



# Nanostructured biocomposites from aliphatic polyesters and bacterial cellulose



Denis Mihaela Panaitescu\*, Adriana Nicoleta Frone, Ioana Chiulan

Polymer Department, National Institute for Research and Development in Chemistry and Petrochemistry ICECHIM, 202 Splaiul Independentei, 060021 Bucharest, Romania

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## ABSTRACT

The fast depletion of fossil fuel reserves, global warming and environmental problems caused by non-biodegradable plastic materials as well as the high toxicity of some synthetic polymers that prevents their use in packaging or medical applications are the main reasons for a greener and more sustainable approach. There is also an imperative demand from the medical sector for more advanced materials with both biocompatibility and specialized functionalities to be used in living systems. High expectations arise from polymers obtained from renewable sources: poly(lactic acid) (PLA), polyhydroxyalkanoates (PHA), poly(butylene succinate) (PBS) and their blends, which are relevant materials for both biomedical and engineering fields. Moreover, bacterial cellulose (BC) has excellent properties and very broad application opportunities. Therefore, considering that these promising biomaterials will play an active role in the future, this review covers the progress made in the study of aliphatic polyesters/BC nanocomposites from the perspective of nanostructure–property relationship. New approaches to obtain aliphatic polyesters/BC nanocomposites with tailored mechanical properties and inherent biocompatibility are also summarized. The updated information from this review will help identifying new directions and strategies to design biocomposites for medical field and other applications.

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## 1. Introduction

At present, crude oil is the most important resource for the fabrication of plastics and other useful materials as well as for power generation. Nevertheless, crude oil is an exhaustible resource, estimated to last only for 100 years. The rapid depletion of petroleum reserves and their uncontrollable price variation, in addition to the growing environmental awareness due to the increasingly negative impact of persistent plastic wastes, have determined intense studies on polymers and composites derived from renewable resources as alternatives to petroleum-based polymers (Armentano et al., 2013; Belgacem and Gandini, 2008; Dufresne, 2013; Gellerstedt, 2015; Rhim et al., 2013; Thakur, 2013; Williams and Hillmyer, 2008). Biopolymers obtained from agro-resources such as starch, cellulose, proteins, lignin, chitosan, some polyamides, poly(lactic acid) or polyhydroxyalkanoates, are increasingly studied as possible replacements of petroleum-based materials (Armentano et al., 2013; de Castro et al., 2016; Dufresne, 2014; Frone et al., 2013; Ghaffar et al., 2015; Moon et al., 2011; Panaitescu et al., 2015;

Thakur et al., 2014). Among all these, cellulose in its nano form has experienced the most rapid progress.

### 1.1. The way from cellulose to nanocellulose

More than 170 billion metric tons of cellulose and other carbohydrates are produced by photosynthesizing organisms every year (Noggle and Fritz, 1983). As the most abundant polymer on the earth, cellulose has attracted great attention from both researchers and industrial manufacturers (Boufi, 2014; Collinson and Thielemans, 2010; Frone et al., 2011; Hurtado et al., 2016; Lavoine et al., 2012; Missoum et al., 2013). At molecular level, cellulose is formed of D-glucose units linked by  $\beta$ -1-4 glycosidic bonds that lead to a flat conformation. This arrangement gives cellulose a great ability to form intra- and inter-molecular hydrogen bonds, which hold the chains packed in the crystalline structure. This explains the high axial strength and modulus of crystalline cellulose. A value of 134 GPa (137 kgf/cm<sup>2</sup>) was determined for the elastic modulus of cellulose crystals by Sakurada et al. (1962), using XRD diffraction and cellulose fibers deformed under a constant stress. This modulus is at the same level with that of Kevlar or other reinforcing fibers but at a lower density (Eichhorn et al., 2010; Moon et al., 2011). Wood and lignocellulosic fibers have much lower elas-

\* Corresponding author.

E-mail address: [panaitescu@icf.ro](mailto:panaitescu@icf.ro) (D.M. Panaitescu).

tic modulus compared to that of crystalline cellulose (about 30 GPa in the case of hemp fibers). For taking full advantage from the remarkable mechanical properties of cellulose crystals, the complex structure of wood or lignocellulosic fibers must be broken down and cellulose crystals released. Although the first TEM image of cellulose nanocrystals prepared by acid hydrolysis of plant cellulose was published by Mukherjee and Woods (1953), it is the merit of Favier et al. (1995) to emphasize the importance of cellulose nanocrystals for polymer reinforcement. Their early studies open a new era, that of nanocellulose and cellulose based nanocomposites, which are still extensively studied and started to be produced in pilot and, even, in full scale plants. Nanocellulose is so important because it brings together in the same material strength, flexibility, biocompatibility, availability and cheapness. The main disadvantages of nanocellulose when it is used for the preparation of polymer nanocomposites, high moisture absorption, limited thermal stability and high hydrophilicity, are not yet fully solved and more research is needed to settle these issues.

Initially, nanocellulose was classified in three types (Klemm et al., 2011): (i) nanofibrillated cellulose fabricated by mechanical treatment as main process (Lavoine et al., 2012; Missoum et al., 2013), (ii) cellulose nanocrystals/nanowhiskers prepared by acid hydrolysis (Habibi et al., 2010; Henrique et al., 2015) and (iii) bacterial cellulose. Nanocellulose produced from solution or melt by electrospinning, using electrical forces, was added at this classification in recent reviews (Pandey et al., 2015; Panaitescu and Frone, 2015; Thakur, 2015). Depending on the source, cellulose can be classified in cellulose synthesized in higher plants including trees, in lower plants such as algae, by some animals (tunicates), fungi, amoebas or by some bacteria (Dufresne, 2012). The purest from all these is the bacterial cellulose, which will be further briefly reviewed.

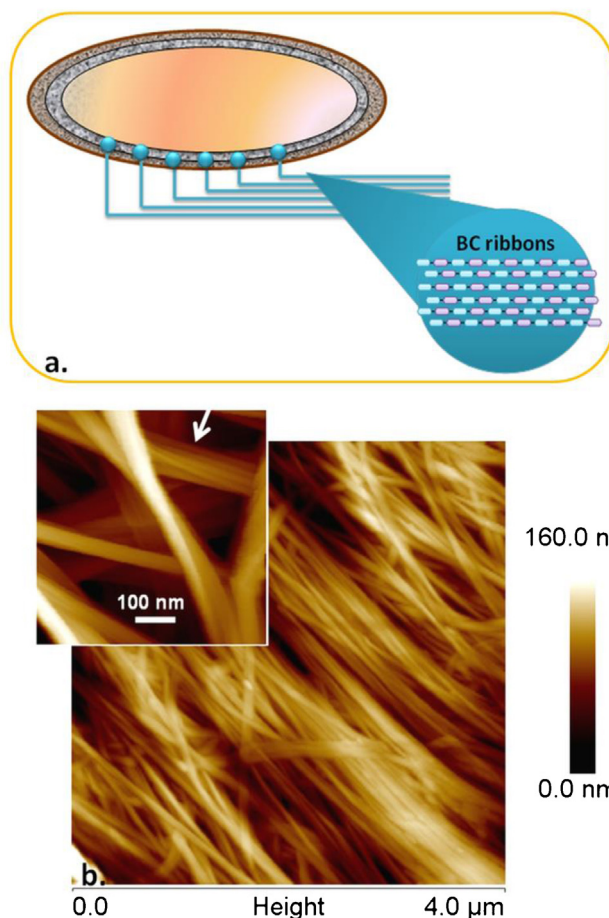
## 1.2. Brief overview on bacterial cellulose and its applications

Bacterial cellulose can be considered as a biomaterial with a bright future in many fields due to its biocompatibility and biodegradability, high purity, fine fiber network structure, high crystallinity, high water-holding capacity and good strength-to-weight ratio. The interest of the academic community in bacterial cellulose is demonstrated by the high number of papers published every year on this topic. For example, more than 1000 papers have been found in the Thomson Reuters databases in the last three years when entering the keyword “bacterial cellulose”. Advances in bacterial cellulose biosynthesis; properties and application have been reviewed in several papers (Brown, 2004; Gatenholm and Klemm, 2010; Huang et al., 2014; Laborie, 2009; Lee et al., 2014; Moon et al., 2011; Panaitescu et al., 2015; Thakur, 2015).

Rapid advancement was observed in the design of the fermentation process for optimum BC production and in the characterization of BC for new applications (Abeer et al., 2014; Castro et al., 2012; Gatenholm and Klemm, 2010; Pourramezan et al., 2009; Sheykhnazari et al., 2011). High attention was also paid to the reduction of BC production costs by using cheaper carbon and nutrient sources, such as agroforestry industrial wastes or byproducts (Carreira et al., 2011; Casarica et al., 2013; Hong et al., 2012).

### 1.2.1. Bacterial cellulose nanostructure

The biogenesis of cellulose by aerobic bacteria as an extracellular polysaccharide membrane is a bottom-up approach whose final result is very pure cellulose. This is different from the top-down method, consisting in the extraction of cellulose from plants and wood (Moon et al., 2011). Bacterial cellulose is produced both as a protection against UV radiation or chemical environment and to access oxygen from the air (Huang et al., 2014).



**Fig. 1.** (a) Schematic representation of microfibril formation and ribbon assembly in the *Acetobacter xylinum* system; (b) AFM topographic image of bacterial cellulose network; inset—detail showing the hierarchical organization of cellulose: the ribbon marked with arrow is formed of 4 microfibrils of about 20 nm in width (Panaitescu and Frone, unpublished).

Biosynthesis of cellulose and its structural organization are not fully understood, but great progress has been made in this field in the last decade (Khandelwal and Windle, 2013a,b; Saxena and Brown, 2013). Synthesis of cellulose by microorganisms consists in the formation of glucan chains and the assembly/crystallization of cellulose chains. A model suggesting at least a 3-level hierarchy of the cellulose chains was proposed based on previous works (Haigler and Benziman, 1982; Brown and Saxena, 2000) and on SEM, AFM, XRD and SAXS analysis results (Khandelwal and Windle, 2013a). Firstly, the cellulose chains synthesized in bacteria (about 16 chains) are spun through the pores giving cellulose first assembly of about 1.5 nm diameter, and microfibrils, 3–4 nm in diameter. These structures assemble to form crystalline microfibrils (of about 20 nm in width) which, at their turn, will associate in flat ribbons, of 80 – 120 nm in width and hundreds of microns in length (Khandelwal and Windle, 2013a). This process is schematically represented in Fig. 1a.

The AFM image of the BC network from Fig. 1b (Panaitescu, unpublished) shows ribbons of about 40–100 nm in width and less than 20 nm in thickness. The detailed image (Fig. 1b, inset) shows the hierarchical organization of cellulose: the ribbon marked with the arrow is formed by an assembly of 4 microfibrils, each of about 20 nm in width. The twist of the ribbons is also obvious in Fig. 1b—inset. The twisted morphology of bacterial cellulose microfibrils and nanowhiskers was previously emphasized by SEM and AFM investigations (Khandelwal and Windle, 2014). Twisted

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