



# Pre-mixing and masterbatch approaches for reinforcing poly(vinyl acetate) with cellulose based fillers



Apiradee Nicharat<sup>a,1</sup>, Janak Sapkota<sup>a,1</sup>, E. Johan Foster<sup>a,b,\*</sup>

<sup>a</sup> Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland

<sup>b</sup> Virginia Tech, Macromolecules Innovation Institute, Department of Materials Science & Engineering, 445 Old Turner Street, 213 Holden Hall, Blacksburg, VA 24061, USA

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## ABSTRACT

Milling of microcrystalline cellulose (gMCC) and poly(vinyl acetate) (gPVAc) was performed, and the milled samples were pre-mixed prior to melt-mixing. Ground samples that were pre- and subsequently melt-mixed (gPVAc/gMCC) showed similar reinforcement (modulus of  $\sim 3$  GPa at 25 °C,  $\sim 9$  MPa at 90 °C) compared to the directly mixed composites containing cellulose nanocrystals isolated by acid hydrolysis from cotton (PVAc/CNC, modulus of  $\sim 3$  GPa at 25 °C and  $\sim 10$  MPa at 90 °C). Highly concentrated masterbatches (up to 60 wt% of gMCC) are shown for the first time with cellulosic filler. These additive concentrates can be first prepared using a solution casting approach, aiding in efficient transport, and then diluted by melt-mixing when needed. Using DMF and water as solvents for preparation, melt-processing schemes that are easier to scale-up and exploit industrially were evaluated in this work.

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## 1. Introduction

Cellulose nanomaterials or nanocelluloses have been studied widely because of their superior reinforcing capability in nanocomposite applications, due to their renewable nature, high aspect ratio, high on-axis stiffness and therewith high reinforcing capability (Beck-Candanedo et al., 2005; Habibi et al., 2010; Lin and Dufresne, 2014; Moon et al., 2011). Cellulose nanofillers are obtained from several bio-sources including cotton (Dong et al., 1998), softwood (Filpponen and Argyropoulos, 2010), hardwood (Beck-Candanedo et al., 2005), bacterial cellulose (Araki and Kuga, 2001), tunicates (Frone and Dufresne, 2000) and microcrystalline cellulose (MCC) (Frone et al., 2011; Bondeson et al., 2006; Capadona et al., 2009). Cellulose nanofillers are usually produced by acid treatments with strong acids, such as sulfuric (Dong et al., 1998), hydrochloric (Araki et al., 1998), phosphoric (Camarero Espinosa et al., 2013) and hydrobromic acids (Filpponen and Argyropoulos, 2010), dissolving away amorphous sections of cellulose while leaving highly crystalline regions. Combinations of acidic treatment and high-pressure homogenization have also been reported (Pan et al., 2013).

Chemical or mechanical treatments of cellulosic material have shown to be efficient in producing nanometer or micrometer sized fillers with exceptional properties, resulting into a plethora of advanced applications (Eichhorn, 2011; Eichhorn et al., 2010; Habibi et al., 2010). However, the production of cellulose nanofillers by acidic treatment requires several neutralization steps that have slowed the mass-scale production of these nanofibers (Bandera et al., 2014; Camarero Espinosa et al., 2013; Capadona et al., 2007; Sapkota et al., 2013). Although several commercial plants producing CNCs have recently come online, MCC has proven to be an interesting alternative. A recent study has demonstrated the impact of different mechanical treatments on commercially available MCC to produce cellulose nanomaterials having similar reinforcement as of the commercially available CNCs (Bandera et al., 2014).

Homogeneous dispersion of CNCs in nanocomposite materials is the primary requirement for effective reinforcement (Bandera et al., 2014; Sapkota et al., 2014). Casting/evaporation based processing techniques have been widely exploited, as they predominantly use hydrogen bonding solvents which facilitates the good dispersion of unmodified CNCs in the nanocomposites thus obtained (Nicharat et al., 2015; Rusli et al., 2010; Shanmuganathan et al., 2009). However, considering the amount of solvent and the time required to obtain the composites, the industrial scaling of casting/evaporation based processing techniques is limited. Eventually, either quick removal of solvent, and/or industrial processing techniques such as

\* Corresponding author at: Virginia Tech, Macromolecules Innovation Institute, Department of Materials Science & Engineering, 445 Old Turner Street, 213 Holden Hall, Blacksburg, VA 24061, USA.

E-mail address: [johanf@vt.edu](mailto:johanf@vt.edu) (E.J. Foster).

<sup>1</sup> Authors contributed equally.

extrusion and injection molding will be preferred for large volume production (Nicharat et al., 2015; Sapkota et al., 2015).

Based on the previous studies, once CNCs are well dispersed in a poly(vinyl acetate) (PVAc) matrix (using solution casting), the resulting composite can be effectively re-processed in low shear melt-mixing conditions, such as those found in a roller-blade type mixer, allowing one to keep the morphology well preserved (Sapkota et al., 2015). When direct mixing PVAc granules with lyophilized CNCs in similar conditions, an effective dispersion of CNCs was predominantly observed, even though the as-obtained composites showed slightly lower reinforcement than the solution cast composites. Considering the need for an industrially viable approach, direct mixing is a more preferable mixing method, and therefore the addition of pre-mixing techniques/steps prior to extrusion/melt-mixing could facilitate the preparation of well-mixed composites. Meanwhile, several studies have demonstrated the masterbatching approach, which involves dispersing a high concentration of nanofiller into a matrix for easier transport, with an end-user diluting the material using straight forward (industrially viable processing methods), as an effective approach to obtain nanocomposites with homogeneous dispersion (Lepoittevin et al., 2003; Prashantha et al., 2009; Shah and Paul, 2004). More recently, Mariano et al. (2015) showed the possibility of using highly concentrated CNC/polycarbonate (PC) composites, and subsequently diluting these composites by extrusion. In this approach, prior to melt-mixing, CNCs were coated with PC, using a dissolution/precipitation process in which an aqueous dispersion of CNCs had the water exchanged to PC solubilizing pyridine. Even though the approach is quite interesting, it involves additional costs and scaling of a prohibitive solvent such as pyridine, what potentially limits the use of this technique in industrial processes.

To balance the high dispersibility advantage of lab-scale solution based approach and the need of an industrially viable processing technique, we implement a masterbatching approach that allows one to have highly concentrated CNC nanocomposites which when diluted via melt-processing techniques such as compounding with roller blade mixer (RBM), maintain a high level of dispersion with virtually indistinguishable mechanical properties compared to the solution cast reference composites.

## 2. Materials and methods

### 2.1. Materials

Poly (vinyl acetate) (PVAc, weight-average molecular weight,  $M_w = 120,000$  g/mol) was purchased from Anhui Herrman Impex Co., (China) and all reagents were purchased from Sigma Aldrich and were used without further purification. Microcrystalline cellulose (MCC) was purchased from FMC Biopolymers (Avicel Lattice NT-100). Cellulose nanocrystals (CNCs) were isolated from MCC via ultrasonication following earlier established protocols (Capadona et al., 2009). Briefly, 8 g of MCC were dispersed via ultrasonication in 400 mL of deionized water for 6 h. The CNCs suspension was allowed to rest overnight, and the upper homogeneously dispersed layer of the suspension was lyophilized using a VirTis BenchTop 2 K XL lyophilizer with an initial temperature of 25 °C and a condenser temperature of –78 °C to obtain dry CNCs.

### 2.2. Preparation of ground PVAc (gPVAc) and MCC (gMCC)

The dry milling of the PVAc (gPVAc) and MCC (gMCC) was performed using Hammer Witt-LAB (Frewitt SA, Fribourg, Switzerland) at hammer side using a screen 'Chevron' 0.2 mm for MCC and 0.35 for PVAc at 7000 rpm 1 kg of PVAc or MCC was milled in 42 s cycle and consecutive cycles (11 for PVAc and 7 for MCC) were operated

in order to obtain finer particles. To determine the milled particle size, Sieve analysis was performed using Retsch Analytical Sieve Shaker AS 200Control for 30 g samples each with a vibration rate of 2 min, amplitude of 2 mm/g and Vulkollan cubes as a sieving aid.

### 2.3. Direct mixing of PVAc composites with MCC, gMCC and CNC using roller blade mixer (RBM)

PVAc composites with 10 wt% filler content were prepared using direct mixing at low shear conditions in a laboratory-scale miniature batch mixer in a twin-cylinder configuration with two counters rotating roller blades (Brabender® 30EHT) at 170 °C and 70 rpm. The polymer was first melted and subsequently MCC, gMCC and lyophilized CNCs were added to the molten PVAc. After mixing for 10 min, the composites were removed in the melt state from the mixing chamber and were allowed to cool at room temperature.

### 2.4. Pre-mixing of gPVAc with MCC, gMCC and CNC prior to melt-mixing using a roller blade mixer (RBM)

gPVAc and the corresponding amount of filler (10 wt% in the final composites in their dry state) were pre-mixed manually in powder state. The pre-mixed powder was fed in the low shear roller blade mixer and melt-mixed at 170 °C and 70 rpm for 10 min. The composites were removed from the mixing chamber and were allowed to cool to room temperature.

### 2.5. Preparation of gPVAc/gMCC masterbatch composites by solution casting

To prepare the masterbatch composites, two different solvents (dimethyl formamide (DMF) and water) were used as processing aid. gMCC was dispersed in DMF at a concentration of 20 mg/mL by sonication for 5–6 h in an ultrasonic bath (VMR™ USC600TH/40 kHz/120W). gPVAc was dissolved in DMF at a concentration of ~20% w/w by stirring for 4–6 h. Aliquots of the gMCC dispersion and the gPVAc solution were combined in a flask and the mixtures were stirred for 1 h with a magnetic stir bar, sonicated for 1 h and finally cast into Teflon® Petri dishes with a diameter of 12.7 cm. The Petri dishes were placed into an oven at 70 °C for 3–4 days to evaporate most of the solvent and the resulting films were dried in a vacuum oven at a pressure of 400 mbar at 70 °C for 2 days to remove any remaining solvent. Masterbatch composites containing 40–60 wt% of gMCC were thus produced. Similar approach was used with water as solvent to obtain composites with similar compositions.

### 2.6. Dilution of gPVAc/gMCC masterbatch using a roller blade mixer (RBM)

gPVAc/gMCC masterbatch composites were diluted to gPVAc/gMCC 10 wt% composition using a roller blade mixer (RBM). Briefly, appropriate parts of masterbatch composite were melt-mixed with gPVAc powder directly in the roller blade mixer at 170 °C and 70 rpm for 10 min. For instance, to dilute gPVAc/gMCC 50 wt% masterbatch, 4 g of masterbatch composite was melt-mixed in RBM with 16 g of gPVAc under similar conditions as described above.

### 2.7. Injection-molding of PVAc/CNCs nanocomposite films

PVAc composites using the above methods, and shaped by injection molding (DSM Xplore micro-injection 10 cc). The materials made by the different methods were vacuum-dried for 24 h in a desiccator at room temperature and polymer was melt-injected

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