

Mechanical Techniques for Enhanced Dispersion of Cellulose Nanocrystals in Polymer Matrices



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1 Introduction

The growing concern regarding the impact of petroleum-based polymers on the environment and the development of biopolymers call for a transition from petroleum-based polymers to sustainable biopolymers. However, such a transition possess a substantial challenge for scientists and industries, requiring innovative materials and the applicable methods for improving the potential application of new materials.

Among all different types of biopolymers, cellulose is one of the most abundant organic compound available on the earth and it is the primary structural component of the cell wall of various plants, many forms of algae and the oomycetes. It is also present in different species of fungi, bacteria, and some sea animals such as tunicates [1]. Cellulose crystallites contain highly ordered, crystalline portions along with some disordered (amorphous) domains [2]; crystallinity index of the celluloses indicates the ratio between the area of the crystalline regions and the total area. Cellulose can be transformed into micro or nano-scale products with different shape and crystallinity using different methods such as acid hydrolysis, combined with mechanical shearing and enzymatic hydrolysis [3–7]. During the process, the amorphous or disordered regions of cellulose are hydrolyzed, and the crystalline regions with higher resistance to acid attack remain intact [8–10]. The resulting crystalline segments with the dimensions of nanometer is called nanocellulose (NC); generally, the family of NC can be classified as cellulose nanocrystals (CNCs), cellulose nanofiber (CNF), and cellulose nanowhisiker (CNW) [11].

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In general, CNCs with a strength over 10 GPa and the elastic modulus of 150 GPa [12] has attracted wide attention as a reinforcing agent and have been employed in the nanocomposite, soft-tissue replacement, and food packaging industry for several decades [7, 13, 14]. The specific structure of CNCs contains several free hydroxyl groups on the surface (Fig. 1). The strong hydrophilic character of CNCs due to the presence of free hydroxyl groups on the surface of CNCs restricts the application of different solvents processing as the medium for solution blending [15].

The hydroxyl group located at C₆ is primary alcohol and at C₂ and C₃ are secondary alcohols. It has been reported that the hydroxyl group located at 6 positions has reactivity ten times higher than the other hydroxyl group [16]. The high reactivity of the hydroxyl groups to form hydrogen bonds strongly influence the overall properties of cellulose such as the reactivity of the hydroxyl groups, hierarchical organization, crystallinity, and limited solubility in most solvents [17, 18].

There are plenty of studied highlighting the optimum characteristics of CNCs as reinforcing agent. It is reported that the homogeneous dispersion of CNCs within the polymeric matrix is an essential step for achieving the superior properties of CNCs in composite materials [19, 20]. In addition, the dispersion of CNCs into the hydrophobic polymer with water-insoluble nature is a big issue. Therefore, several techniques have been experimented to decrease the affinity for moisture of the CNCs and improve the compatibility with a nonpolar polymer. The presence of hydroxyl groups on the surface of CNCs provides an opportunity for application of different surface modification techniques to alter the hydrophilicity and improve the compatibility with different nonpolar polymer matrices [21, 22]. Much research has been devoted to moderate the hydrophilicity of cellulose nanocrystals using physical and chemical modifications [23].

The application of different chemical-oriented surface modification methods is the most common method to alter the hydrophobicity nature of CNCs and enhance the compatibility between CNCs and nonpolar polymer. However, the need for developing new manufacturing processes capable of scaling up motivated the academia to find out innovative processing techniques. In the literature, two innovative manufacturing processes can be found: the application of liquid feeding and the application of masterbatch approach. This chapter contains contributions to the field of cellulose nanocomposites in the area of mechanical processing reporting new advances of the emerging ideas about manufacturing processes, which mainly focus on the achieved mechanical improvement.

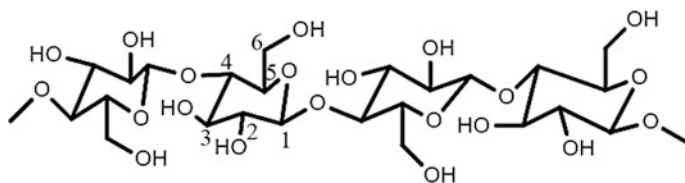


Fig. 1 Schematic representation of a cellulose molecule

2 Liquid Feeding

The application of extruder to shape thermoplastic materials dates back to 1935 when the first extruder machine was built by Paul Troester [24]. Since then, it has become the most broadly used processing technique through the development of different types of extruders capable of serving in different fields. The dramatic growth in plastic processing industry makes it essential to feed solid and liquid phases into extruders. In solid feeding extruders, the forces generated from rotating the screw and the stationary barrel move the materials down in the screw channel. In Liquid feeding extruders, the liquid can be fed into an extruder through a liquid injection nozzle.

It is reported that the drying process of cellulose nanocrystals results in the formation of irreversible aggregates which cannot be re-dispersed through an extrusion process. The application of liquid feeding seems to be a possible option to limit the formation of cellulose nanocrystal agglomerates. The incorporation of liquid and solid phase in an extruder could be difficult and the liquid feed rate, as well as liquid temperature, need to be monitored carefully, since the liquid temperature can strongly influence the viscosity and the change in liquid viscosity can result in pellet slippage on the barrel wall and consequently form undesirable product [25].

The first report of liquid feeding application of cellulose nanofillers into a polymer was by Oksman [26]. The extrusion process was implemented using an extruder equipped with a peristaltic pump which controlled the liquid feeding rate. Two different feeding methods were used: the dry materials were fed into the extruder from a top mounted hopper into the barrel taking advantage from gravimetric feeding and the aqueous cellulose nanowhisker suspension was fed into the extruder using a vacuum pump to ensure the constant liquid feeding rate. In the extrusion process, the existing solvent in the liquid phase was removed by atmospheric venting (Zones 7 and 8) as well as vacuum venting (zone 10) (Fig. 2).

The elaboration of achieving uniformly dispersed cellulose nanowhisker in this work resulted in the generation of the high amount of solvent vapour during the extrusion process. TEM analysis of the composite samples exhibited partly dispersed cellulose nanowhisker into the matrix as well as thermal degradation of cellulose nanowhisker [26].



Fig. 2 Schematic image of extrusion process with liquid feeding [26]

In another work similar to cellulose nanowhisker liquid feeding, cellulose nanofibers were fed into PLA in a liquid phase. The high viscosity of cellulose nanofiber suspension reduced the uniform dispersion thorough composite samples [27]. The need for a specific extruder capable of feeding liquid and dry matter was reported as an essential need for incorporating liquid cellulose nanofiber into the polymer matrix.

3 Masterbatch Approach

The incorporation of cellulose nanocrystals into the different polymer matrix in a step-wise manner is one of the most commonly used preprocessing techniques in nanocomposites preparation. It is reported that the application of masterbatch can maximize the dispersion of cellulose nanocrystals in a polymer matrix, however, the time-consuming nature is the main weakness of the masterbatch approach [28, 29]. In masterbatch approach, a selective polymer is employed as a carrier for cellulose nanocrystals. The polymer can be either the same or different than the host polymer in the nanocomposite [30–34]. The highly concentrated masterbatches can be diluted in the extrusion process by adding polymer using the let-down ratio or mixing ratio (CNCs: polymer, generally between 1:14 and 1:20). The let-down ratio is of paramount importance since high mixing ratio might limit the uniform dispersion of CNCs in the polymer matrix [35]. Solvent casting and spin-coating are two methods employed in preparing CNCs masterbatches in literature.

3.1 Solvent Casting

Solvent casting has a widespread use in different applications owing to its simplicity and low-cost processing [36–39]. Solvent casting technique contains solubilization, casting, and solvent evaporation steps [40–45]. In solvent casting method, a polymer melt or polymer solution is applied on a flat surface, the solvent is then evaporated leaving a solid film. The evaporation rate of the solvent depends on the boiling point of the solvent, the viscosity of the solution, the pressure and the ambient temperature [46]. The rheological properties of the polymeric solution are of huge importance since the film thickness and the roughness of the film depends on the viscosity of the solution.

The solvent casting is a century-old method for nanocomposite films production [47–49] and is the most common method for preparing highly concentrated masterbatches. The application of solvent casting in composites manufacturing was reported for the first time by Favier et al. [50]. In that study, a tunicin-based nanocrystal in a latex matrix of poly(styrene-*co*-butyl acrylate) was studied and the competitive mechanical properties in corresponding composites confirmed the capability of solvent casting technique in composite films preparation.

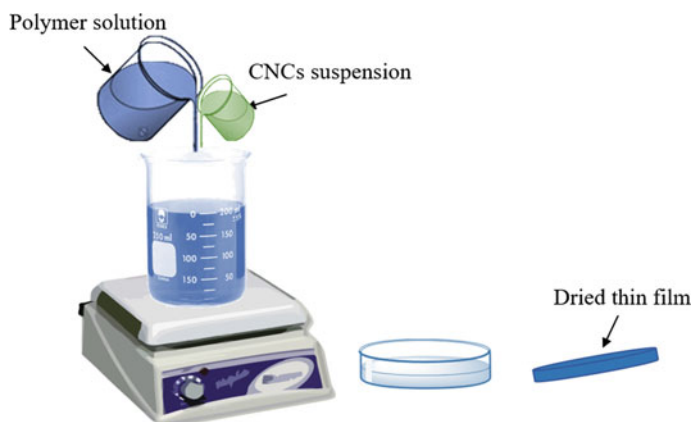


Fig. 3 Schematic depicting of solvent casting method

The preparation of thin films with uniform thickness, maximum optical clarity, and low haze were some advantages reported for solvent casting technology [51–53]. In general, the literature regarding the preparation of cellulose nanoparticles masterbatches involves the solvent casting as the main technique [20, 30, 54].

In solvent casting method, a polymer is first dissolved in a selective solvent either at room temperature or at elevated temperatures [55, 56]. The nanocelluloses are dispersed in either same or different solvent separately. The application of sonication and homogenization techniques can be used to increase the dispersion of nanoparticles through the solvent prior to the addition to the polymer solution [57]. The solution of polymer and CNCs suspension are then mixed together using magnetic stirrer and then poured into a flat-bottomed glass Petri-dishes and the solvent is evaporated and consolidate the films (Fig. 3).

3.1.1 Formation of Aggregates in Masterbatch Films

The morphology of thin film masterbatches generally affects the mechanical properties of final composites since the high concentration of CNCs in masterbatches tends to form CNCs' aggregates [35]. The time-intensive drying process in solvent casting method can intensify the formation of micro-sized cellulose aggregates in the masterbatch. The slow evaporation rate in solvent casting permits solvent molecules to exclude the nanoparticles and pushing them into closer proximity and leading to the formation of unavoidable CNC aggregates [35, 58]. In a recently published work, the formation of CNC aggregates in the masterbatch films was explored. In the aforementioned work, chloroform was used as the solvent and the percentage of CNCs in masterbatch films was 15% and the ultimate thickness was kept constant at 1.12 mm. Figure 4 illustrated the SEM image from a cross-section of the masterbatch.

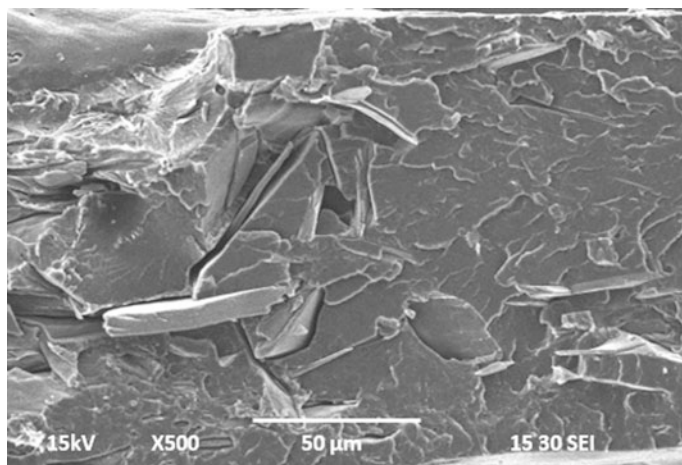


Fig. 4 Cross-sectional SEM image of solvent cast masterbatch film [35]

The formation of permanent CNC aggregates with relatively large effective size suggested strong aggregation in solvent cast masterbatches. It was reported that CNC aggregates formed during masterbatch preparation are difficult to separate during the extrusion process and those aggregates might result in poor adhesion between cellulose nanocrystals and polymer matrix [59].

3.2 Spin-Coating

Spin-coating is a common method employed to prepare thin films with thickness in the order of micrometre to nanometers. In this method, a liquid is deposited on a substrate, which can either be static or rotate at a specific angular velocity [60–62]. The deposited liquid generally consists of volatile solvents and non-volatile solute, and the non-volatile solute forms a thin film after solvent evaporation. Spin-coating involves four consecutive stages: deposition, spin-up, spin-off, and evaporation with some overlap in spin-off and evaporation steps [63]. During spin-off state, a film of liquid tends to spread with a uniform thickness, and after reaching a uniform thickness it tends to remain the uniform thickness. This behaviour suggests that mixture viscosity does not depend on shear and it would be constant throughout the substrate [64]. The equilibrium between centrifugal force generated from rotating substrate and the hydrodynamic (viscous) force evolving from the viscosity of mixture governs the efficiency of the formation of thin films with desirable thickness [35, 65]. In another word, the solution viscosity and the spinning speed mainly influence the film forming procedure. In general, the uniformity of thin film depends on the spinning speed, the concentration of mixture, and the volatility of

the solvent [66]. The desired film thickness can be achieved by adjusting the spinning time and speed [67].

The most common application of spin-coating method is in the field of micro-electronic thin films preparation. This method was first used by Emil et al., who studied the thin film formation of Newtonian fluid on a rotating substrate [68]. The application of this method in polymer films has been investigated in several theoretical and experimental studies [65, 69, 70].

A recently published work introduced an efficient spin-coating method for masterbatch preparation [35]. In this study, thin films with the thickness of the order of micrometres were spread evenly over the glass substrate using a combination of centrifugal force and the surface tension of the solution (Fig. 5).

In this work, the PLA-CNCs mixture was loaded in a syringe and injected through a needle (diameter = 500 μm) onto the centre of the rotating glass substrate with 100 mm diameter. The solvent evaporates simultaneously as the solution is applied to the substrate [62]. The spinning speed was kept constant at 400 rpm. The PLA-CNC mixture was loaded onto the centre of rotating substrate for 180 s.

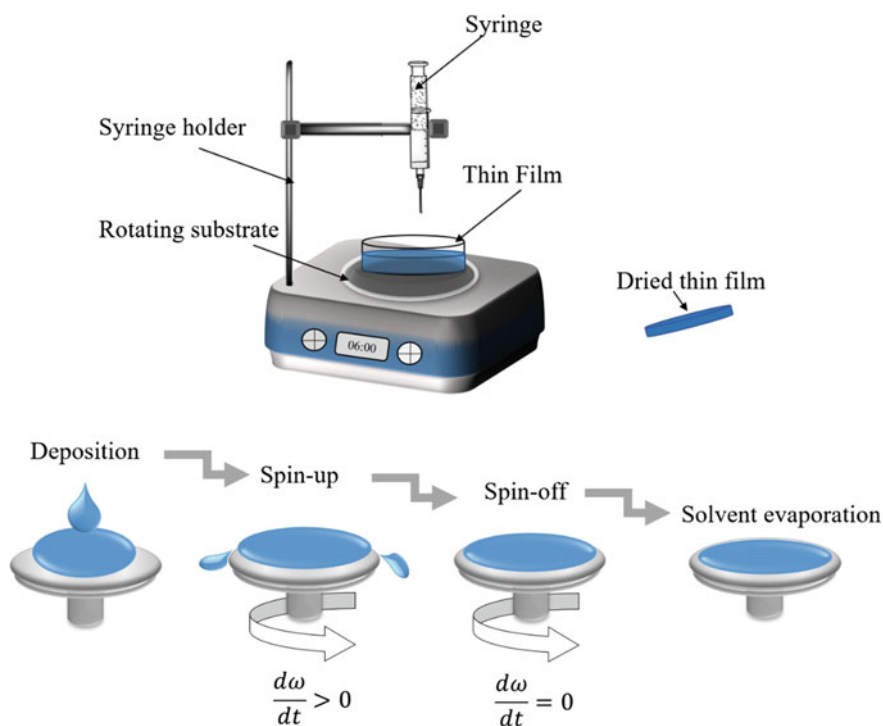


Fig. 5 Schematic illustration of the spin-coating method and four consecutive stages of the spin-coating method

3.2.1 Formation of Aggregates in Masterbatch Films

The volatile solvents used in spin-coating technique with a high evaporation rate can influence the formation of CNC aggregates through the polymer matrix. In fact, the high evaporation rate and low vaporizing time of the solvent from thin films in spin-coating method limit the movement of CNCs through the matrix and inhibits their assembly into micro-sized aggregates [35]. In fact, the rapid increase in the viscosity of solution as a result of the high evaporation rate of solvent kinetically traps the CNCs in the polymer matrix and hinder their movement for making more CNCs bundles. In the spin-coating method, thin film masterbatches are effectively dried out during spinning step. It is reported that in the spin-coating process as the solution is injected onto rotating substrate, the solvent evaporates and this, in turn, results in trapping the individual cellulose nanocrystals from forming big aggregates (Fig. 6).

The SEM micrograph of the free surface of spin-coated masterbatch exhibits that the high evaporation rate results in the formation of widespread voids on the free surface of masterbatches (Fig. 7).

3.3 Variation of Aggregates in Masterbatch Along the Cross-Sectional Thickness

The CNCs concentration and the formation of CNC aggregate through the thickness of the thin film masterbatches are shown in Fig. 8 (CNCs aggregates are pointed by arrow). In the solvent cast masterbatch, since the solvent evaporation occurs at a

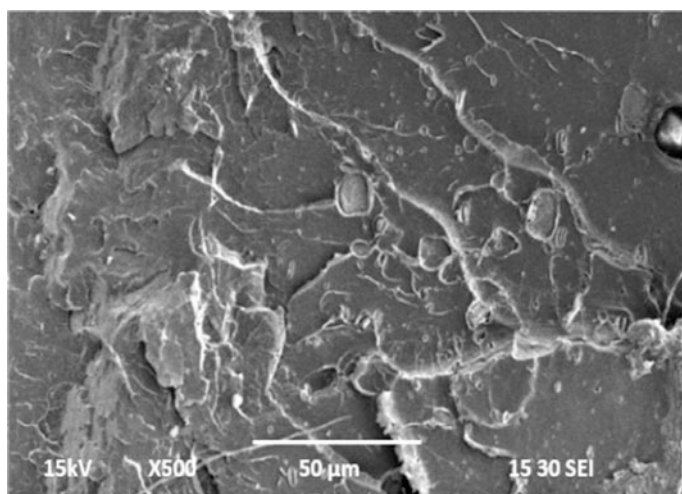


Fig. 6 Cross-sectional SEM image of solvent cast masterbatch film [35]

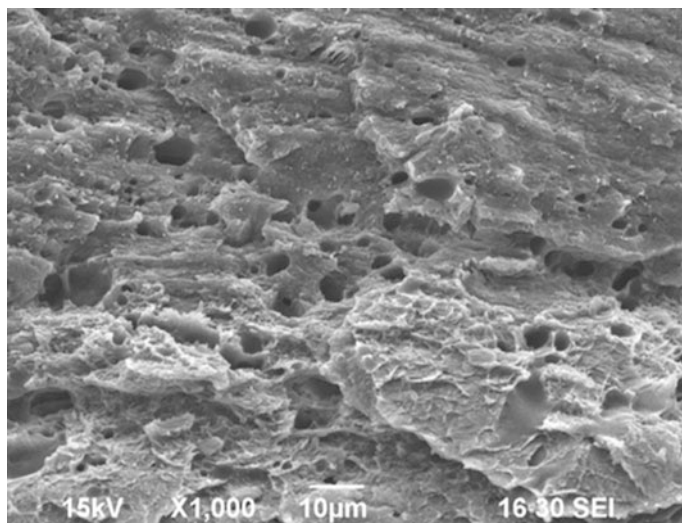


Fig. 7 The presence of voids on cross-sectional SEM image of spin-coat masterbatch film

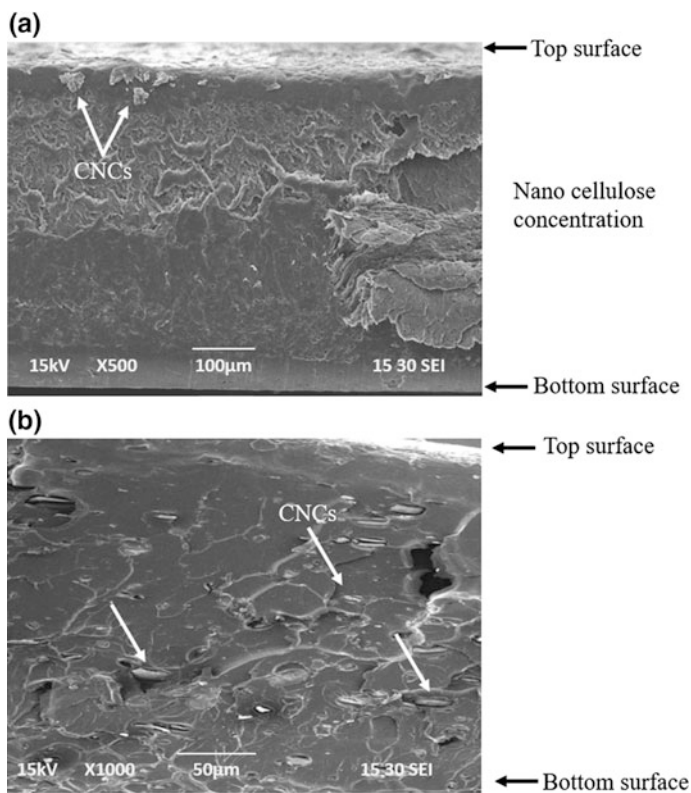


Fig. 8 The comparison of CNCs aggregates formation in the masterbatches: **a** solvent cast, **b** spin-coated

relatively low rate from the free surface of the film, the concentration of CNCs varies vertically along with the thickness of the thin film and the highest solute concentration happens close to the free surface. The increasing CNCs concentration can lead to the formation of CNC aggregates (Fig. 5a), however, in the spin-coated masterbatch, the CNC aggregates with perpendicular orientation with respect to the film thickness are scattered throughout the masterbatch thickness (Fig. 5b). These observations confirm the lower CNCs mobility in the spin-coated masterbatch as a result of the high evaporation rate of the solvent as well as the centrifugal force generated from rotating substrate [35].

4 Conclusion

The potential of nanocellulose to improve material properties has been widely accepted, however, application of nanocellulose in commercial polymer products has been lacking. One of the main hurdles is a uniform dispersion of nanocellulose material through polymer matrices. This review shows clearly that besides surface modification treatment, the application of mechanical pre-processing techniques has a great potential for improving the dispersion of nanocellulose through polymer matrices. This, in turn, results in higher compatibility between the polymer matrix and cellulose nanocrystals. The different techniques discussed in this chapter demonstrated an improvement in the performance characteristics of corresponding nanocomposites. All these techniques are expected to widen the domain of different mechanical pre-processing techniques for using nanocellulose materials.

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