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Review Article

POLLUTION & SKIN: ROLE OF POLYSACCHARIDES
From Waste Material to Innovative Cosmeceuticals

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Abstract

Skin as principal barrier protects our body from the inside and outside environmental aggressions represented principally from air pollution and the pathogenic microorganisms.The fundamental protective parts of the skin are the Stratum Corneum and the dermal compartment largely composed of dense collagen-rich fibrils which, embedded into the Extracellular matrix, provide structural and mechanical support.This complex structure degrades during the aging processes due to genetic factors and the environmental polluted environment .To protect and try to rejuvenate the skin both women and men are looking for cosmetic products made by natural ingredients,produced by sustainable technologies and packed by containers able to safeguard human health and the environment. Polysaccharides seem to be the best ingredients to make natural-based active ingredients and carriers for Pharmaceutical and Cosmetic use, being skin- and environmentally-friendly,and obtainable at low cost from the food waste.

At this purpose, a new category of biocosmetic products has been proposed, which are made by smart non-woven tissue-carriers,

embedded by micro-nanoparticles of nanochitin-nanolignin, encapsulating different active ingredients. Natural polysaccharides used as carriers and active ingredients characterize the different activities of these innovative cosmeceutical-tissues. So doing it could be possible to reduce part of the food waste, safeguarding natural raw materials and biodiversity of our planet for the future generations.

Keywords: skin; polysaccharides; chitin nanofibrils; nanolignin; cosmeceuticals, cosmetics; packaging; biodegradability; sustainability; non-woven tissues

Introduction

Skin is an important multilayered barrier which externally protects the human body from threats**,** such as infectious microoganisms and chemicals, while internally helps to maintain homeostasis with a reduced loss of water [1]. This protective structure, less than 2 mm thick, is composed of several layers: epidermis, dermis and hypodermis (figure 1).

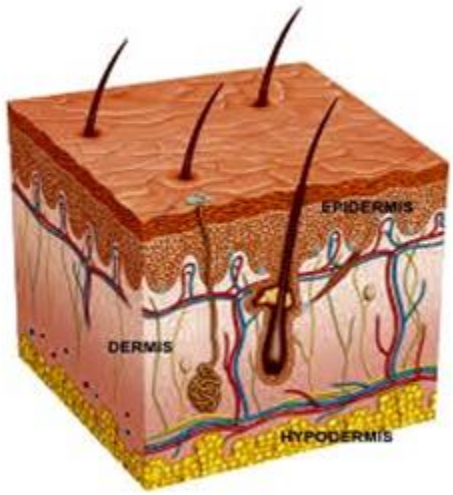

Figure: 1 The skin layers

The outermost epidermis' layer, the stratum corneum (SC), represents the primary barrier to balance the excessive water loss, the ingress of exogenous chemicals and pathogens, as well as to protect from the UV radiation' activity and regulate the transdermal delivery of compounds applied on its surface [1,2]. Keratinocytes, as sentinels of skin homeostasis, are the major cell population of epidermis, representing the first line of immune protection against the microbial infection and expression of the antimicrobial beta defensins involved.
SC is composed of corneocytes, cells filled with keratin fibrils enclosed by an envelope of proteins and surrounded by a lipid' matrix [1-3]. Dermis is largely composed of dense collagen-rich fibrils, which provides structural, and mechanical support to the skin together with hypodermis that, consisting largely of fat, insulates the skin from cold and aiding shock absorption.

Collagen, produced from fibroblasts and embedded into the complex and dynamic extra cellular matrix together with elastin (ECM),provides the main skin' structural and mechanical support, maintaining its fundamental functions for all the lifecycle[1-3].During the aging phenomena this polymer is fragmented by the activity of complex extracellular and intracellular pathways which, include the activity of the Metalloroteinase-1 (MMP1),impair of collagen integrity, fibroblast attachment and the keratinocytes migration [3]. Skin aging, in fact, is a complex process which is characterized by an alteration of all the ECM components in both dermis and epidermis, involving oxidative, epigenetic and genotoxic stresses, and modified collagen turnover, telomere shortening and mitochondrial dysfunction [3,4].Both genetic factors and environmental conditions,which include UV exposure and pollution nanoparticulates,provoke changes in the ECM' network organization with collagen fragmentation, elevated presence of MMP-1 enzymes,cross linking of amino acids side chains, and the consequent skin wrinkling (figure.2) [3-**5**].

It isn't to be forgotten that structural-integrity and functionality of dermis depend primarily on the intact ECM network with its tightly packed and well-organized long collagen-1 fibrils [2].Thus to slowdown the aging processes, it results fundamental to live in an healthy environment with a regular lifestyle which, as previously reported, balance and influence part of the genetic factors and skin structure[2,4,5].Regarding the many functions of collagen, it's to remember that its fragments are also mediators of Inflammation during the wound re-epithelialization process,acting as chemoattractants for neutrophils,thus enhancing immune responses and modulating gene expression[6,7]. There fore, with the aim to find solutions for slowdown the skin wrinkling formation as well as to accelerate and remodeling the skin affected by wounds and burns, some authors have proposed the hydrolized collagen that, used by nutracosmeceuticals formulations, have been applied topically and/or taken by oral route[7-9].

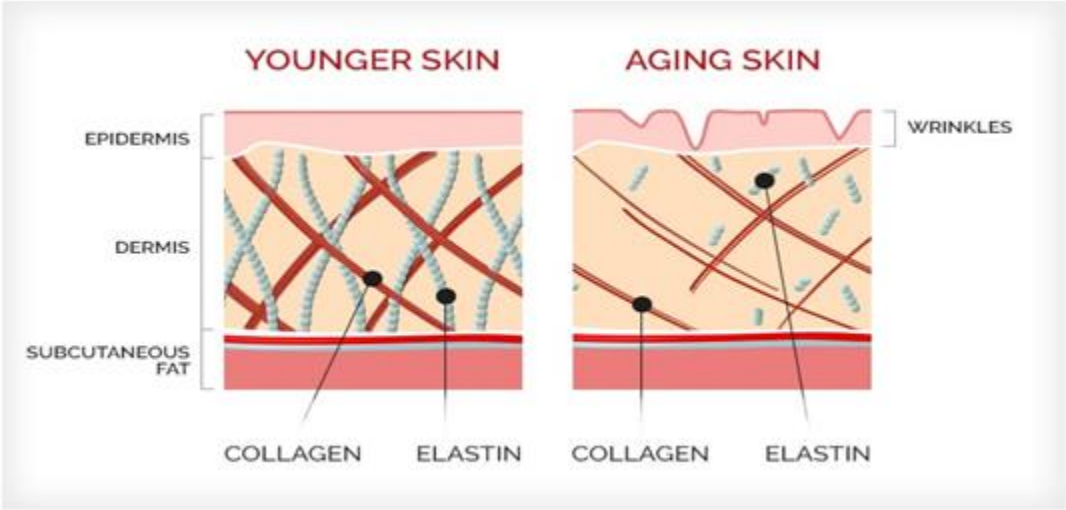

Figure: 2 Collagen fragmentation in aging skin.

The obtained collagen peptides,in fact, seem to act as antioxidant compounds for their capacity to donate electrons,neutralizing the free radicals' activity in dependence on their molecular weight :the lower the molecular weight the greater their effectiveness [8].

Consequently, the use of natural active ingredients, as collagen, loaded and released from biodegradable natural carriers of products to be applied on the skin and/or taken by oral routes, is among the actual consumers' request [9-11]. People,in fact, are looking for natural cosmetics and skin care with a positive impact on the environment due to the biodegradable ingredients and packaging materials used for their formulations [12].Thus the necessity to reduce pollution and waste adopting the circular Economy and producing innovative skin- and environmentally-friendly cosmeceuticals by the use of polysaccharides obtained by food by-products[13-15]

Pollution, climate changing and human health

The level of pollutants are constantly increasing worldwide, causing many health-related problems and risks of microbial and virus infection, such as COVID-19. The WHO 2016 report states that around 7 million people globally and 400,000/580,000 in China only die prematurely annually, due directly or indirectly to pollution problems (figure 3)[16].

Figure 3: Pollution is a silent killer (by the courtesy of WHO)

Moreover the long-term exposure to outdoor and indoor fine particulate matter with a size less than 2.5 millimicrons on diameter (PM2.5) represents the largest environmental risk factor for human health with an estimated 4.1 million attributable deaths in 2019[17-9]. Thus, air pollution as well as both water pollution and soil depletion are the principal causes of the climate change. Thus, the amount of water in rivers has been influenced and, depending on the region and the time of the year, it resulted in more flooding or brought **[**20**].** The worldwide deforestation, is another important cause of climate changing. Forest, in fact, as well as oceans store massive amount of carbon, off setting about 10% of the country's annual greenhouse gas (GHG) emissions, thus helping to mitigate climate change [21**]**. Thus, pollution, nature loss, and changing climate are inextricably linked together. They need to be urgently slowed investing in natural climate solutions, including better land conservation and management' actions able to increase carbon storage and avoid GHG emissions which are increasing day by day due to the different human activities (Figure 4) [22].

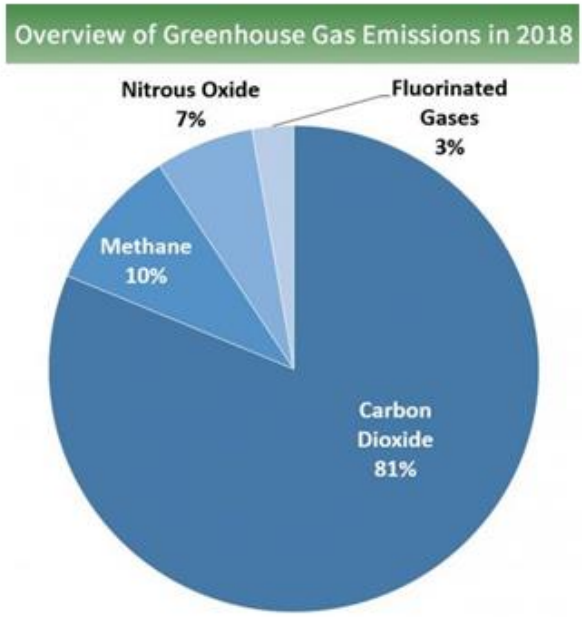

Figure 4: Worldwide GHG emissions by 2018 due to to different human activities.

Moreover, the environmental contaminants have a negative impact on the skin causing premature aging, pigmented spots and inflammation phenomena. Additionally pollutants, weaken the skin barrier function and penetrating through the skin layers, may cause serious dermatological issues such as atopic dermatitis, psoriasis and other systemic toxicity[23].At this purpose it is also to underline the further plastic waste caused from the COVID-19 pandemic due to the great quantity of surgical masks and medical dressings used as protective means to avoid the virus infection, estimated to range worldwide 129 billion of face masks and 65 billion of gloves every month[24,25]**.**These protective means, in fact, are prevalently made by the non-degradable polypropylene (PP) as petrol-derived polymer. As a consequence, it is enormously increasing the interest for natural and biodegradable products, including polysaccharides, which are able to
protect skin and mucous membranes from airborne particulate matter, because of their positive impact on the environment.

Food loss and Role of polysaccharides.

Among the many polymers**,** the natural polysaccharides and other macromolecules such as pullulan**,** chitin**,** lignin and the natural-derived synthetic compounds polylactic acid **(**PLA**)** and Polyhydroxyalcanoates **,**are the more known carriers used in the medical**,**food and cosmetic fields also as packaging raw material**,** because of their skin- and environmentally-friendly effectiveness and safeness **[**26-28**].**Food lost and packaging waste**,** in fact**,** has become a great problem for the consequential air pollution that represents a serious global threat to human health and welfare. According to Food and Agricultural Organization **(**FAO**),** in fact**,**1/3 of the total food production is lost during all the distribution supply chain and harvesting**,** contributing to the estimated value of around USD 1 trillion annual loss **[**29**].** It has been estimated,in fact**,** that approximately 30**%**-50**%** of food intended for human consumption is wasted at different stages of the food system**,** with **a** loss of productivity**,** energy and natural resources**[**30**].**This great quantity of food waste is estimated to be further increased because directly proportionated to the increased demand of food produced and consumed from the world population projected to increase from 7.8 billion people in 2020 to 9.9 billion by 2050 and 11 billion by 2100 **(**figure**.** 5)**[**30-32**].**

Figure 5 The previsional worldwide increase of population by 2100(by the courtesy of Our World in Data)

On the other hand, packaging constitutes roughly 46% of global plastic waste, increased in the European Union by 9.4% for reaching 77.7 million metric tons (Mt) in 2018, also if municipal waste landfilled decreased by 56% in 2019 from 121 Mt in 1995 (fig 6)[32,33].

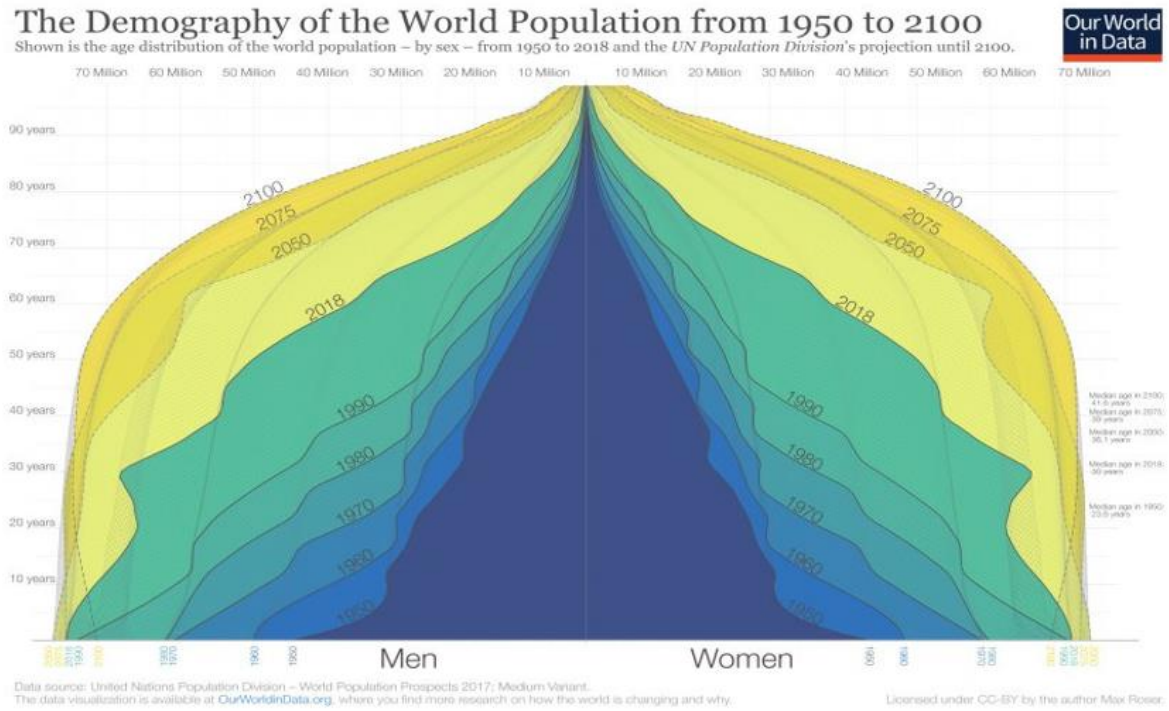

Figure :6 Changing of generation and disposition of comunal waste

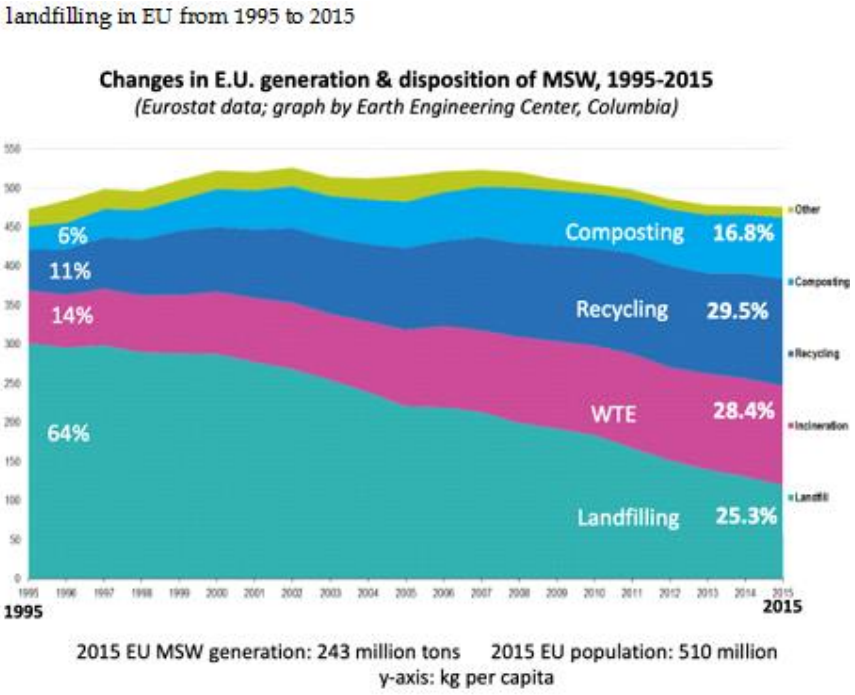

Figure 7: Effectiveness of the CN-LG tissue on the face wrinkling of

However, the use of food waste as a source of precious raw material to produce goods and packagings, remains an urgent need.Food loss in fact represented from vegetables, fruits, grains, fish and seafood, meat, etc, is rich of biopolymers such as proteins, nucleic acids, and polysaccharides, including alginates, pectins, agar, pullulan, cellulose, lignin and chitin which for their similarities to ECM make them one of the key players in designing scaffolds for tissue engineering[34-38].It is to underline, in fact, that an efficient scaffold to be used for tissue regeneration should be able to allow a platform necessary to assist interactions between cells and the surrounding tissues' bioactive factors [34-38].

And the ability of these natural polymers to generate biological-like scaffolds has been linked to their glycan units [36,37].

At this purpose, it is to remember that polysaccharides are the most abundant naturally occurring macromolecules which, present in all living systems, act as structural materials and supplier of water and energy, playing a crucial role in the survival of both animals and plants [37]. Obtainable from many different sources, such as plants, microorganisms, algae and animals, these polymers are constituted by long chain units of monosaccharides jointed each other by glycosidic linkages. Due to their physicochemical characteristics and for enhancing their properties, polysaccharides are susceptible to chemical and physical modifications, resulting more stable than proteins and nucleic acids, without being denatured irreversibly by heating [34,36]. Moreover, they possess different properties characterized by their variable high or low molecular weight and poly-dispersivity, and a linear or branched structure enriched by functional groups such as hydroxy, carboxy, amine, etc. Thus, some polysaccharides are water-soluble like gum arabic or pullulan, while other like cellulose and chitin are water-insoluble, but all are non-carcinogenic and immunogenic and with a low toxicity being skin- and environmentally-friendly [34,35,37]. Due to their characteristics, it is possible to easily realize physical modifications of these polymers by blending two or more of them to obtain composite compounds which**,** possessing physicochemical properties, including porosity, structure, softness, swelling capacity, and elasticity, result similar to biological systems [38,39]. These composites may be also blended with nanomaterials (micro-nanoparticles) extracted from natural sources or chemically synthesized by natural-derived ingredients such as PLA, or obtained by microbiological synthesis as PHAs [40].

At this purpose it is to underline again that utilizing waste by the use of microoganisms (bacteria and algae) to produce polysaccharides not only it will be possible to reduce the environmental pollution, but also to make different kind of tissues and goods skin- and and environmentally-friendly [41,42]. The actual research, in fact, is working on polymers which, already existing in nature as compounds synthesized by plants or microorganisms, result rapidly biodegraded under natural conditions, also when used to produce bioplastics [43,44].

Chitin Nanofibril-Nanolignin on skin, hair and Mucous Membranes

Recently,the natural polymers Chitin and Lignin have been complexed each to other, in their micro-nano dimension, for realizing block polymeric particles useful to encapsulate different and selected active ingredients [45].These particles(Pls) may be bound to the natural fibers of non-woven tissue/films by electrospinning [45],casting techniques[46] or by extrusion [47].Apart the technology used, it is important to control the fibers' nature, the incorporation of the *actives* encapsulated into the realized particles and their bonding onto the tissue/film surface, and naturally effectiveness and safeness of the final product realized [45-56].The final obtained dressings may be utilized to make biodegradable advanced medication and surgical masks ,food supplements ,or innovative cosmeceutical-tissues, more or less effective related to the specific biological characteristics of the selected and encapsulated *active* particles and, naturally, the polymers used to make the non-woven tissues[45-56].

At this purpose, by the use of natural polymers and the electrospinning technique it has been realized a non-woven tissues embedded by chitin nanofibrils-nanolignin (CN-LG) particles, encapsulating peptides from fish collagen hydrolysate together with vitamins C and E .From the first obtained results obtained into a plastic surgery department,this tissue has shown to be effective in reducing both fine lines and wrinkles on women affected by premature aging after 60 days of treatment(Figure.7)(57).It is interesting to underline the recovered anti-aging effect that some authors have obtained by the use of fish collagen' peptides [58] used from our group as part of the realized tissue (59).These peptides, in fact, complexed with chitin nanofibrils(CN) and applied on the skin by a non-woven innovative tissue, confirm to be effective" not only when used topically(59) but seem to possess the same antiaging effectiveness when taken by oral route (8,58), women affected by photoaging(premature aging)

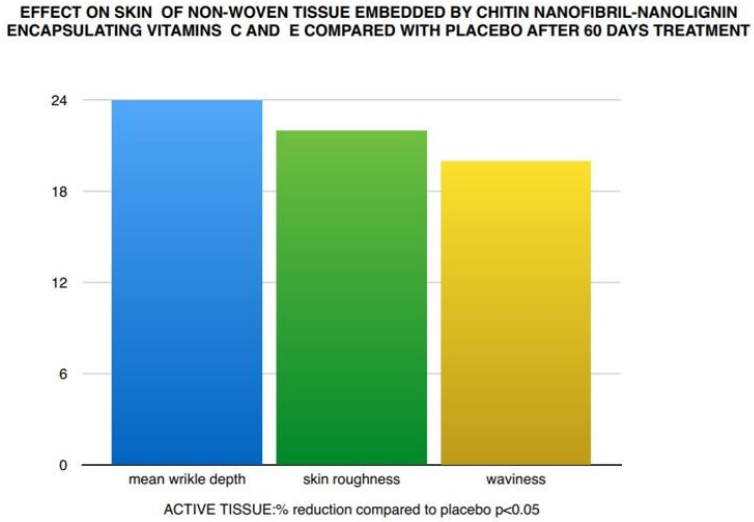

Figure 8: Significance of Active Ageing

Our studies are going on to deeply understand the mechanism of action of these polypeptides when released from the proposed tissues alone and in combinations with other natural ingredients, including the reported vitamins [57]. Thus, the utilization of these specialized tissues as innovative carriers for a new category of cosmeceutical products may be of high interest, as also reported elsewhere [45-56]. They, in fact, may be formulated as multifunctional cosmetics, having the capacity to load a combination of active ingredients, released at different dose and time. Thus, by the selection of the right natural ingredients encapsulated into the Chitin-lignin (CN-LG) complex it may be possible to formulate and make smart cosmeceutical-tissues characterized for their different effectiveness as skin active-aging **(**figure 8) [55]and moisturizing,

whitening, lipid-balancing and anti-pollution products or as protective and hair repairing agents (figure 9) [56].

Figure: 9 Repairing activity of Chitin nanofibrils on a hair' longitudinally tricloclasy

Moreover, by the use of a specific tissue-diet supplement it could be possible to balance the gut microbiota, favoring the growth of saprophytic microbiota and reducing the presence of the pathogenic ones [60,61]**.** It is to remember, in fact, that mammalian mucosal immune systems play an essential role in maintaining the gut and vaginal homeostasis connected with the global health of the human body. Consequently, gut microbiota affect its own development by stimulating the innate and adaptive immune responses. Thus, while the external pathogenic microoganisms are eliminated, the indigenous microbes are tolerated [60,61].

Therefore, the formulation of these innovative multifunctional products requires a planned, organized approach for their structural composition [62]**.** Therefore the need to identify the most appropriate and active ingredients which have to be included on the tissue-films' surface as well as bound to the polymer used.Thus,to yield the designed effect, both selected actives and the carrier' components have to remain stable from the time of the product' production until its use by the consumer, being biodegradable, biocompatible and skin- and environmentally-friendly also.At this purpose,it is necessary to consider molecular size, pH, ionization parameters, melting point, solubility, odor and color of both active ingredients and polymers[62]. Moreover, other than the product formulation,it is also necessary to consider other important factors as, for example, the active ingredients' penetration at level of skin and its structures [62].This includes region of the body,skin condition and degree of hydration as well as size and thickness of the application site.These factors are needed to understand the time necessary for obtaining the cosmeceutical-tissue' effectiveness and safeness. The active ingredients, in fact, should penetrate into the skin, but not through the skin and the active ingredients selected have to be compatible and stable into the tissue-carrier, acting synergistically without interacting with each other [63]. They, therefore, need to be delivered to either the skin surface, including stratum corneum, viable epidermis and/or dermis, and not to the systemic circulation. At this purpose it is also to underline the specific characteristics of the CN-LG complex that acts not only as biodegradable carrier, but also as *active* ingredient **(**27,**64).** In fact, on the one hand chitin, hydrolyzed to glucosamine, acetyl glucosamine and glucose from the human enzyme chitotrosidase, is used as nutrient and energy for the cell growth and reproduction, acting also as antioxidant and antibacterial polymer[27,64,65].On the other hand lignin, acting as antioxidant, antibacterial and UV protective polymer results to be synergistic to the chitin activity [66,67].However, both carriers and ingredients have to be evaluated in advance to verify their impact on the final formulation. Additionally, these innovative cosmeceutical-tissue result not only stable because packed and distributed at the dry state, but are also free of preservatives, emulsifiers, fragrance, color, and chemical which are often the main cause of allergic and sensitizing phenomena [68,69]. Additionally, these smart tissues, packed into container made by biodegradable paper or aluminium foils, are recyclable and to be considered at zero waste.

Naturally, commercial success of these new category of cosmetics will depend from their functional properties and the perceived performance characteristics which have to follow the consumer' request of natural-based safe and environmental-friendly products, which has been estimated by Statista to reach USD 54.5 billion by 2027(figure.10)in a global market of USD 511 billion in 2019 (figure 11) [70,80].

Figure 10 Natural products market (by the courtesy of Common Thread [80])

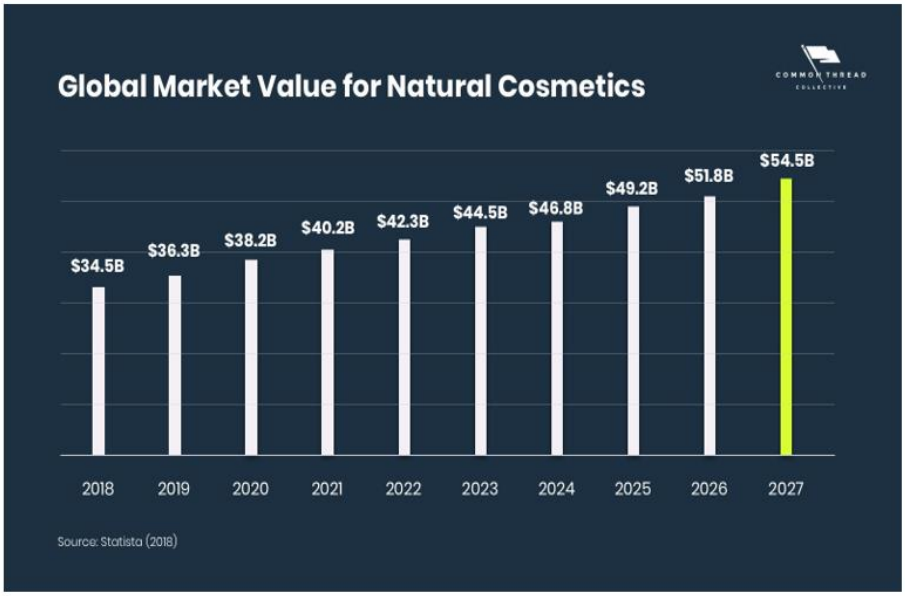

Figure: 10

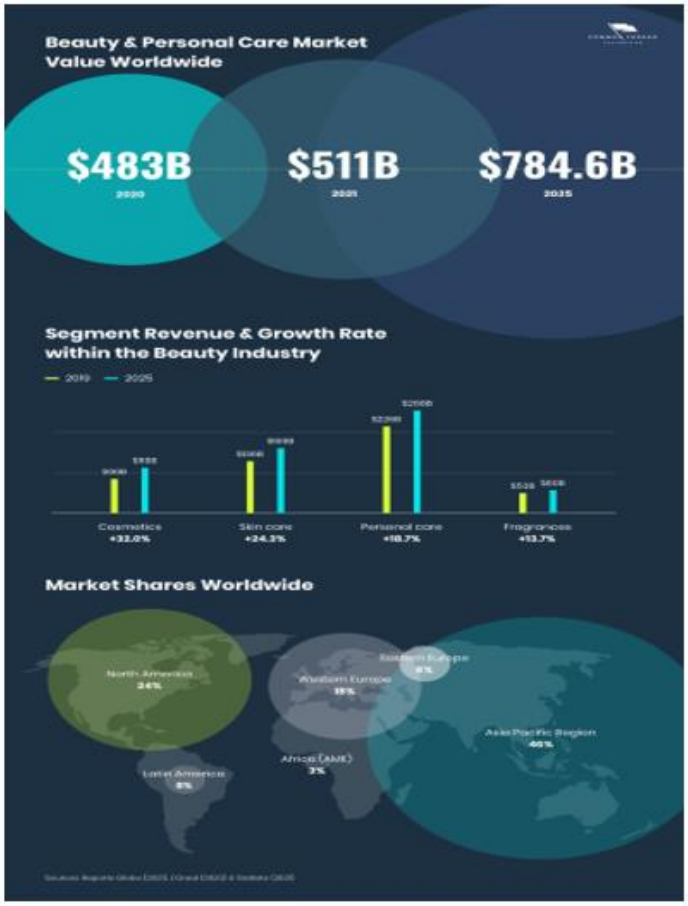

Figure: 11 The worldwide previsional global Beauty and Personal carecosmetic market by 2020-2025(by the courtesy of Common [Thread 80])

Conclusion

Skin, as protective barrier of the body through the SC, is also composed by an extracellular matrix embedding various dermal components, including collagen fibrils and hyaluronic acid (1,2,4,5,23).This complex dynamic system which provides the skin by a structural and mechanical support, undergoes individual physiologic changes with age, including the fragmentation of collagen, with formation of fine lines wrinkles and black spots (72,73).Thus consumers are looking for cosmeceuticals which, natural-based and made by elevated engineered ingredients

carriers and sustainable technologies, may be able to neutralize the pollution micro-nanoparticles and slowdown the aging processes ,thus safeguarding health and the environment (71,74,75).Millennials (26-44 years old) and Gen Z (6-25 years old) are the biggest drivers of the actual cosmetic business, doubling the consume of Baby Boomers (57-75 years old).Their purchasing decisions, based on media or on line reviews, consider more important the product effectiveness with the ingredients and packaging used ,rather than its price. Moreover, they are shifting the focus from aging to longevity (75,76).Thus,COVID-19 pandemic has increased the willingness of all the consumers to pay a premium for sustainable healthy personal care products and prioritize safety and hygiene (77).Therefore, purchasing decisions are increasingly motivated by the quest for an health and *green* living with a best life expectancy (78,79).Consequently, the pursuit of prevention and wellbeing is driving innovation, regarding the cosmetic ingredients used for both products and packagings (81-83).The growth rate for consumer goods marketed for sustainability,in fact ,is nearly four timer higher than the market average (82**).** European customers have understood that the food sector plays a critical,role in climate change and is responsible for about 25% of worldwide GHG emissions,50%of the arable land,and consume most of freshwater (16,33,81)

Therefore, considering polysaccharides as natural, biodegradable and biocompatible polymers obtainable from waste food materials, their use to produce non-woven tissues and films is certainly in line with the actual consumer requests[83]. Moreover, as previously reported, the obtained polymeric composites easily personalized embedding their fibers by CN-LG micro-nanoparticles encapsulating different active ingredients, may be used to produce not only the proposed antiaging cosmeceutical-tissues, but also biodegradable Facial Beauty and

Surgical masks together with one-day Doctor Dressings [45-56,81-91]. Realizing the proposed products by the use of it could be possible to reduce pollution and eliminate part of food waste, thus safeguarding natural raw materials and the earth's biodiversity for the future generations.

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