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Acid functionalized cellulose nanocrystals and its effect on mechanical, thermal, crystallization and surfaces properties of poly (lactic acid) bionanocomposites films: A comprehensive study

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ABSTRACT

This work reports the fabrication of four varieties of cellulose nanocrystals(CNCs) through hydrolysis with different acids which leads to their tailored physical, structural, thermal and surface characteristics. The hydroxyl groups of CNCs are substituted with anionic-moieties from acid which alters its interfacial interaction with PLA matrix, as predicted from dispersion surface energy and work of adhesion values. Interestingly, tunable aspect ratios of various acid-derived CNCs have substantial effect on mechanical reinforcing-efficiency and thermal behavior of nanocomposites. CNCs with high aspect ratio improved the elastic modulus of nanocomposites whereas with low aspect ratio accelerated the crystallization rate. The different acid-derived CNCs shows heterogeneous nucleation-driven crystallization phenomenon with propagation of PLA spherulites in three dimensions. Lauritzen-Hoffmann parameters shows that growth of PLA crystals are restricted requiring higher activation-energy to initiate nucleation process. Therefore, this study provides an alternative approach of selecting the appropriate acid-hydrolyzed CNCs for fabrication of CNC-reinforced polymeric nanocomposites with desired properties.

1. Introduction

'Nanocellulose' is a high performance nanomaterial of the 21st century with interesting structural and physical properties which have attracted researchers and subsequently led to increase in demand among industries for development of cellulose-based value added products. Some of the noteworthy exceptional properties of nanocellulose include tunable aspect ratio, controlled morphology, improved structural (mechanical) properties, high specific surface area and most importantly, non-toxicity and biocompatibility [1]. However, the physicochemical and structural properties of nanocellulose are found to be strongly dependent on the initial biomass type or microbial source selected [2], cellulose polymorphs [3], pretreatment process of cellulose extraction and acid hydrolysis [2] or enzymatic treatment [4] followed for nanocellulose fabrication. Nanocellulose consists of primarily crystalline domains of cellulose which are of three different types depending on the degree of crystallinity and morphology of such crystalline segments: (i) cellulose nanocrystals (CNCs) or cellulose nanowhiskers (CNWs) with high crystallinity generally have small crystalline fragments, are of low aspect ratio and are usually fabricated through controlled acid hydrolysis, (ii) cellulose nanofibrils (CNFs) are of comparatively lower crystallinity with high aspect ratio and are generally fabricated trough mechanical disintegration process using intense homogenization or ultra-sonication and (iii) bacterial cellulose (BC) composed of thin bundles of randomly assembled microfibrils which are microbially produced through the fermentation process [5].

Nanocellulose such as CNCs or CNWs are usually fabricated through controlled, stringent acid hydrolysis process which depends on the type of biomass and the acid systems used. The initial biomass selected can be classified into either softwood or hardwood subject to the degree of adhesion between the microfibrils, its geometry and cell dimensions, composition of the cellulose, hemicellulose and lignin content which tends to vary drastically. CNCs fabricated from cotton (usually with higher cellulose content than higher plants) are generally of aspect ratio ~10 whereas CNCs from tunicin or green algae (highly crystalline) have higher aspect ratio (~67) [6]. Similarly, CNCs extracted from coconut fibers (which have higher lignin content) were ultrathin with diameter of ~2–3 nm consisting of 16–30 cellulosic units [7]. In addition to the

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biomass source, the pretreatment reaction conditions must be optimized in order to yield cellulose with higher purity, crystallinity and degree of polymerization which strongly affect the properties of fabricated CNCs [2]. The mechanism of cellulose hydrolysis usually includes dissociation of acids into protonated ions followed by diffusion into amorphous layers of microfibrils disintegrating the glycosidic bonds of cellulose chains. The diffusion of protonated ions is strongly affected by the selected biomass type which have different degrees of cellulose micro-fibril packing density and presence of impurities such as hemicellulose or lignin. However, the degree of acid protonation depends upon the selected acid type, ionic strength of acidic media and ratio of cellulose to acid used for hydrolysis. In literature, the use of several strong or weak acids such as sulphuric acid [8], hydrochloric acid [9], acetic acid [10], lactic acid [11], phosphoric acid [12], ammonium persulfate [13], hydrobromic acid [14] and 2,2,6,6-tetramethyl-1-piperidinyloxy(TEMPO) [15] has been reported till date for fabrication of CNCs. The fabricated CNCs using different acids have tunable morphology (rod-shaped, circular or elliptical), surface functionality, different degrees of crystallinity, inter/intra-chain hydrogen bonding and dispersion quality in polar/non-polar solvents. In one of our recent study [3], three different categories of CNCs were fabricated from two polymorphs of cellulose (cellulose I and cellulose II) which were found to have significant variation in morphological dimensions, crystallinity, intra/intermolecular hydrogen bonding structure and thermal/dispersion stability. Crystalline cellulose is known to exist in four different polymorphs namely cellulose I, II, III and IV with variable elastic modulus of 138, 88, 58 and 75 GPa respectively [16]. Interestingly, mechanical property investigations of CNCs fabricated from diverse biomass sources, different acids used for hydrolysis reactions and different cellulose polymorphs have revealed anisotropic mechanical behavior [17] with tailored transverse and longitudinal elastic modulus in the range of ~2–50 GPa and 140–220 GPa [18] respectively. Therefore, it could be inferred that the intrinsic properties of CNCs could be finely tailored depending upon the end product applications by appropriately selecting the biomass, pretreatment methods for cellulose extraction, polymorphs of cellulose and the type of acids used for hydrolysis reaction.

Incorporation of such CNCs with tunable inherent properties is expected to tailor the thermal, mechanical, barrier and crystallization behavior of fabricated polymeric nanocomposites as well as affect the processability. Several studies have been reported in literature which takes into consideration the variable aspect ratio, crystallinity and morphology of CNCs or CNFs fabricated from different raw material sources [19], chemical functionalities due to different degree of hydrogen bonding in cellulose polymorphs [3] and variation in the inherent mechanical properties [20] on the reinforcement effects of CNCs in polymeric nanocomposites. Studies by Xu et al. [21] showed that CNFs with larger aspect ratio formed dense fiber entanglements with polyethylene oxide matrix thereby creating a percolated network structure which significantly improved the modulus of nanocomposites by two times. Saciu et al. [19] reported fabrication of CNCs/CNFs from seven different cellulosic precursors using different hydrolysis conditions such as acid based, enzymatic hydrolysis, (2,2,6,6-tetramethylpiperidin-1-yl) oxyl (TEMPO)-based oxidation and mechanical disintegration followed by detailed investigations of their fundamental properties. CNCs/CNFs fabricated from such precursors were found to have different fractions of crystalline segments with varied polymorphisms, surface functionality, charge and total surface energy. Fabrication of polylactic acid (PLA) based nanocomposites with the different polymorphs of CNCs (from cellulose I and II) shows tunable structural and physical properties [3]. Incorporation of CNCs with cellulose II polymorphism led to the formation of high degree of intermolecular hydrogen bonding and better adhesion with PLA matrix thereby improving the mechanical and barrier properties significantly. Camarero Espinosa et al. [12] isolated CNCs from different acid sources viz. sulphuric, phosphoric and hydrochloric acids and investigated their thermal and dispersion stability in polar solvents. Comparison of the thermal behavior showed that phosphoric acid-hydrolyzed CNCs were thermally stable up to ~300 °C which was significantly higher compared to sulphuric and hydrochloric acid-hydrolyzed CNCs [12]. Moreover, phosphorylated CNCs when dispersed into polyurethane foams have been found to improve the mechanical strength by ~4.3 times and incorporate flame retardancy characteristics increasing the time of ignition ~2.6 times [22]. Recently, Henrique et al. [22] extensively studied the thermal degradation kinetics of CNCs fabricated from the different cellulose polymorphs, various bio-based sources and different acid types which showed significant variation in the activation energy and reaction order of degradation process. It was observed that keeping the raw material source for cellulose fixed (for e.g. cellophane) the CNCs hydrolyzed with hydrochloric acid and CNCs with cellulose II polymorphs have higher activation energy thereby leading to higher thermal stability [23]. It is known that extrusion of polymer-CNC nanocomposites with sulphuric acid-hydrolyzed CNCs leads to degradation of polymers (reduction in molecular weight) and CNCs causing black coloration in fabricated films [24]. CNCs hydrolyzed with various acids would lead to substitution of the hydroxyl groups with different chemical moieties, which might enhance the compatibility with the polymer and subsequently improve the dispersion of CNCs within the matrix. However, to the best of our knowledge, the effect of the variable surface characteristics of CNCs introduced during hydrolysis with different acids on their degree of dispersion, reinforcement, crystallization and thermal behavior of fabricated polymeric nanocomposites have not been reported in literature.

In the present work, CNCs were fabricated utilizing four different acid types viz. sulphuric acid, hydrochloric acid, phosphoric acid and nitric acid using the cellulose extracted from filter paper as the precursor. The filter paper (Whatmann grade I) are purified from of the cellulose with minimal content of the hemicellulose or lignin components and can be used directly in fabrication of the CNCs through hydrolysis process. The influence of acid types on the morphology, chemical modification of hydroxyl functional groups of CNCs, crystallinity, surface characteristics (especially the energy/charge) and thermal/dispersion stability were investigated in details. The four different acid-derived CNCs with variable physico-chemical and structural properties are extruded with polylactic acid (PLA) to fabricate biopolymeric nanocomposites with various CNC loadings. The main aim of this study was to utilize the tunable intrinsic properties of CNCs to fabricate the polymeric nanocomposites with tailored mechanical, thermal and crystallization properties. The effect of acid-based surface modifications of CNCs on the dispersion quality and microstructural changes occurring in polymers (for example, degradation in molecular weight etc.) during extrusion of nanocomposites (in the presence of CNCs) was also studied. Further, study of the isothermal crystallization kinetics was carried out to understand the influence of variable aspect ratio and chemical functionalities of CNCs on the crystallization behavior and mechanism of the growth of spherulites. The variation in activation energy and reaction order of thermal degradation process of the four different CNCs were calculated. Processing of polymers usually occurs at high temperature and shear conditions, in the presence of nanofillers such as CNCs which leads to degradation of the polymer backbone. Therefore, according to the thermal stability, appropriate CNCs should be selected for fabrication of nanocomposites which will however depend on the processing techniques followed.