EXTRACTION OF CELLULOSE NANOCRYSTALS AS A POTENTIAL REINFORCING MATERIAL FOR POLY(LACTIC ACID) BIOCOMPOSITES

BORŮVKA Martin, LENFELD Petr

Technical University of Liberec, Department of Engineering Technology, Liberec, Czech Republic, EU,
martin.boruvka@tul.cz

Abstract

Usage of plant source-based stiff fillers as reinforcement material in polymer composites has attracted significant interests of researchers during last few decades. The crystalline parts of the semicrystalline cellulose chains represent the most highly potential bio based reinforcing agents for polymers. This paper covers the extraction of cellulose nanocrystals (CNCs) from commercial microcrystalline cellulose (MCC) and their polylactic acid (PLA) nanocomposite films preparation by solvent casting. The nucleation effect of CNCs on PLA matrix crystallization was investigated. The production of biodegradable nanocomposites based on cellulosic biomass waste suggests the possibility of using these new bio-nanocomposites in industrial and environmental friendly applications.

Keywords: Cellulose nanocrystals, biodegradable, biopolymer, nanocomposites

1. INTRODUCTION

During the last years constantly increasing demands of modern society to products made from renewable and sustainable resources that are biodegradable, non-petroleum based, carbon neutral, and have low environmental, animal/human health and safety risks [1]. Cellulose is the most common organic compound affecting the Earth's surface, meets the above mentioned requirements and finds its application in many branches of the modern industry. Existence of the cellulose as structural member of plant cell-walls was firstly detected by Ansalm Payen in the 1838. Cell-wall represents the functional structure for every kind of plants [2]. Mankind uses the natural cellulose based materials (wood, hemp, cotton, flax, etc.) for thousands of years and their use in various spheres of the industry continues till today (timber industry, paper, textiles, etc.) [1]. Materials in plant and animal kingdom are entirely based on composite principle. These natural composites were created during millions and millions of years of evolution for a specific purpose, a specific strain and the desired function, with ingeniously crafted structure [3]. However, properties, functionality, durability and uniformity, which are required for the new generation of cellulose based materials and engineering applications, cannot be achieved using these traditional materials. With a view to sustainable development is so necessary evolution both science and technology [1]. Plant fibers are reinforced by helically arranged semi-crystalline microfibrils of cellulose. Cellulose is a polysaccharide with unique but simple structure. It is a linear macromolecule consisting of D-anhydroglucose ($C_6H_{11}O_5$) repeating units joined by β-1.4-glycosidic linkages (**Fig. 1.**).
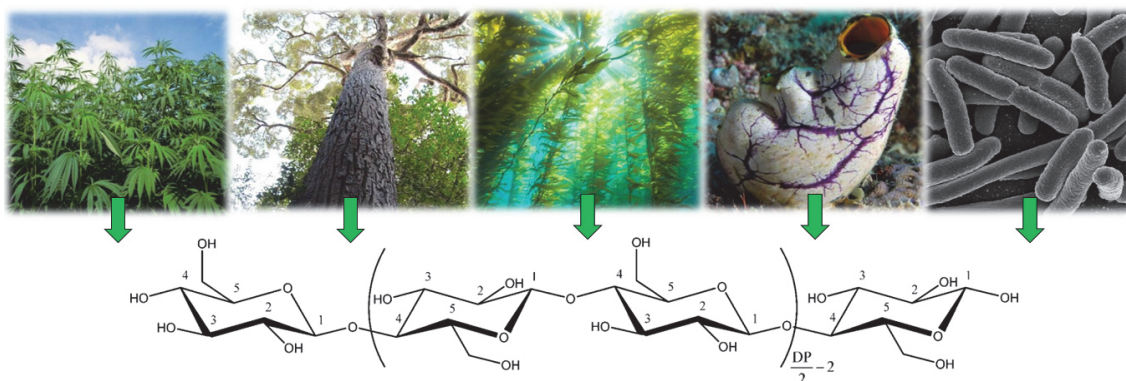

Fig. 1 Examples of cellulose-synthesizing organisms and cellulose chemical structure

Degree of polymerization is around 10 000. Each microfibril is a string of cellulose crystallites, linked along the chain axis by amorphous domains [4]. Crystalline regions considerably predominate and are called cellulose nanocrystals (CNCs). These crystals are essential reinforcing element that nature synthesizes to strengthen all the supporting structures of trees, plants and algae's. Although it is exclusively plant material, it can be synthesized by some marine creatures (tunicates) and even produced by certain types of bacteria called Gluconacetobacter xylinus (reclassified from Acetobacter xylinum). Extraction of cellulose to nano dimensions can eliminate a major cause of defects associated with the hierarchical structure and thus creating a new plant based reinforcing element, that opens the imaginary door for future generation of "green" nanocomposites [1].

Cellulose nanocrystals (or whiskers) occur as high aspect ratio rod-like nanoparticles (**Fig. 2**). Their geometrical dimensions depend on the origin of the cellulose and hydrolysis conditions. The most commonly used extraction method is hydrolysis using concentrated acids (hydrochloric, sulphuric, hydrobromic, phosphoric, etc.). Extraction process is based on penetration of amorphous regions by hydronium ions, followed by hydrolytic cleavage of the glycosidic bonds and releasing individual CNCs after mechanical treatment [5]. Additionally have been recently reported other promising extraction processes, such as selective TEMPO oxidation [6], enzymatic hydrolysis treatment [7], and treatment with ionic liquids [8].
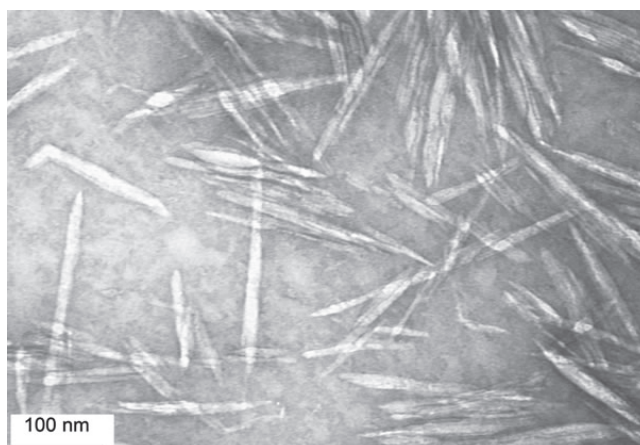
Fig. 2 TEM of freeze-dried cotton CNCs [9]

Desired property for a reinforcement fiber in composite system is certainly high stiffness. For determination of the axial modulus of CNCs have been used both theoretical and experimental strategies. Eichhorn et al. [10] summarized some obtained values of cellulose crystal modulus. Reported have been values in the range 100-160 GPa. In comparison with other conventional construction materials (**Table 1**), moreover, when one takes into account the low density (1.5 g cm^{-3}) of the cellulose, the value of specific modulus (Young's modulus / density) is significantly high [10]. The main cause of failure in the processing of the nanocomposite is inhomogeneous dispersion and distribution of CNCs in the polymer matrix. There is strong tendency of CNCs to agglomerate and form clumps and interconnected networks due to hydrophilic nature (omnipresence of hydroxyl groups on the surface) and because of the formation of additional hydrogen bonds between nanoparticles [5]. To avoid irreversible agglomeration of CNCs during composite processing and improve the potential of mechanical reinforcement, adsorption of polyethylene oxide (PEO) onto CNCs was performed. The nucleation effect of PEO-adsorbed CNCs on PLA matrix crystallization was investigated.

Table 1 Moduli of engineering materials compared to cellulose [10]

Material	Modulus (GPa)	Density (Mg m^{-3})	Specific modulus (GPa Mg^{-1} m^3)
Aluminium	69	2.7	26
Steel	200	7.8	26
Glass	69	2.5	28
Crystalline cellulose	138	1.5	92

2. EXPERIMENTAL METHODS

An extraction process is shown in **Fig. 3**. Initial cellulose material for extraction of CNCs was cotton microcrystalline cellulose (MCC). Material was purchased from ZIBO ZIMAO TRADE CO., LTD (China). Used extraction conditions was based on work of Ioelovich [11]. The initial MCC was mixed with deionized water

(DIW) in a lab glass, and then was slowly added highly concentrated sulphuric acid (H_2SO_4) to obtain required final concentration of acid from 55 to 60 wt. % and acid/cellulose ratio from 8 to 10. To prevent burning of MCC due to exothermic reaction between acid and water, reaction was carried out at cooling in ice bath. The glass with solution was then placed into water bath having temperature from 45 to 55℃ and heated at stirring for 45 to 60 min. Hydrolytic reaction was then terminated by pouring the suspension into tenfold of deionized water. The solid phase has been separated from the liquid by series of centrifugation in a laboratory centrifuge at 3200 g for 10 minutes. After each series followed replacement of the supernatant above sediment and replacing it with deionized water until pH 6 was reached. The suspension was then placed into ice-cold ultrasonic bath at 80% power for 10 minutes. Obtained aqueous suspension of CNCs were stored in refrigerator.
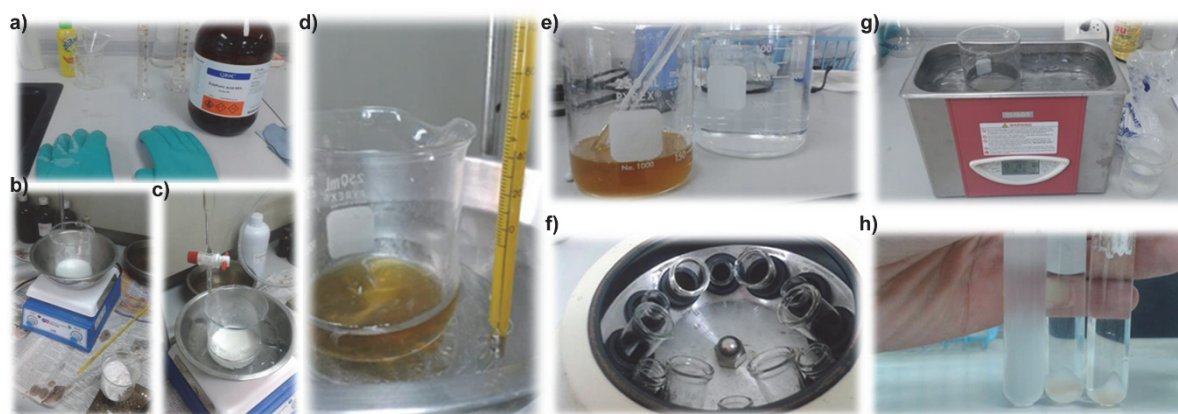
Fig. 3 CNCs extraction procedure (in alphabetical order)

Extracted particle size analysis was conducted by Dynamic light scattering (DLS) using Zetasizer Nano ZS (Malvern, UK). Method of PEO adsorption onto CNCs was adopted from procedure described in the literature [12]. PEO with two different molecular weights (M_w= 200,000 g/mol and M_w= 400,000 g/mol) were obtained from Sigma Aldrich. The concentrated CNCs/DIW suspension was transferred to glass beaker to reach desired concentration. After that, required amount of PEO was added to reach 2 wt. %. Final solution was stirred for 2 hours with magnetic stirrer at ambient temperature. The control CNCs a PEO adsorbed CNCs (PEO-A-CNCs) were then freeze dried. Further than both control CNCs and PEO-A-CNCs were homogenously re-dispersed in chloroform and PLA (Ingeo™ 3251D, NatureWorks, USA) was added to reach desired 5 wt. % concentration of CNCs. The solution was maintained at ambient temperature under stirring until PLA was completely dissolved. Finally was applied sonication 60% output power for 10 min and resulting materials were then vacuum-dried in an oven for two days at 60°C. Study of crystallization was conducted by differential scanning calorimetry (DSC) (DSC 1/700, Mettler Toledo). The samples amount was 15 mg and analysis run at 10 °C min^{-1} heating/cooling ramp in one heating-cooling cycle in a nitrogen atmosphere (flow rate 50 ml.min^{-1}). From resulted thermograms we studied effect of unmodified CNCs and modified PEO-A-CNCs on crystallization of PLA and thermal properties such as exothermic peak cold crystallization and premelting temperature (T_{PCC}), endothermic peak melting temperature (T_{Pm}), peak melt crystallization temperature (T_C), cold crystallization and premelting enthalpy (ΔH_{CC1}, respectively ΔH_{CC2}), fusion enthalpy (ΔH_f), melt crystallization enthalpy (ΔH_C) and degree of crystallinity (χ_C). The crystalline fraction χ_C (%) of PLA nanocomposite samples can be calculated based on the enthalpy value of a 100 % crystalline PLA from the following equation [13]:

$$\chi_C(\%) = \frac{\Delta H_f - \Delta H_{CC}}{\Delta H_f^0 \cdot W_m} \times 100 \tag{1}$$

where ΔH_f^0 is melting enthalpy of totally crystallized PLA sample (ΔH_f^0 = 93 J g^{-1}) [4] and W_m is PLA matrix weight fraction in the nanocomposite sample (W_m=0.95).

3.   RESULTS AND DISCUSSION

Based on investigations have been found ideal conditions for extraction of CNCs from cotton MCC (**Table 2**). Samples treated with lower concentrated H_2SO_4 (< 55 wt. %) showed micro-scale particles under optical microscope investigations. This phenomenon could be addressed to strong lateral contacts between CNCs that is hard to break with diluted acids and crystallites than remained intact. Higher concentrated H_2SO_4 (> 60 wt. %) hasn´t been investigated due to dissolution of MCC in acid and formation of low crystalline amorphous ellipsoidal nanoparticles that is described elsewhere [11]. Lower treatment temperatures further than resulted in longer extraction times and higher temperatures resulted in burning of samples. Average spherical hydrodynamic diameter obtained from dynamic light scattering (DLS) measurements of samples has been found to be 220±42 nm. This number could be assigned to average length of extracted CNCs. The interaction of solvent molecules and agglomeration must be taken into account with DLS analysis. Since DLS is suitable analysis for spherical particles measurements, for rod-like CNCs larger dimensions has been probably found. This proposition will be compared in future investigations with AFM or TEM analysis that provides an estimation of the projected area.

Table 2 Ideal CNCs extraction conditions

H_2SO_4 concentration	H_2SO_4/cellulose ratio	Treatment temperature	Treatment time	Ultrasonication time
55 - 60 wt. %	8 - 10	45 - 55°C	40 - 60 min	10 min

In the DSC measurements an distinct exothermic peak of amorphous PLA can be found, related to the cold crystallization above T_g, and an endothermic peak, relate to the melting. When PLA is recrystallized prior to measurement, the exotherm in the DSC curve is not present. Recrystallized PLA products also carry a huge advantage compared to amorphous products, related to higher mechanical properties and heat deflection temperature (HDT). The resulted degree of crystallinity (χ_C) from DSC heating and cooling scans (**Fig. 4**) is shown in **Table 3**. Compared with pure PLA, addition of unmodified CNCs (5 wt. %) (e.g. PLA/CNCs-5) rise value of χ_C from 8.6% to 18.1%. Slightly increased value of χ_C=19.2% compare to PLA/CNCs-5 (18.1%) has been calculated for samples with surface modified CNCs by adsorption of lower molecular weight PEO (M_w= 200,000 g/mol) (e.g. PEO2) marked as PLA/PEO2-A-CNCs-5. On the other hand nanocomposite samples marked as PLA/PEO4-A-CNCs-5, where CNCs were surface modified by adsorption of higher molecular weight PEO (M_w= 400,000 g/mol) (e.g. PEO4) significantly increased value of χ_C from 8.6% to 40.5%. In DSC heating scans exothermic peak of cold crystallization (ΔH_{CC1}) was not presented for PLA/PEO4-A-CNCs-5 samples and thus can be postulated that samples were recrystallized prior to measurements. This could be addressed to more homogeneous dispersion and distribution of CNCs in the polymer matrix where CNCs works as bio based nucleation agents. After adsorption of PEO molecular chain on CNCs surface, works as steric hindrances and prevent formation of aggregates during processing.
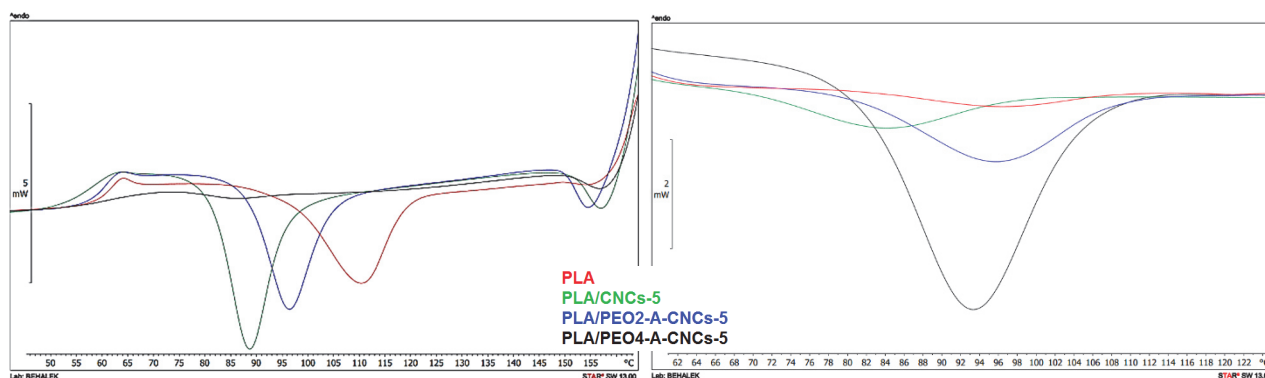
Fig. 4 DSC heating (left) and cooling (right) scans

Table 3 Thermal parameters of PLA, PLA/CNCs and PEO adsorbed CNCs nanocomposites

Material	ΔH_f (J g^{-1})	ΔH_{CC1} (J g^{-1})	ΔH_{CC2} (J g^{-1})	ΔH_C (J g^{-1})	χ_C (%)
PLA	35.6	26.9	0.7	-	8.6
PLA/CNCs-5	36.2	18.2	2.1	4.2	18.1
PLA/PEO2-A-CNCs-5	34.6	15.3	2.3	8.9	19.2
PLA/PEO4-A-CNCs-5	36.6	-	0.8	25.9	40.5

4. CONCLUSION

In this work renewable, sustainable and bio based stiff cellulose nanocrystals (CNCs) have been extracted from microcrystalline cellulose (MCC). The effect of ideal conditions on extraction process has been studied: H_2SO_4 concentration (55 - 60 wt. %), H_2SO_4/cellulose ratio (8 - 10), treatment temperature (45 - 55°C), treatment time (40 - 60 min) and ultrasonication time (10 min). Average spherical hydrodynamic diameter obtained from dynamic light scattering (DLS) measurements has been found to be 220±42 nm. Nanocomposites based on unmodified and modified CNCs and PLA matrix have been prepared. Nucleation effect CNCs on PLA matrix crystallization were investigated. To avoid irreversible agglomeration of CNCs during composite processing and improve the potential of mechanical reinforcement, adsorption of polyethylene oxide (PEO) onto CNCs surface was investigated. Study of crystallization was conducted by differential scanning calorimetry (DSC). The crystallization rate calculated from DSC scans was strongly increased by addition of both unmodified and modified CNCs. Compare with pure PLA, degree of crystallinity for PLA/CNCs-5 samples increased from 8.6% to 18.1%. Slightly increased value 19.2% was observed for PLA/PEO2-A-CNCs-5 samples reinforced with modified CNCs by adsorption of lower molecular weight PEO2 (Mw= 200,000 g/mol). Most promising results has been found for PLA/PEO4-A-CNCs-5 samples modified by adsorption of higher molecular weight PEO4 (Mw= 400,000 g/mol). Degree of crystallinity was significantly increased compare with pure PLA from value 8.6% to 40.5%. Adsorption of higher molecular PEO molecular chain on CNCs surface avoid irreversible agglomeration during processing due to steric hindrances, improve homogeneous dispersion and distribution of CNCs in the polymer matrix and significantly increase crystallinity degree of nanocomposite.

ACKNOWLEDGEMENTS

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