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Nanotechnology - Methods of Manufacturing Cellulose Nanofibres

Abstract

Nanotechnology is still a new science, but already fully developed and increasingly used in everyday life. Cellulose is a polymer of low cost and is also hydrophilic, chiral and can be easily subject to chemical modifications. Moreover, cellulosic material is biodegradable and socially acceptable. All these features make cellulose an attractive replacement for plastics used as composite fillers or reinforcement. A polymer composed of cellulose nanofibres, whose functional properties are determined by the fibril structure, is called nanocellulose. The article discusses the methods of producing nanomaterials and presents different concepts of cellulose nanofibre production of plant biomass

Key words: nanotechnology, manufacturing nanofibres, cellulose nanofibres.

Introduction

Nanotechnology is the science of technology. The enormous development of science and technology that occurred in the second half of the twentieth century has resulted in not only new, bold ideas, but it has also created tools that enable to perceive atoms in surrounding matter. Scientific achievements, especially those made at the end of the twentieth century, have contributed to the significant development of nanotechnology. It was a kind of fait accompli achieved with the cooperation of many fields of science, which has made nanotechnology develop very intensively using the achievements of basic and applied sciences that originate from electronics, biotechnology, medicine, mechanics, chemistry, pharmacy and computer science, as well as the humanities, such as philosophy, economics and ethics.

Sources, definition and application of nanotechnology

Nanotechnology was 'invented' by nature. This type of technology 'has been chosen and perfected' by nature for 5.5 billion years, building up, atom by atom, the environment of life on Earth. The development of science and technology in the twentieth century, showing the undeniable merit of the people, laid theoretical and practical foundations, thanks to which it was possible to look into the structure of matter and see items on a nano-scale (10^{-9} m).

One of the criteria currently used that defines nanotechnology is the size of objects manufactured, which should have at least one dimension not greater than 100 nm. During the production of such objects, their chemical and physical properties should be controllable, and it should be possible to build larger objects from them [1].

Due to the interdisciplinarity of nanotechnology it is often superfluous and sometimes even impossible to subdivide it by placing the nano- prefix before the name of a particular field of science (e.g. nanochemistry, nano-biotechnology). Therefore, this area of science and technology should be treated as one common nanotechnology (*Figure 1*). Nanotechnology plays the role of a platform joining together various disciplines in order to produce successful, easy to sell products.

History of nanotechnology

The beginning of nanotechnology as a field of science and technology dates back to 1959, when the physicist Richard Feynman gave a visionary talk at the convention of the American Physical Society. His lecture – "There is plenty of room at the bottom" – on the construction of machines from individual atoms, which would have the ability to self-assemble and create various objects, forever revolutionised the world of science, although Feynman did not use the term nanotechnology [2]. The term "nanotechnology"



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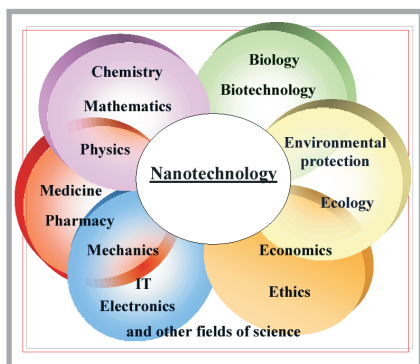


Figure 1. Interdisciplinarity of nanotechnology.

was coined in 1974 by Norio Taniguchi as an explanation of the possibility of engineering materials on the nanometer level [3].

Currently, measuring equipment used in nanotechnology and machinery for the production of nanoparticles is becoming much better and cheaper every year. Scientific and popular literature literally engulf their readers in various information, and research laboratories and industries are designing and producing a broader and broader range of nano-products that are placed on the market.

Methods of producing nanoproducts

Both animate and inanimate matter contain nanostructures made of atoms, which - assembled and organised - are the building blocks of the environment.

There are two basic approaches for creating nanostructures - bottom-up [4, 5] and top-down [6]. The bottom-up method involves construction on a molecular scale from scratch using atoms, molecules and nanoparticles as building blocks. This method uses chemistry- and physics-derived technologies which are based on chemical synthesis or strictly controlled mineral growth [7].

The top-down method involves the disintegration of macroscopic material to a nano-scale by the following methods: mechanical (e.g. grinding), chemical (e.g., partial hydrolysis with acids or bases), enzymatic (e.g., treatment with enzymes hydrolysing cellulose, hemicellulose, pectin and lignin) and physical (e.g. techniques using focused ion beams or high-power lasers) [7].

Products of nanotechnology

Nowadays, still at the very beginning of the road of development, several hundred laboratories conduct research and produce many nano-products, such as powders, lotions, liquids and fibres [8 - 14], which can be used by consumers directly or are vital additives to traditional products. The nanoparticle content imparts extremely useful properties to the new products, hence the technologies used to produce them are often defined as revolutionary. The value of world production of nanomaterials in 2010 reached the level of \$ 1.7 billion, with an average annual growth in the last five years amounting to 10.4%. It is anticipated that by 2016 the worldwide market for nanomaterials will reach U.S. \$ 5.8 billion, an increase of 23%. [15]. Other estimates suggest that by 2016 the volume of the production of nanomaterials will more than double, to about 44 thousand tons due to increased demand from areas such as electronics, energy production and processing, pharmaceuticals, chemical manufacturing, coatings, and catalysts [16].

Nanofibres

Nanofibres have diameters of less than 100 nm, which is several thousand times smaller than that of a human hair, hence you can observe them only using an electron microscope. Their properties are unique, often impossible to describe by traditional laws of physics. Nanofibres have such a large surface area, but 1 m² of them weighs only 0.1 - 1 gram [17].

Such fibres are largely obtained by the bottom-up approach using the electrospinning of polymer melts or solutions such as fibre formed from synthetic polymers such as PVA [18], PLA [19] or their mixtures and processed raw materials such as cellulose, chitosan, keratin, starch or their mixtures [20-30].

The top-down method can also be used to obtain nanofibres. In this case, for example, natural vegetable fibres contained in the biomass are disintegrated to a nanosize with the use of thermal, chemical [31-33] or biotechnological processes using biorefining [34].

Nanofibres produced from cellulose

Cellulose is a material widespread in nature, and it may be obtained from many natural sources, such as wood, cotton and vegetable biomass [35]. Cellulose is also

synthesised by algae and some bacteria. Another interesting source of cellulose are tunics of marine animals – tunicates [36,37].

Cellulose nanofibres derived from plant biomass are a particularly desirable group of nano-products. The almost unlimited availability of the raw material, its biodegradability and biocompatibility with the animated world make a lot of laboratories conduct research on the development of nano-fibre manufacturing technologies [35 - 38]. Both the bottom - up and top - down processes are applicable to the production of cellulose nanofibres. In the bottom - up method such techniques as electrospinning can be used [39 - 42], where nano-fibre is spun from cellulose solution, which initially may also contain solid nanoparticles [43]. The top-down method uses physical [44 - 47] or chemical refining [31, 45, 48], biorefining [34] or combinations of these methods [36], consisting in the removal of plant cell constituents other than cellulose, such as pectin, hemicellulose, lignin, and minerals. Moreover the appropriate treatment of cellulose fibres can increase the availability of hydroxyl groups, change the degree of crystallinity, develop the inner surface, and break hydrogen bonds, which increases the reactivity of cellulose [49, 50]. Conducting the process under appropriate conditions can lead to the separation of cellulose fibres in macro- and micro-fibrils [36, 51, 52]. Micro-fibrils in cellulose are composed of elongated crystalline areas separated by amorphous regions. It is assumed that the amorphous regions may act as structural defects of the material, which are responsible for the lateral division of micro-fibrils into nanocrystals during the hydrolysis of cellulose [53].

Cellulosic materials intended for use as nano-fillers in composites are usually subjected to hydrolysis by strong acids such as sulfuric or hydrochloric acid, which causes a selective degradation of amorphous regions of cellulose and, consequently, the splitting of micro-fibril beams. As a result of cellulose hydrolysis, the disintegration of its hierarchical structure takes place to form crystalline nanofibres or nanocrystals, usually referred to in literature as nanowhiskers. The morphology of the nanocrystals obtained depends on the source of cellulose and hydrolysis conditions used, such as acid concentration, the ratio of acid to cellulose, temperature and reaction time.

In general, cellulose nanocrystals obtained from plant materials are characterised by a length in the range 100 - 300 nm and width of 5 - 20 nm [54, 55], and those extracted from cellulose derived from tunicates - marine invertebrates and from cellulose synthesised by certain bacteria may have a length of several micrometers and width of 5 - 50 nm [36, 56]. As a result of cellulose hydrolysis with sulfuric acid nanocrystals are obtained forming stable suspensions in water due to the presence on their surfaces of a mutually repulsive negative electrostatic charge. This is because of the surface esterification of hydroxyl groups of cellulose with sulfate groups. Unfortunately, in addition to the favorable reduction of nanoparticle aggregation, the presence of sulfate groups on the surface of cellulose considerably reduces the thermal stability of the material [55], which is undesirable, especially in the application of cellulose nanofillers to reinforce composites based on thermoplastic polymers. The solution to this problem may be the neutralisation of remaining acid after hydrolysis, which allows to obtain cellulose nanocrystals with a thermal stability enabling their processing at temperatures above 200 °C.

The oxidation of cellulose using 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) as a catalyst allows the formation of carboxyl groups in the C6 position from hydroxyl groups present on the surface of the fibres. Since the dissociated carboxyl groups are negatively charged, there are repulsive forces between micro-fibrils, thanks to which cellulose nanofibres with a diameter of 3 - 4 nm may arise from the simple mechanical treatment of the oxidised material. The reaction can be carried out under alkaline or acidic conditions with the addition of various reagents as oxidants. Films formed from TEMPO-oxidised cellulose are characterised by good transparency, thermal stability and low permeability to oxygen. Both TEMPO and its analogs are soluble in water [32]. The product of cellulose oxidation catalysed by TEMPO is, in contrast to native cellulose, resistant to acid hydrolysis and susceptible to alkaline hydrolysis. It is also resistant to the depolymerisation carried out using typical cellulase. However, it may undergo biodegradation catalysed by enzymes produced by microorganisms that occur naturally in the environment, such as bacteria of the genus *Brevundimonas* [57].

Another method of obtaining microfibrillar cellulose, known since the early eighties of the twentieth century [58], is the delamination of cellulose fibres dispersed in water using a high-pressure homogeniser at a pressure of 150 - 200 MPa. Cellulose microfibrils obtained in this way have a length of several micrometers, while their diameters are in the range of 25 - 100 nm.

For the production of nano-cellulose, enzymes can also be used which, in combination with refining methods, is called biorefining [59, 60]. For this purpose multi-enzyme preparations are usually applied which contain enzymes degrading both cellulose and other accompanying polymers, such as pectin, hemicellulose and lignin. Enzymes can be used in two ways: Firstly the treatment of biomass with enzymes such as pectinase, hemicellulase and ligninase may lead to the removal of non-cellulose materials. Secondly, in order to obtain nanofibres, industrial cellulases can be used, which are enzymes with various activities that can hydrolyse cellulose into smaller structural elements, as well as into oligosaccharides, cellobiose and ultimately – into glucose.

One of the components of the celololytic complex is endoglucanase - an enzyme that selectively hydrolyses amorphous areas of cellulose in a random manner, causing the breakdown of cellulose fibres into smaller fragments [61] and resulting in different fractions of products. This treatment allows to obtain cellulose nanoparticles [39, 62].

The crystalline areas of cellulose, in contrast to the amorphous regions, show a large number of hydrogen bonds, making them more resistant to the action of enzymes.

The advantage of enzymatic hydrolysis, in contrast to acid hydrolysis, is the fact that the fibre surface is not esterified e.g. by sulfate groups. Nano-cellulose thus obtained is a biocompatible material and can be used to produce biomedical and pharmaceutical products [63]. Enzymatic processes are widely considered to be 'clean', i.e. environmentally friendly, unlike conventional methods of acid hydrolysis.

The inclusion of additional enzymatic hydrolysis to the nanofibre manufacturing process, in addition to mechanical treat-

ment, enables the separation of fibrils in nano-fibrils with diameters smaller than those extracted using only mechanical methods. Enzymatic hydrolysis compared to acid hydrolysis provides longer nano-fibres characterised by a greater number of connections between nanofibrils. These are desirable characteristics for nano-cellulose used as a reinforcement in composites.

Enzymatic hydrolysis applied prior to grinding or homogenisation allows the reduction of energy consumption in these processes, thus reducing the cost of producing nano-fibres [64].

Application of nano-fibres

Because nanofibres can be produced from polymers which do not always fall within the concept of classical fibre-forming polymers [17], it is anticipated that the scope of use of these nanoproducts may be far beyond the use of standard fibres, micro-fibres or fibrous materials.

The bottom-up method allows the introduction of additional modifiers (at a molecular or supramolecular level of fragmentation) into a polymer/polymer blend before the formation of fibres, which gives them new, specific properties favourable from a practical point of view.

Some of the areas in which the use of nanofibres is expected include the following: medicine (drug carriers, surgical materials, prostheses, dressings), cosmetics (creams and nutritional ingredients, tampons, masks), the environment (sensors, filters, nanofilters, adsorbers), energy (electric cells, hydrogen storage), chemistry (catalysts with high efficiency, ultra-light materials and composites), electronics (computers, shields for electromagnetic radiation, electronic equipment), textiles (clothing and functional products), defense (special-purpose clothing, face masks) [64 - 69].

■ Summary

It should be noted that the development of technological sciences, including nanotechnology, can be hindered or even halted due to a lack of public acceptance. For this reason, a broad information campaign is needed, besides considerable funding and spectacular scientific progress, in order to promote the expected benefits of nanotechnology but with-

out neglecting any possible costs that society will have to bear.

In our opinion, cellulose nanofibres will form a reliable starting point to produce a whole range of useful polymeric materials.



Acknowledgment

- This paper was written within the promotional action of a research project of Operational Programme Innovative Economy: 'The use of biomass for the production of environmentally friendly polymeric materials', with the acronym BIOMASS No 01.01.02-10-123/09.
- One of the aims of this program, conducted in 2010-2013, is to produce cellulose nanofibres from plant biomass. These intentions will be realised in two task packages: PZ 2.1. 'Multi-enzyme preparations for targeted degradation of plant biomass' and PZ 3.1. 'Preparation of cellulose nanofibres from plant materials'. These tasks aim to produce cellulose nanofibres from selected biomass (e.g. flax, hemp, rape) using enzymatic, chemical and physico-chemical treatment, and then to process them into innovative, biodegradable composite materials.

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Received 16.07.2010 Reviewed 10.12.2010

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