourced from woods, grasses, tunicates, algae or bacteria CNCs and CNFs are extracted via acid hydrolysis or combinations of chemical and mechanical processing respectively.^{5,6} Exhibiting rod and fibril-like morphologies CNCs and CNFs have many advantageous mechanical, rheological and optical properties, yielding potential applications ranging from electronics and biomedical devices, to catalytic supports and coatings.⁷ Yet much like nanoclays, the hydrophilic nature of CNCs and CNFs limits compatibility with hydrophobic polymer matrices. Moreover, the relatively low thermal stability can lead to discolouration and degradation in traditional extrusion and injection molding processes.⁸ To address this, many researchers have sought to modify nanocelluloses to improve both compatibility and thermal stability. The most widely used approach is to chemically or physically graft small molecules or polymers to or from the particle surface. For example, the use of surfactants can aid dispersion in non-polar solvents,^{9,10} altering charged groups and selection of counter-ions can increase thermal stability,^{11–13} and grafting polymers improves compatibility within hydrophobic polymer matrices.¹⁴ However, as the number of modification steps and additional components increases so too does the economic cost. Moreover, due to the high specific surface area of nanocellulose the degree of substitution and molecular mass must be considerable for modifications to be effective thus, reducing the cellulose content (by mass) and the overall

sustainability of the final material. Ideally, CNCs and CNFs should be used as unmodified materials.

As we continue to progress towards more advanced nanoscale devices, new materials and insights can yield new opportunities for old ideas. One such example is the interfacial polymerization of polyamides. While to achieve high molecular weights at the industrial scale polyamide producers have long sought to eliminate water by using batch autoclaves, vented extruders or flashing tubes^{15,16} the interfacial polymerization of polyamide at the oil/water interface has often been considered as a simple laboratory demonstration. Yet, interfacial polymerization is a tremendously active field and is an excellent method to prepare ultrathin films, membranes, capsules and fibres.¹⁷

Recently, there has been significant interest in using CNCs to create supported thin film polyamide composite membranes via interfacial polymerization.^{18–22} In these works aqueous dispersions of CNCs and diamines are deposited on an ultrafiltration membrane from which an oil phase, containing an acidic chloride, is filtered through and the resulting interfacial polymerization forms a submicron composite polyamide layer on top of the ultrafiltration membrane. Although, inclusion of CNCs generally improves flux through the membrane, and in some cases selectivity,^{20,22} these composites are bound to the underlying polymer support, and are limited to a single architecture.

Other high aspect ratio nanoparticles such as carbon nanotubes and graphene have been used to prepare reinforced, support free composites^{23–25} yet surfactants or surface functionalization are often required to form stable suspensions in either the aqueous or oil phase during preparation. Moreover, the sp^2 carbon structure of carbon nanotubes and graphene does not natively support hydrogen bonding within the polyamide matrix,^{26,27} and surface modification is often used to improve compatibility.²⁸

To demonstrate that unmodified CNCs have potential as reinforcing agents or as functional components in composite materials herein we show the fabrication of

polyamide/CNC nanocomposites via a one-step interfacial polymerization method. We prepare nanocomposites with different form factors including films, fibres and capsules (Figure 1) to demonstrate the simplicity and flexibility of the method. Additionally, we specifically examine the interaction between CNCs and diamide monomers to understand the mechanism that drives composite formation. Using this method, we create Janus-like materials that are not possible with conventional processing techniques, (extrusion, solvent casting, etc.) giving rise to materials with controlled wetting properties and potential applications as separators/barriers, drug delivery devices or as internally wicking fibres.

Figure 1: Schematic representation of nanocomposite formation and accompanying photographs of the nanocomposites. The oil phase containing acid chlorides is shown in yellow, the aqueous phase containing amine monomers and CNCs is shown in blue, and the nanocomposite is shown in purple.

Nanocomposites were prepared by combining sulfuric acid extracted CNCs²⁹ and m-xylylenediamine (MXD) in the aqueous phase (AP) and sebacoyl chloride and trimesoyl chloride (TMC) in the oil phase (OP). MXD was selected due to the interesting crystallization behaviour^{30,31} and excellent barrier properties,^{32–34} however nanocomposites can be similarly formed using more traditional linear diamines such as hexamethylenediamine (Figure S1

Supporting Information). Nanocomposites were formed by either layering the OP on top of the AP (and pulling the interface to form fibres) or by dripping the diamine/CNC dispersion through the OP to form aqueous containing capsules.

The interfacial polymerization reaction is rapid, however within this process there are several limiting steps (incipient film formation, slowdown of film formation, and diffusion limited growth) that have proved challenging to model effectively.^{35–37} In general, the polymerization follows a step growth mechanism, where amine monomers diffuse through the interface to condense with acidic chlorides from which, the polymers reach a high enough molecular weight to precipitate out of solution.³⁸ As polymerization progresses the interface grows towards the OP where the thickness of the polymer layer can be controlled by altering the time of polymerization or the concentration of the monomers in solution (Figure S2 Supporting information).

Inclusion of CNCs into the final composite structure requires CNCs to either diffuse to or be drawn to the interface, such that they can be incorporated during polymerization. CNCs are well known to be good Pickering emulsion stabilizers however, they often require significant energy input via sonication to migrate to the oil/water interface.^{39,40} When small molecules, such as surfactants are adsorbed, they can more effectively migrate to the interface,^{41,42} yet inclusion of additional components increases economic and environmental costs in comparison to native materials. For nanocomposite films where the polymerization is relatively static (i.e. the reaction is left undisturbed until completion) CNCs have sufficient time to diffuse to and interact with interface. This is in contrast to fibre formation, where the drawing process continually creates new interfaces to which CNCs must rapidly migrate in order to be incorporated in the nanocomposite. As a result, we aim to use diamine molecules to perform two distinct functions during composite formation: i) serve as monomers for polymerization and ii) adsorb to CNCs to promote migration to the oil/water interface.

Adsorption behaviour was investigated upon the addition of MXD to CNC dispersions. Zeta potential measurements (Table 1) and isothermal titration calorimetry (ITC) (Figure 2) show that MXD adsorbs to the CNC surface and thus promotes particle migration and incorporation during polymerization. Notably, adsorption is observed at both pH 10.5 and pH 3, above and below the pK_a of MXD ($pK_a \sim 9.2$) respectively.⁴³ Fitting the ITC curves to a generic binding process with independent sites indicates that MXD spontaneously adsorbs to the CNC surface ($\Delta G < 0$) however, the mode of adsorption is dependent on pH.⁴⁴ (See Supporting information for ITC fitting details) At pH 3, MXD is cationic and thus adsorption is entropically driven through the release of counter ions with the anionic sulfate half esters on the CNC surface. However, significantly above the pK_a MXD is no longer charged and adsorption occurs via an enthalpy driven process, suggesting that while specific interactions between MXD and CNCs do not drive adsorption, they do play a role. Adsorption at both high and low pH is beneficial as the pH is expected to vary throughout the interfacial polymerization. Specifically, during the initial phases of polymerization, high monomer concentration in the AP (2 wt.%) yields a pH above the pK_a of MXD. As the polymerization progresses, condensation of the amine and acidic chlorides produces HCl which locally reduces the pH. While adsorption will primarily occur during initial mixing of MXD and CNCs, from the ITC and zeta potential data, we do not expect desorption to occur as polymerization progresses.

Table 1: Zeta potential and apparent particle size measured by DLS for CNC and MXD dispersions.

[MXD] (wt.%)	pH	Zeta potential (mV)	Apparent Particle Size (nm)
0	6.5	-44 ± 4	75 ± 1
0.125	6.5	-17 ± 1	74 ± 1
1.0	11.0	-22 ± 2	76 ± 1

Figure 2: Baseline corrected raw heats for 0.1 wt% MXD injected into 1 wt% CNC dispersion at pH 3 and pH 10.5

Due to adsorption, CNCs can potentially alter the interfacial polymerization as it is dependent on both the diffusivity of MXD and the interfacial tension at the oil/water interface.¹⁷ Interfacial tension measurements between aqueous solutions of MXD and dodecane show that above 1 wt.% MXD the interface becomes saturated and CNCs do not significantly impact the interfacial tension between the two phases. (Figure S4 Supporting Information) As a result, it is expected that CNCs do not have a significant effect on the polymerization of the nanocomposite. This is supported by results in Figure 3a and Figure 3d where nanocomposite films with 0 wt.% and 0.5 wt.% CNCs, the lowest and highest concentrations investigated, have similar thicknesses and structure when imaged by SEM. The impact of CNCs on polymerization is further investigated by ATR-FTIR spectroscopy and is discussed below.

Figure 3: Scanning electron microscopy images of MXD/CNC nanocomposite films formulated with 2 wt.% MXD, 0.25 wt.% TMC and (a-c) 0 wt.% CNC and (d-f) 0.5 wt.% CNC. The images show the edge, OP surface, and AP surface from top to bottom respectively. Inset in (d) shows interior pore morphology.

The interior structure of the nanocomposite is highly porous with a cellular-like morphology, typical of interfacially polymerized membranes and films.⁴⁵ Each cell is separated by thin polymer walls that are void of CNCs (Figure 3d inset). Currently, the connectivity between the cells is unclear however, the morphology and selectivity of the membrane can potentially be tuned by altering monomer type and concentration.⁴⁶ Examining the surface of the nanocomposite reveals that CNCs are incorporated largely only at the surface facing the AP where they form a dense network of overlapping particles that lay parallel to the nanocomposite surface (Figure 3f). This can be further seen in atomic force microscopy images (Figure S5

Supporting Information). In contrast, few or no CNCs are observed at the oil facing surface. We propose this Janus-like structure results from the rapid polymerization of the polyamide at the interface, whereby the initial film formation limits CNCs from penetrating deeper into the composite structure. As a result, CNCs have little impact on the surface facing the oil phase, with both native and CNC modified materials exhibiting rough, globular like structures, typical of polyamides formed by interfacial polymerization.⁴⁷ Moreover, with CNCs only present at the surface facing the AP they constitute a relatively small percentage of the overall composite mass and have limited impact on the thermal properties of the nanocomposite, as measured by thermogravimetric analysis (Figure S6 Supporting Information).

Similar to the films both the fibre and capsule nanocomposites show Janus-like morphology with different interior and exterior structures (Figure 4). Specifically, as the fibres are pulled out of the interface a tubular structure is formed, in which the interior and exterior surfaces face the AP and OP, respectively, and thus confine CNCs to the interior of the fibre (Figure 4d). CNCs were observed along the entire length of the fibre, demonstrating that even though new interface is rapidly created as the fibre is drawn from solution, the CNCs are sufficiently mobile in the AP to be incorporated during polymerization. The unique structure of these fibres, have potential applications as internally wicking fibres or as hollow fibre membranes for filtration applications.

Figure 4: Scanning electron microscopy images of MXD/CNC nanocomposite (a, b) capsules and (c, d) fibres formulated with 2 wt.% MXD, 0.25 wt.% TMC and 0.5 wt.% CNC. The images show the (a,c) OP surfaces and (b, d) AP surface of the nanocomposites.

During the formation of the capsules rapid polymerization around the droplet creates a polyamide shell which contains the AP and CNCs. Similar to the nanocomposite films, amine monomers seem to diffuse through the capsule wall and continue to polymerize with the TMC in the OP. As a result, the capsule wall is highly porous with a cellular morphology (Figure S7 Supporting Information) and CNCs are only present at AP surface, as detected for the films and the fibres. Regardless of the formulation method, the resultant nanocomposites incorporate CNCs only at the surface facing the AP, creating unique Janus-like architectures.

While the CNCs are only present at the AP surface, a sufficient number are incorporated into the nanocomposite such that they impact the overall material properties and performance as evidenced by ATR FTIR spectroscopy and contact angle measurements. For all nanocomposite films, ATR FTIR spectra of the AP surface show characteristic aromatic polyamide bands at 1633 cm^{-1} , 1524 cm^{-1} , 1425 cm^{-1} and 1281 cm^{-1} , attributed to $\nu(\text{C}=\text{O})$, $\delta(\text{N}-$

H), $\delta(\text{C-H}_2)$ and $\delta(\text{C-H})$ vibrational modes respectively (Figure 5a).^{34,48} The intensity and width of these bands remain relatively unchanged with the addition of CNCs, indicating that the polymerization is largely unaffected by CNCs, in good agreement with SEM images. However, evidence of CNCs within the nanocomposite structure is observed by the development of peaks at 1057 cm^{-1} and 1033 cm^{-1} . These peaks are assigned to $\nu(\text{C-O})$ at the C6 and C3 position of cellulose, respectively, and show an increase in signal intensity with CNC concentration.⁴⁹ In addition to the characteristic cellulose $\nu(\text{C-O})$ peaks, CNCs are observed at higher vibrational frequencies; specifically within the $\nu(\text{C-H})$ and $\nu(\text{O-H})$ regions of the spectra (Figure 5b). Broadening of the peak at 2925 cm^{-1} and development of band shoulders at 2967 cm^{-1} indicate that additional $\nu(\text{C-H})$ modes, resulting from CNCs, are present for the nanocomposite. Furthermore, Figure 5b shows that with increasing CNC concentration a new peak develops at 3664 cm^{-1} . While, $\nu(\text{O-H})$ modes from the alcohol groups within cellulose range from $3200 - 3500\text{ cm}^{-1}$,⁴⁹ the vibrational modes from $3700 - 3600\text{ cm}^{-1}$ are attributed to weakly bound or free $\nu(\text{O-H})$ modes and are typically observed within highly structured clays.⁵⁰ The development of this peak suggests that when CNCs are incorporated into the nanocomposite, a portion of the alcohol groups cannot effectively hydrogen bond with other CNCs or the N-H within the polyamide, and can be speculated to be due to an immobilization of the CNCs parallel to the nanocomposite surface. Additionally, ATR FTIR spectra of the OP surface (Figure S8 Supporting Information) show no characteristic cellulose bands and further demonstrates that CNCs are only present at the AP surface.

Figure 5: ATR FTIR spectra of polyamide CNC nanocomposite films from a) 1800 – 950 cm^{-1} showing the amide and CNC regions and b) 3800 – 2800 cm^{-1} displaying the O–H, N–H and C–H stretching regions (c) Contact angle measurements of polyamide CNC nanocomposite films at the oil facing surface (OP) and aqueous facing surface (AP) of native and 0.1 wt.% CNC.

As shown in Figure 5c CNCs significantly alter the wetting behaviour of the polyamide nanocomposites. Native films have a contact angle of $57 \pm 10^\circ$ for both OP and AP surfaces, demonstrating that the different morphology, observed by SEM (Figure 3), has little impact on the wetting behaviour. Comparatively, nanocomposites containing CNCs wet significantly more at the AP surface, with 0.1 wt. % CNC yielding the lowest contact angle of $14 \pm 7^\circ$ (Figure 5c). See Table S2 in the Supporting Information for complete list of contact angles. The presence of hydrophilic CNCs only at the AP surface creates a higher surface energy in comparison to the aromatic polyamide at the OP surface, resulting in Janus-like films. While not specifically investigated in this work this controlled wetting behaviour has potential to increase flux and specificity for filtering and separation applications. Moreover, incorporating CNCs into the nanocomposites provides an opportunity to graft specific moieties, such as enzymes, antibodies, or ligands directly into the nanocomposite.⁵¹

In conclusion, we have demonstrated a versatile one-step method for producing nanocomposites via interfacial polymerization of polyamides. This procedure makes use of unmodified CNCs and is capable of producing various architectures including films, fibres and capsules, with unique Janus-like structures and properties. The formation of nanocomposites

occurs initially via amine adsorption to the CNC surface in the aqueous phase, from which CNCs are incorporated into the nanocomposite during polymerization. Amine adsorption was observed to occur above and below the pK_a of the monomer via zeta potential and ITC measurements and promotes migration of CNCs to the oil/water interface. The resulting nanocomposites, were found to have a Janus-like structure with CNCs only present at the AP surface as observed via SEM, AFM and ATR FTIR. Immobilizing CNCs at the nanocomposite surface created films with unique Janus-like wetting behaviour, with only the AP surface becoming more hydrophilic. While this simple one step process has been demonstrated for aromatic amides, material properties can be further tuned by altering both the aqueous and oil phase monomers. Moreover, this methodology goes beyond filtering and separations, to potential applications including drug delivery via capsules and advanced fibres with core shell morphologies. Additionally, modification of the CNCs prior to or post polymerization has the potential to impart specific functionalities and material properties.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Materials and Methods, AFM and SEM images showing composite morphology, ITC data and fitting, interfacial tension data, TGA, FTIR characterization and contact angles.

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