Letter to the Editor

Material science and bionanotechnology: extracts of a meeting

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Introduction

Natural products, widely used in traditional medicine, are a common source of bioactive molecules used as active ingredients, carriers and biodegradable packaging. Thus, one of the major goals of the delivery system is to increase the efficacy of the selected ingredients that should penetrate the designed site of interest. Moreover, biodegradable and biocompatible natural polymers are the best materials to be used as carriers of pharmaceutical and cosmetic active ingredients that enhance their stability characteristics. Moreover, skin penetration and the consequent product efficacy seem to be increased when the ingredients are used at their nano-size dimension, therefore made by the nanotechnology (1, 2).

This technology makes it possible to make minute particles on an atomic or molecular scale, whose size is measured in nanometers (nm) (i.d., one billionth of a meter). However, on the other hand, the consumer's request is for effective and safe products made with natural ingredients (3). Consequently, the so-called green and sustainable chemistry was born, based on natural ingredients made possibly at their nanoscale. Thus, sustainable chemistry is defined as "the utilization of a set of principles that reduces or eliminates the use of generation of hazardous substances in the design, manufacture and application of chemical products" (4, 5).

All the products should aim to maintain good health for humans and the environment, coping with nature's way of producing without producing waste. According to James Lovelock, the physicochemical and biological processes of the inhabitants of our planet are capable of self-regulation to maintain the best rules for living together (6). As a consequence, humans and animals depend on energy produced during plants' photosynthesis, and, in turn, plants depend on carbon dioxide, produced by mammals, and nitrogen from bacteria. Therefore, no one can survive alone but, living together, it's possible to maintain the general condition of life. Thus, the necessity to change the way of producing, consuming and transforming the actual linear economy into a circular green economy, re-designing, reusing and recycling all the goods without producing waste material (Fig. 1). The expanding fossil-based economy has created local and global environmental and social problems and tensions, including climate changing, biodiversity loss and increased pollution (7).

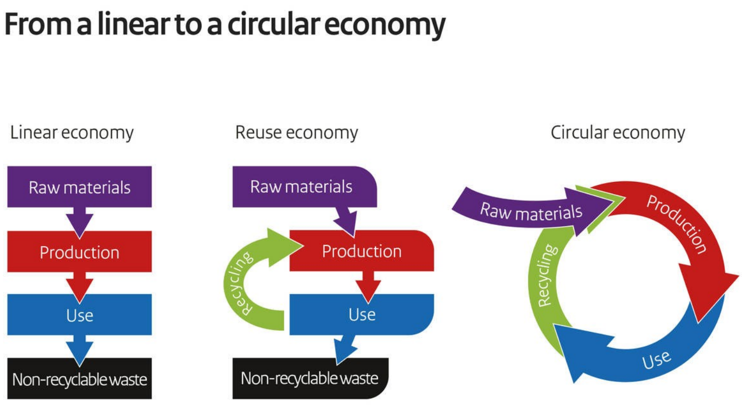

Fig 1. *From Linear to a circular economy, possibly green.*

For all these reasons, there is an increasing worldwide recognition that the transition to a green bio-based and sustainable economy could generate more sustainable growth and address some of the systemic problems of the current economic balance, such as the decline of eco-systems and the consequent increase of biosphere temperatures, which have caused frequent disasters in the last years. According to the World Commission on Environment and Development, "sustainable development is a development that meets the needs of the present without compromising the ability of future generations to meet their own needs" (8). Thus, the use of waste by innovative bio-nanotechnologies with lower water consumption and green renewable energy could deliver climate-resilient development and a healthier eco-system, ameliorating the global habitat and maintaining the planet's biodiversity also.

Such was the aim of a one-day international meeting held in Rome on October 5 of the current year on the topic: Material Science & Bionanotechnology: Natural Ingredients, Carriers and Packagings of Pharmaceutical and Cosmetic use.

Most of the papers presented reported the possibility that natural polymers (biopolymers)should be used as carriers to produce innovative, safe, biodegradable, noninvasive drug delivery products. Through these polymers, it is possible to produce innovative goods such as smart tissues, which, mimicking the productive processes that occur in nature, may minimize the environmental impact.

A view to the meeting's papers

Under the direction of prof Giuseppe Marceca and the undersigned in the First session and prof Marceca and prof Torello Lotti, University G. Marconi, Rome, Italy, in the Second session, many papers were reported and discussed during this international meeting. Most of the reported topics regarded the activity of bio (natural) polymers, such as chitin, lignin, and other biocomposites obtained by nanotechnologies.

Biopolymers are monomeric units covalently bonded, forming macromolecules produced by living organisms. These natural molecules, often represented by multifunctional porous, self-repairing materials, are made of stiff and soft components organized in hierarchical structures that, able to retain strength and flexibility, provide valid paths for mass transport (9-11).

Thus biopolymers, obtained from organic and forestry waste and opportunely engineered, offer new possibilities in several applications and demonstrate special properties, such as the use of biodegradable bio-nano materials to create active ingredients, carriers and packaging for the medical, cosmetic, textile, and agricultural market (9-11). For example, they may be used in the medical field to realize drug delivery systems, surgical implant devices, wound closure and healing products. Furthermore, biopolymers may also support cell growth and proliferation by their porous structure due to their excellent stability and mechanical properties, biocompatibility, biodegradation to non-toxic end products, and high bioactivity (12, 13). Moreover, helping to eliminate worldwide waste is fundamental to saving human health and the environment.

For this purpose, prof Vladimir E Yudin, Head department of the Institute of Macromolecular Compounds, Russian Academy of Science, St Petersburg, reported interesting data on chitosan as an anti-burn drug and drug delivery system to make medical devices and to develop innovative cosmetic products. Thus, a cosmetic serum was developed composed of chitosan (CS) and chitin Nanofibrils (CN) based on the film-forming property of CS and the skin' penetrating property of CN. In addition, nanofibers scaffolds explicitly made by CN and its complexes with hyaluronic acid and biolignin (CN-LG). This complex provides, in fact, an excellent binding affinity as well as an entrapment and loading capacity of active ingredients, releasing them continually for a longer duration after applications on the skin (14-16) (Fig. 2).

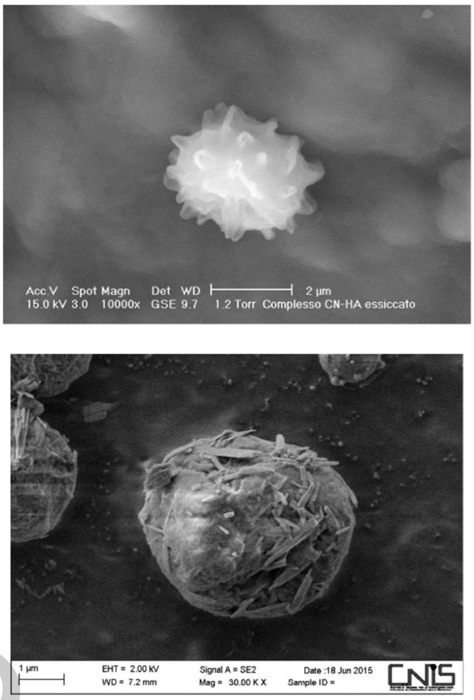

Fig 2. *Chitin Nanofibrils-hyaluronic acid complex (up) and Chitin Nanofibrils-Nanolignin (down).*

These natural nanofibers are also used to make innovative and biodegradable tissues (17) and possess an adequate and open interconnected pore structure which allows the best interaction with bioactive molecules to help cell growth and proliferation. However, it is important to remember that pore interconnectivity and pore size distribution are essential for most applications together with the total porous morphology (11-13). Going back to the topic discussed by Prof Yudin, Professor Beatrice Coltelli from the Department of Civil and Industrial Engineering, University of Pisa, Italy, and the undersigned have reported and discussed the method to produce chitin nanofibrils with the relative films and tissues through electrospinning and casting technologies.

The tissues that consist of natural polymers have been shown to possess anti-inflammatory and regenerative skin properties, demonstrating the considerable immunostimulatory activity, being compatible and safe for human skin and the environment, and may find application in both the medical and cosmetic fields (17,18). They are created by fibres bonded together and organised similarly to the natural ones recovered in the extracellular matrix (ECM), providing an ideal environment for cellular growth. Thus, chitin nanofibers are promising when used as scaffolds to repair or replace damaged tissues for tissue engineering applications. However, it is to underline that, to characterise their different activities, these tissues were embedded in various natural ingredients, encapsulated into the complex Chitin Nanofibrils-nanochitin (CN-LG), easily obtained by mixing the two polymers in a water solution; therefore, the surface of these polymers that are covered by electropositive and electronegative charges can form a polymeric block complex encapsulating the designed ingredients via the gelation method.

Regarding CN, it is also to underline that their positively charged Nanoparticles can be more adsorbed on the cell membranes negatively charged, resulting in subsequent cellular internalization. Consequently, and as previously discussed, the micro/nanocapsules created were bound to the fibres of the tissue during the electrospinning process to characterise their activity. To better understand the chitin nanofibril's function and reactivity, it must be underlined that chitin is a linear semicrystalline polymer consisting of nano fibrillar bundles called microfibrils. This polymer, isolated from crabs, shrimps, krill, lobsters, insects, and fungal and yeast walls, represents the second most abundant natural polymer in nature, after cellulose, being present in its beta gamma and alpha form. Alpha Chitin, the most abundant, has a more compact form, and having the chains arranged in an antiparallel fashion, favours strong hydrogen bonding. In contrast, Beta Chitin has major stability, having wearers intermolecular forces and gamma-Chitin is a mixture of alpha and beta chitins (Fig. 3) (19).

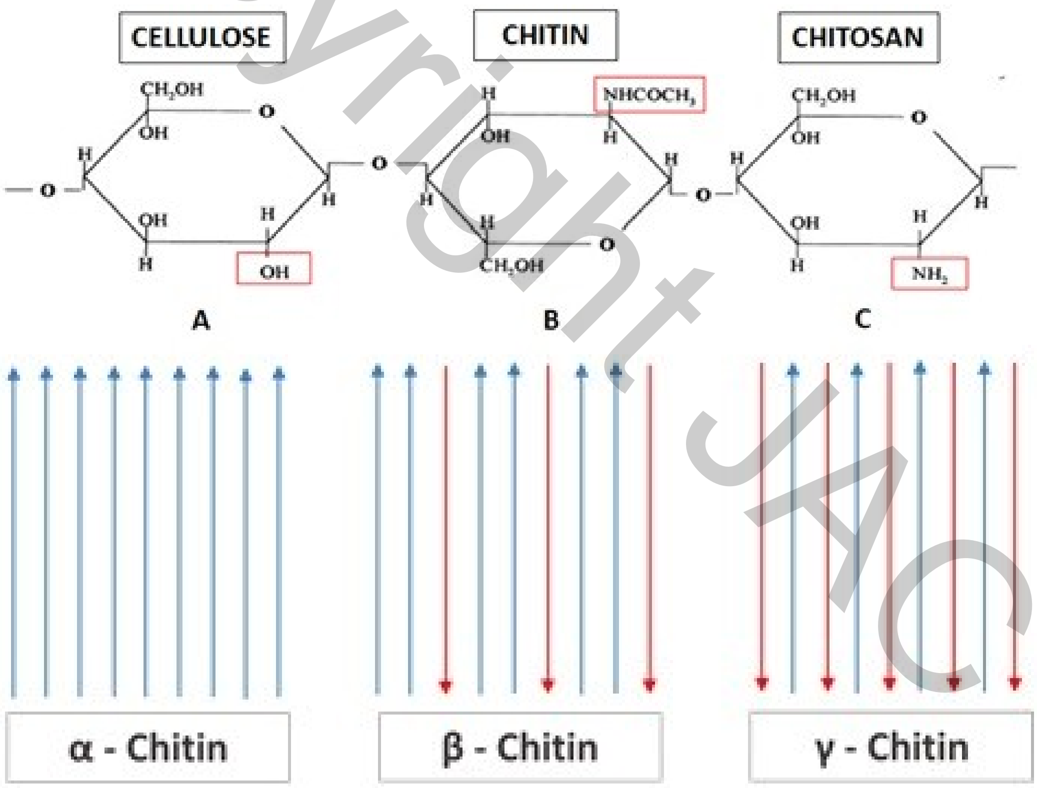

Fig. 3. *Chemical differences among cellulose, chitin and chitosan (up) and the different form ofchitin (below) (by courtesy of Broqua et al. (19).*

Chitosan is the deacetylated chitin form, recuperated industrially by a 70 to 90% deacetylation process, while chitin Nanofibrils are obtained when deacetylated at 50 to 60%. Moreover, 1 ml of the aqueous colloid CN dispersion contains about 300 trillion nanocrystals enveloped with water. At the same time, chitin nanofibril crystal with about 15.000 amino groups for 1 nm3 appears as a needle-like crystal with a mean dimension of 240x7x5 nm and a water uptake capability of about 400 wt %, in comparison with normal chitin (20).

As previously reported, chitin and chitosan may also be obtained from insects, such as Hermetia illucens; their extraction, production and characterization are amply discussed in various papers by Carmen Scieuzo and by Dolores Iannicello and Anna Guarnieri from the department of Science, University of Basilicata, Campus Macchia Romana, Potenza, Italy, brilliantly and masterly directed by Prof. Patrizia Falabella. These studies have shown the possibility of making Nanoparticles of chitin and chitosan by the ionic gelation method, determining their morphology and size and confirming their antimicrobial activity against both gram-negative and gram-positive bacterial species, according to their previous published papers (21).

Prof Patrizja Cinelli, Department of Civil and Industrial Engineering, University of Pisa, Italy, has reported a study conducted with her collaborators on these polymers, showing how nanochitin-nanolignin can be electrosprayed on cellulose tissues or to other natural polymers to be used not only for skin application but also to make sustainable, biodegradable packaging (22-23). Thus, for example, the bamboo fibres and the electrospun tissues may be used for bone reconstruction due to the similarities of the two hierarchical structures (Fig. 4) (11, 24).

As previously reported, the focus on electrospun nonwoven polymers came from a desire to create possible biomimetic scaffoldings made by the same structures found in living tissues (23). Using natural polymers such as collagen and chitin nanofibrils and lignin obtained from renewable sources, it is possible to develop natural biocompatible systems capable of enhancing tissue repair and regeneration and/or making biodegradable packaging (23-25). Furthermore, through the electrospun of these biopolymers, it is possible to obtain biodegradable and biocompatible porous scaffolds which, acting as templates, facilitate the diffusion of cells anabolism and catabolism with the consequential enhancement of their growth and survival.

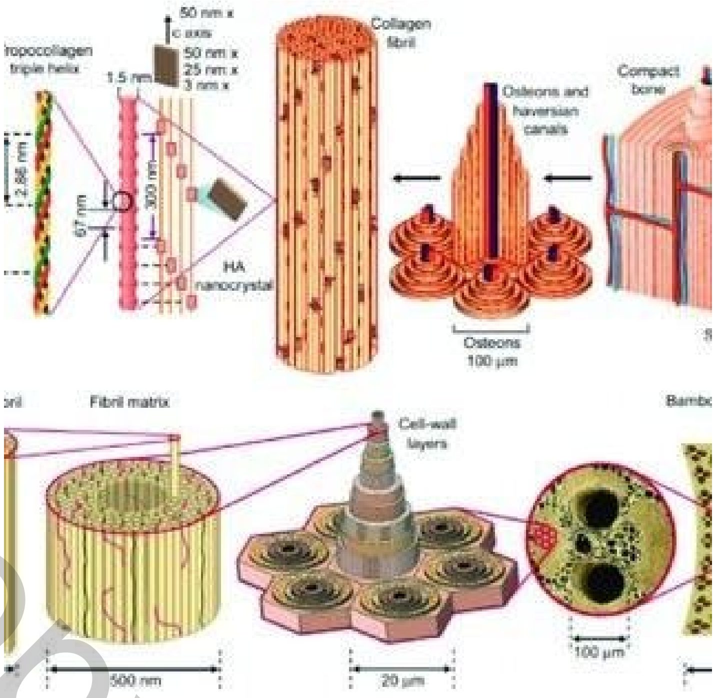

Fig. 4. *the similarities between the hierarchical structures of bone and bamboo (by courtesy of Weigst et al (11)).*

The properties of lignin used to make the Chitin-Lignin Complexes were reported and discussed from Dr Bouchra, R&D Department of CIMV, Labege, France. She has shown the added value and high purity of the sulfur-free bio-lignin, produced industrially from the biomass obtained from forest residues, sugar cane, wheat, corn and rice straw. By the same process, CIMV produces cellulose pulp, xylose, glucose, silica and bioethanol to be used as energy fuel, fine chemicals and bioplastic (25).

In regards to the use of bamboo fibres to make Nonwoven tissues, Dr Alessandro Gagliardini, together with Dr Carmine Cimini and Valentina Di Fazio (R&D Unit, Texol Srl, Alanno (PE) Italy), have focused their presentation on the production process, the physicochemical characteristics and the biological properties of this interesting polymer, to use as nonwoven fabric in the production of table clothes, hygienic and wet wipes for personal care, specialized medical devices and automated applications.

The authors also reported the undoubtable naturalness and biodegradability of Bamboo Lyocell and Bamboo viscose, reminding the audience that viscose was produced for the first time industrially in Italy by the Arundo donax plant and milk proteins by the year 1935. For further data on the industrial use of bamboo, Dr Barbara Ottaviani, Product specialist R&D Unit of Calzificio Pinelli, Castel Goffredo (MN), Italy, has reported the interesting, graduated compression, thermoregulation, breathability and comfort of stockings produced by the Company. The interesting effectiveness of these stockings is due to the great experience of Pinelli's hosiery factory, well known worldwide, especially for the fibres made of natural bamboo, Merino and silk.

Prof Vittorio Calabrese, Head Department of Biomedical and Biotechnological Sciences, School of Medicine, University of Catania, Italy, presented another interesting paper. The topic has regarded the family of polyphenols which, as protective compounds recovered in fruit and vegetables known for their interesting antioxidant properties, are used for the prevention and/or treatment of many diseases. Thus, many research studies have shown how these natural polymers, contained in many oils, such as olive oil, a fundamental component of the Mediterranean diet, may prevent oxidative stress-inducing cardiovascular disease or chronic Alzheimer's. Furthermore, and just on the probable solution of some aspects of Alzheimer, prof Calabrese reported interesting new results obtained from his laboratory, arousing many enquiries from the attendants.

Regarding the polyphenolic family, Dr Graziana Bonincontro, Environmental Department of Biology at La Sapienza University of Rome, Italy, under the direction of prof Giovanna Simonetti and Gabriella Pasqua, reported an interesting research paper regarding the antifungal activity of Pterostilbene, which derives from Resveratrol obtained from the leaves and the grapes of the V. vinifera plant, which has been encapsulated into a polylactic polymer. It was, therefore, evidenced that Pterostilbene, entrapped into the polymeric structure, demonstrated a higher and more stable antifungal effectiveness.

Speaking of the healthy activity of natural polymers, Alessandra Fusco from the Department of Experimental Medicine, Section Microbiology and Clinical Microbiology, Campania University "Luigi Vanvitelli", Naples, Italy, coordinated by prof Giovanna Donnarumma, focused the discussion on the activity that nano-composite polymers have on the microbially-induced tympanic membrane perforation. After an interesting description of the tympanic membrane activity and its defence mechanisms from aggressions, Alessandra presented some interesting experimental data; the effectiveness of nano-composite polymers in loading and delivering local antibiotics and other antibacterial agents, preventing and impeding bacterial infections at the level of the ear membrane.

On the other hand, Dr Emanuele Limiti, Department of Engineering, Campus Bio-Medico University of Rome, Italy, reported the effectiveness of hyaluronan-based nano gels for controlling the Delivery of doxorubicin in ovarian cancer treatment. Through numerous data, the author has brilliantly reported the synthesis realized to make the Hyaluronan-Nanoparticles which, without the use of surfactants and other chemicals, were used to encapsulate, load and release the antibiotic compound at the level of the tumor cells.

Prof Umberto Cornelli, Loyola Medical School of Chicago, USA, presented a paper regarding the polymers used to control human health conditions, Loyola Medical School of Chicago, USA, who, before entering his specific topic, reported an amply and interesting panoramic on the physicochemical characteristics and biological activity of chitosan. Based on its structure-property relationship, this polymer is effective and feasible in many applications. However, the activity and effectiveness of the polymer are strictly connected to molecular weight (MW), polydispersion Index (PI), and degree of deacetylation and crystallinity, all parameters which influence its solubility and penetration through the mucous membranes, controlled explicitly by the shifting intestinal fat absorption. Intestinal absorption is molecular-weight-dependent and increases with decreasing chitosan MW, affecting its degradation rate. For this purpose, Prof Cornelli has shown the data obtained using chitosan that, controlled for its MW and PI, was characterized by 80% deacetylation and added with 6% ascorbic acid and 3% tartaric acid. The product, generating a network capable of adsorbing fats and binding cholesterol, makes it useful to reduce the food intake and therefore seems useful for hypercholesterolemic subjects. The last two papers, one on the market and the other on the cosmetic EU rules, were presented as closure of this interesting meeting.

These papers have been reported on the program to underline the importance of the Italian cosmetic market for speakers and attendants. It represents the third in Europe by a turnover of €11.8 billion, 16 % of which are natural-derived/organic and sustainable products. Moreover, according to the data reported by Dr Gian Andrea Positano, Statistics development manager of Cosmetic Italia (i.e., the association representing the majority of the Italian cosmetic industries), it is known that the Italian cosmetic industry employs 54% of women compared to 28% in other manufacturing industries. Finally, 67% of the make-up sold in Europe is manufactured by Italian Companies.

The final paper was presented by the lawyer Dr Sonia Selletti, Studio Legale Astolfi, Milan, Italy. Sonia Selletti, head of this famous lawyer's office, considered the first in Italy and one of the most important in the EU, is undoubtedly a great expert for her deep knowledge of the many laws regarding the pharmaceutical and cosmetic sectors of human health in general. Regarding the use of nano polymers in cosmetics, it was underlined that Regulation (EC) 1223/2009 "contains rules dedicated to nanomaterials and their presence in cosmetic products", given their potential impact on human health.

Reporting the various interventions of the EU Commission to modify the first definition of nanomaterial focused in the low of 2009 -, the paper focused on the responsibility the producer has to control the product before placing it on the market regarding both the ingredients used and the cosmetic labelling. However, also if another revision of the regulations regarding cosmetics should happen by the end of 2022, the consumer remains responsible for using the product in the reported conditions. After the closure of the meeting, the day brightened from the possibility of drinking the excellent Morganti-Coffee marketed since 1890; a visit to the Medical Museum of the Academy was organized, illustrated by its Secretary General Prof Giuseppe Marceca (Fig. 5).

Fig. 5. *Partial view of the Academy medical museum with some participants on the left (top) Prof Giuseppe Marceca, Dr Andrea Cividini from IRA Company and Prof Maria Beatrice Coltelli.*

The visit was integrated with a view of the famous Lancisiana Library and some well-known ancient rooms of Santo Spirito Hospital, one of which (Sala del Commendatore) the Academy Museum was founded on April 22, 1920. This visit was directed by Dr Patrizia Ricca, Director of the reported medical ancient library (Fig. 6).

The one-day Congress was closed by a happy and interesting wine-testing of the best Italian wines produced by the famous Italian agrarian company Casale del Giglio, located near Rome.

Fig. 6. *Partial view of the Commendatore Hall with a group of the Congress' speakers. From the right: Prof Giovanna Donnarumma, Dr Andrea Cividini, Dr Graziana Bonincontro, Dr Alessandra Fu Fusco, the lawyer Sonia Selletti, Prof Maria Beatrice Coltelli, Prof Angelo Chianese and others clever Congress' speakers.*

Conclusive remarks

Today scientists are fascinated by the particular qualities of the elegant and complex architectures of natural structures made with low water and energy consumption. The possibility of mimicking the features of natural material by nanotechnology opened a large spectrum of new ideas for making bio-inspired structural materials, such as biopolymers, for applications in the field of medicine, nutrition, cosmetics and agriculture (11-13). In doing so, it will be possible to reduce the use of chemicals and synthetic ingredients used in many households, and cosmetic products that can cause undesirable side effects. Consequently, in the past decade, there has been a significant increase in the demand for natural ingredients used, for example, to make drugs, cosmetics and food. All these products must be loaded, carried by natural carriers, and released at the tissues, such as the skin, at the designed dose and time.

Thus, biopolymers, such as chitin and lignin fibres, were engineered to increase the production of biodegradable products extracted from food and forestry waste at their nano-size (20, 26). To better understand the use of these natural polymers, chitin and lignin are utilized as nanofibers with a mean diameter of 240 nanometers or less (nm) and 80-781 nm, respectively, characterized by a large surface-area-to-volume ratio, extremely small pore dimensions and interesting mechanical and biological properties (20, 24). Therefore, the need to use waste for producing goods has become a must of our society because of the increased pollution invading lands, oceans, rivers, bays, and estuaries, especially by plastic materials (27, 29).

It has been estimated that around 12,000 million metric tons of plastic waste will be in landfills or the natural environment by 2050 (27, 28). The purpose is to underline that plastic containers and packaging materials suspended in water are transformed into tiny particles by the microorganisms' enzymes that use the sun as energy. In turn, this plastic debris, called microplastics and erroneously ingested as food by marine organisms, has been recovered into the stomach of fishes, sea birds and mammals (27, 28). Therefore, this waste may impact biodiversity, Eco-system services, food security and human health (27, 28), being found not only in commercial salt and tea bags but also in human blood and placenta, impacting and affecting the cells and tissues' organisation by their content of toxic compounds (29-31). It is also to underline that pollution, considered today the largest cause of disease and premature death, represents 16% of all the deaths worldwide, with 9 million in 2015 (32).

Thus, as reported from this meeting, the urgent need for making biodegradable, bio and Eco-friendly biopolymers, such as chitin and lignin extracted by food and industrial by-products, has to be considered a good idea to reduce pollution and waste. This use seems particularly useful for biomedical applications such as tissue engineering scaffolds, wound dressings, separation membranes and antibacterial coating, as well as for making innovative natural-oriented cosmetic active agents, carriers, packaging and products. Moreover, it is also necessary that specialised teachers educate, encourage, support, and train the participation of a diverse body of students in the environmental sciences to maintain nature and the planet's biodiversity for the next generations.

In conclusion, the aim and result of this interesting meeting have been the hope that we may go toward a more sustainable green environment to save the health of humans and the planet.

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