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Nanopackaging Of Food: An Overview.

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ABSTRACT

Nanotechnology has been a boon to the society and has been used to improvise the products and services in numerous sectors like chemical, pharmaceuticals, agriculture and also in the medical sector. Food crisis has always been a serious global issue and food spoilage is a major menace in the food and dairy industry. Mankind has effortlessly worked to devise better food preservation and packaging techniques so that the shelf life of food can be enhanced. The efforts have however employed crude processes and hence, a permanent solution needs to be discovered. Nanomaterials are seen to impart remarkable and unique properties that can not only be used to increase the shelf life of the food products, but also monitor the internal and external condition of the packed food. Nanopackaging helps to combat the problem of food spoilage effectively without compromising the taste, flavour and odour of the food. However, there are certain limitations pertaining to the technology that needs thorough research. The review gives a comprehensive description on the various types of nanomaterials that have the potential of being used as food packaging materials. The major concerns related to nanopackaging of food have also been highlighted in the article.

Keywords: Food spoilage, Shelf life, Nanopackaging, Food industry.

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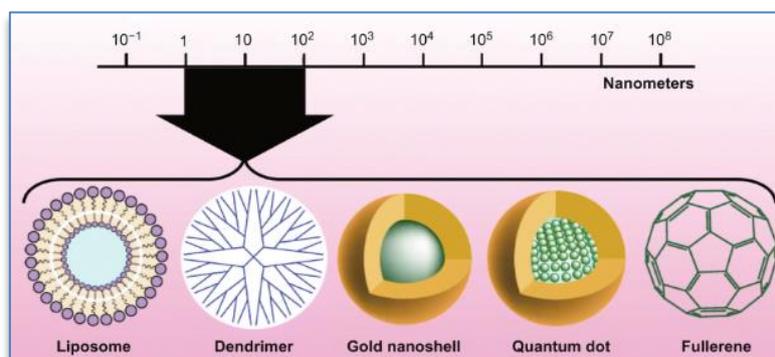
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INTRODUCTION

Efforts for devising and improvising better food packaging and preservation techniques have been a never-ending attempt by man since time immemorial. The processes of fermentation and drying have been into existence since 10,000 B.C. and it is the principle behind these basic processes that have been modified and improvised by the current food industries in order to increase the shelf life of food [1]. The processes of salting, pickling, fermenting, roasting, canning and irradiation and use of various artificial and chemical preservatives mainly slow down and decelerate the multiplication of the microorganisms that break down and degrade the food components [2]. Artificial refrigeration was the first innovative breakthrough for food preservation and was introduced by William Cullen in 1784 [3]. Preservation by using sugar and honey was introduced by the Greeks. They transformed the food into jelly-like form to increase the shelf life [2]. In 1862, Louis Pasteur introduced the process of pasteurization, which could eventually be employed for the preservation of milk, wine and beer [4]. These crude methods however, were not very reliable solutions for preserving food for a long duration and hence, there was a necessity for better preservation techniques.

In 1959, Richard Feynman introduced the various developments of nanoscience and nanotechnology [5] and the applications of these new materials with nano-meter scale dimensions (1-100 nm.), called “nanomaterials” have been widely used by the food industries for both food packaging and food preservation [6,7]. The nanomaterials are classified as zero-dimensional like nanoparticles and nanoclusters, one-dimensional like nanorods and nanotubes, two-dimensional like nano-films and three-dimensional like nanofibers and composites [8]. These nanomaterials have high ductility, surface area and greater strength and are hence used in various industries [9,10]. The potential applications of the nanomaterials to upgrade the quality of food, improve packaging of the food and produce various food products with improved function and nutrition have been reported by many food scientists [5,6,10-12] and hence, different sizes of nanomaterials are used for different production and processing techniques in the industries [13,14] as shown in **fig.1**. Also, these novel food products have shown higher thermal stability, great oral bioavailability and better solubility [15]. Nanotechnology hence, is immensely important in the food industry for both improving the food quality and safety and also increasing the shelf life of the food products [16].

Figure 1: Different sizes of nanomaterials used in the food industry [13,14]

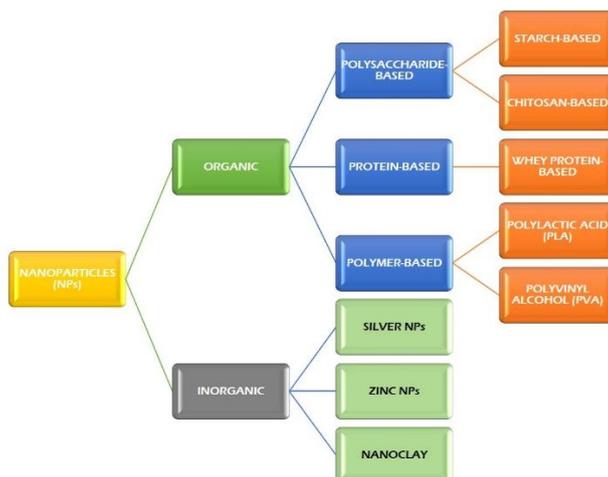


TYPES OF NANOMATERIALS USED IN FOOD PACKAGING

The process of enclosing food components in order to avoid contamination or tampering of food by any physical, chemical or biological sources and for preserving the food products for a period of time is called Food Packaging. Food spoilage due to the various external agents is the prime concern for the food industry and various advances in food packaging technology are being adopted in order to combat this menace. The outbreak of food-borne microorganisms therefore, serves to be the most important reason for the evolution of food packaging technology [17,18]. These food-borne organisms are not only responsible for degrading and deteriorating the food quality but also for causing various food-borne diseases when consumed by people. Hence, a good food packaging material provides protection against all the contaminants and also maintains the suitable physicochemical environment that is required to increase the shelf life of the food [18,19]. The properties of an ideal packaging material include (i) zero toxicity (ii) low cost (iii) easy availability (iv) controlled transmission of gases and moisture (v) high stability over a wide temperature range (vi) ability to include proper

labelling (vii) protection from loss of flavour and odour (viii) resistance of leaching from package (ix) good closure characteristics such as opening, sealing, resealing and pouring [20]. Most of the nanopackaging materials are used either as Active packaging materials or as Smart Packaging materials. Active packaging mainly serves as an inert barrier between the external surroundings and the food material that is enclosed in it. Smart packaging, on the other hand, helps to monitor the condition of the food that is packed, such as pH and moisture content, as well as the external environment, such as concentration of the gases and temperature. **Fig. 2** illustrates the various sources from which nanoparticles are derived for preparing nanopackaging materials.

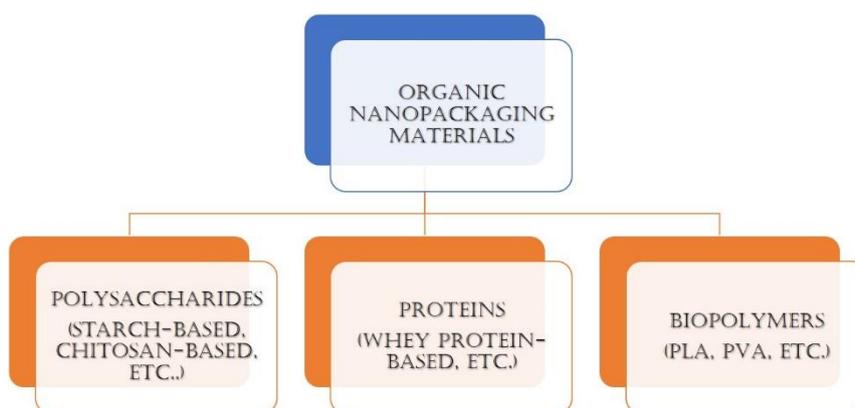
Figure 2: Overview of the various sources to derive nanoparticles for preparing nanopackaging materials.



ORGANIC BIOPOLYMER NANOPARTICLES

The use of biomaterials in every industry is being promoted greatly and a number of strategies are being developed using various renewable organic materials like polymers, polysaccharides and proteins [2,21]. The research on such ‘green materials’ mainly focuses on the prevention of pollution and reduction of waste generation [22-24]. The organic nanoparticles are derived from polysaccharides, proteins and certain biopolymers [25] and are illustrated in **fig. 3**.

Figure 3: Overview of nanoparticles derived for making organic nanopackaging materials [25].



Polysaccharide Based Nanoparticles:

Starch-based Nanoparticles: Starch is a polysaccharide which is non-toxic, biodegradable and renewable and is widely being used as food, pharmaceutical and other packaging material. It is cost effective, has wide availability and is environment-friendly [26]. Starch is composed of amylose and amylopectin, which occurs in partial

crystalline forms. So, the amorphous and crystalline complexes that naturally exist in native starch must be separated in order to produce nanostarch. The processes generally employed for the separation include microfluidizer-based mechanical treatment [27], precipitation techniques [28], and hydrolysis techniques using acid [29,30] or enzyme [31].

Nanostarch have enhanced mechanical properties, barrier properties, flexibility and strength. They are hence, used as reinforcement materials and fillers for food packaging [32]. Also, nanostarch are potential alternatives to the synthetic emulsion latex that are used. The nanostarch latex are used as adhesives for the container boards [33]. The blend of Polyvinyl alcohol and starch can serve as good O₂, CO₂ and other odour barriers and also retain the aroma and flavour of the food. This hence, has a great potential to replace LDPE films [34]. A biomaterial company named EcoSynthetix has developed a nano-sphere starch that has great adhesive property. It has presently replaced the traditional adhesives used in packaging and is currently used in the US by McDonald's for their hamburger clamshells [35,36].

Chitosan-based Nanoparticles: Edible chitosan films were prepared and eventually incorporated in nanocapsules containing EGCG (Epigallocatechin gallate) and then the antioxidant studies were carried out by Liang et. al. [37]. Moreover, tensile strength of certain chitosan hydrochloride films was increased greatly by adding nanocapsules. The films developed prove to be better nanopackaging materials. A packaging film containing an ethanol solution-coated PE surface was prepared by Buslovich et. al. using ultrasonic techniques and vanillin and chitosan particles were incorporated in it [38]. This was then used to increase shelf life of fruits as these packaging films showed good antimicrobial properties.

Polymer-based Nanoparticles:

Poly-Lactic Acid (PLA)-based nanoparticles: PLA has proved to be the most preferred biopolymer due to its incredible properties of biodegradability, crystallinity, renewability and great mechanical characteristics [39,40]. A nanopackaging film was prepared by firstly incorporating ZnO powder doped with Cu into PLA samples and these samples were functionalised using Ag nanocomposites. This was done by Vasile et. al. using the melt blending process [41]. The crystallinity of PLA was increased with an increase in the nanoparticle content. Similarly, Aframehr et. al. studied the barrier and biodegradability properties of PLA incorporating CaCO₃ nanoparticles. They found an increase of 5 wt% on barrier properties and also found that with an increase in feeding pressure, the gas permeability of N₂, CO₂ and O₂ could be decreased [42].

Poly-Vinyl Alcohol (PVA)-based Nanoparticles: PVA has good mechanical properties, biocompatibility, solvent resistance and higher hydrophobicity [43]. PVA-based nanocomposite films were incorporated with Ag-NPs and the thermal, mechanical and physical properties were studied by Sarwar et. al. The films showed greater microbial growth inhibition, especially against *S. aureus* and *E. coli*. Moreover, the cytotoxic studies were carried out on HepG2 cells and the films had no cytotoxic effect [44]. In another study conducted by Yang et. al., lignin nanoparticles were embedded in PVA/chitosan hydrogels by using freezing-thaw techniques [45]. The nanopackaging materials showed great thermal and mechanical properties.

Protein-based Nanoparticles:

Whey protein-based Nanoparticles: TiO₂ nanoparticles were incorporated into chitosan-whey protein films by Zhang et. al. and they found that there was an increase of 11.51% in the tensile strength of the nanocomposite film [46]. Hassannia-Kolae et. al. used the casting procedure to work on the incorporation of SiO₂ NPs into pullulan/whey protein nanocomposite films and they found that the films had enhanced tensile strength, barrier and water resistance properties [47].

INORGANIC NANOPARTICLES

For various food packaging applications, different metal nanoparticles like Ag, Zn, Au, etc. and metal oxide nanoparticles like ZnO, TiO₂, SiO₂, etc. have been researched [48]. These nanoparticles have excellent antimicrobial and barrier properties and have tremendous potential to enhance the shelf life and quality of the packed food [49].

Zinc Nanoparticles: ZnO nanoparticles have excellent antimicrobial activity against *S. aureus*, *B. atrophaeus* and *E. coli* [50-53] and are of particular interest to the researchers as they have very less toxicity in humans and animals and are comparatively cheaper [54,55]. The antibacterial activity of ZnO NPs in ready-to-eat meat was studied by Akbar et. al. and they found greater inhibition in the growth of *S. typhimurium* [56]. A glass bottle made of allyl isothiocyanate and nisin and incorporated with ZnO NPs was developed to store liquid egg albumin, by Jin et. al. and the bottle inhibited the growth of *Salmonella* [57]. A nanocomposite packaging was developed by Emanifar et. al. using ZnO NPs and LDPE (Low Density Poly-Ethylene) and it showed biocidal effects against *L. plantarum*. The packaging was used for storing orange juice [58].

Silver Nanoparticles: Silver has been known to show biocidal activities against various microorganisms like bacteria, fungi and algae and have been extensively used for the storage of food and beverages [59, 60]. Silver nanoparticles have biocidal activities against a wide range of bacteria, that are mainly responsible for food degradation like *B. subtilis*, *K. mobilis*, *S. aureus*, *E. coli*, *S. epidermidis*, etc. [61] and these organisms are primarily responsible for causing various food-borne disorders in humans. Presently, Ag-NPs are being investigated and also being used for both active and smart packaging of food materials. A South Korean company named Baby Dream Co. Ltd., launched a milk bottle that contains Nanosilver for storing and feeding milk to babies [62] and is shown in **fig. 4**. The US market has employed numerous nanosilver containers that are used for storing food. Examples of a few companies would include Oso Fresh Food Storage, FresherLonger™, BlueMoonGoods™ and Kinetic Go Green. The companies claim that the containers not only inhibit microbial growth but also enhance the quality of food by increasing the taste, freshness and safety of the food [63-66].

Figure 4: Nanosilver based milk bottles for feeding milk to babies, launched by Baby Dream Co. Ltd., South Korea [62].



Nanoclay: Nanoclay is basically a polymer nanocomposite that is known to enhance numerous physical properties when used as a nanopackaging material. In fact, it is the first nanopackaging material that has been launched into the market [67] due to its excellent moisture and gas barrier properties. Moreover, in recent times, it is the most extensively used nanopackaging material in the market [68,69]. Montmorillonite (MMT), the most commonly used nanoclay, is an octahedral sheet of aluminium hydroxide ($Al(OH)_3$) that is sandwiched between two tetrahedral layers of silica [70,71] and these are further linked together by weak intermolecular electrostatic forces [72]. The nanoclay serves to be a great nanopackaging material as it increases the mechanical and tensile strength of the biopolymers like polycaprolactone (PCL) and polylactic acid (PLA) [73,74] and also acts as a great barrier to both moisture and gases [75-77], thereby, enhancing the quality and shelf life of the packed food. The incorporation of the nanoclay at a lower concentration in the biopolymers, also increases the barrier properties of the biopolymers and also enhances the creep resistance. The biodegradability of the polymers also remains intact [78,79].

SMART/ INTELLIGENT NANOPACKAGING-NANOSENSORS

Smart or Intelligent Nanopackaging is the use of nanomaterials to monitor the changes that take place in the packed food and also its external environment. They are basically nanosensors that help to detect the changes in the condition of the packed food [80,81]. This is shown in **fig. 5**. The nanosensors detect the gases and chemicals that are resulted due to food degradation or spoilage and are usually sensitive to gases like NH_3 , H_2S , SO_2 , H_2 , and nitrogen oxides [82]. Au, Pt and Pd NPs are usually used to make gas nanosensors due to their high selectivity and sensitivity [83].

Figure 5: Nanosensors can help to detect the quality of the packed food by changing the colour of the sensor [111].



Au-NPs are also used to detect certain toxins that are present in milk like aflatoxin B1 [84]. The moisture content detection was studied by Luechinger et. al., who developed nanosensors using Cu-NPs and coated them on carbon film [85]. When Au-NPs are functionalized using cyanuric acid, the sensors developed can be used to detect melamine and certain adulterants by changing colour [86]. Changes in pH can be detected using nanosensors developed by incorporating engineered Pt- nanoparticles [87]. Pradhan et. al. demonstrated the potential of TiO₂ and silica-based nanosensors to detect presence of O₂ in food [88]. ZnO, and TiO₂ based nanosensors also help to detect presence of certain volatile compounds like gaseous amine and ethanol, which help to indicate fish or meat degradation and spoilage. Nanocomposites of titanium dioxide and tungsten oxide also help to detect ethylene gas, which plays a very important role in fruit ripening [89]. Nanosensors therefore, play a very important role in the maintenance of food quality [90] and also help to prevent the consumption of foods that are unfit for consumption and that would be detrimental to health.

COMMERCIALY AVAILABLE PRODUCTS

Nanotechnology has found its applications in various sectors and the 21st Century saw the beginning of numerous applications of nanoparticles in the form of commercially available products. The use of nanoparticles has been found in cosmetics, clothing, household appliances, disinfectants, fuels and also in the agricultural and environmental sectors. Nanoparticles are extensively being used in medicine and drug delivery. Similarly, numerous applications of nanomaterials are seen in the food and dairy industry as well and the products are listed in **Table 1** [91].

Table 1: List of the commercially available nanomaterial products.

S. No.	Nanomaterial	Product	Company	Applications	References
1.	Nanosilver	Nanosilver Food Containers	A-DO Global, Korea	Food storage	[92]
2.	Nanosilver	Nano Storage Box	BlueMoonGoods™, USA	Food storage	[92]
3.	25 nm of silver nanoparticles	Fresher Longer™ Miracle	Sharper Image®, USA	Antimicrobial protection	[92]
4.	Nanosilver	Food storage containers	BlueMoonGoods, LLC, USA	Food storage	[92]
5.	Plastic	Fresher Longer™ Food Containers	Sharper Image®, USA	Longevity of food products	[92]

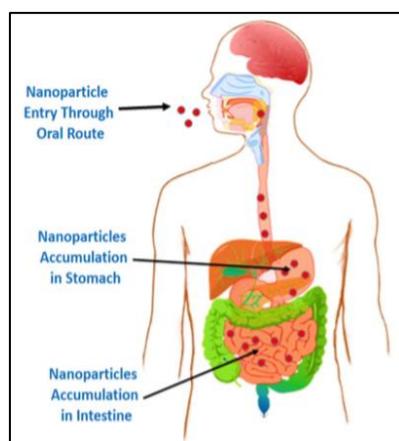
6.	Nanosilver	Large Kitchen Appliances	Daewoo® Refrigerator, Korea	Strong disinfection and storage power	[92]
7.	Nanoparticles of silver	Antibacterial kitchenware	Nano Care Technology/NCT	Increased antibacterial properties	[93]
8.	Nanoparticles of silver	Nanosilver cutting board	A-Do Global	Potent antibacterial	[93]
9.	Nanosilver	Nanosilver Salad Bowl	Changmin Chemicals, Korea	Food storage	[94]
10.	-	OilFresh™ Nanoceramic product	US-based Oilfresh Corporation	Suppresses oil breakdown	[95]

MAJOR CONCERNS RELATED TO NANOPACKAGING

The properties of nanoparticles like greater surface area, increase the chemical reactivity of nanoparticles and hence, these nanoparticles have greater potential to participate in many biochemical reactions than bulkier materials. This may in turn have a negative impact in the health of individuals and therefore, many unintentional yet detrimental effects may be observed [96].

TOXICITY OF NANOPARTICLES: The use of different materials in food products require very strict assessment before the products reach the consumers. As nanoparticles have health risks associated with them, many researchers have particularly carried out many toxicity and migration studies of various nanoparticles used in food packaging [97,98]. Nanoparticles, when ingested, may get accumulated in the gastrointestinal (GI) tract as shown in **fig. 6**. In fact, the enzymes and the acids that lower the pH in the stomach, may help to process the nanoparticles [99]. The nanoparticles hence, may produce certain toxic components as they get a fairly good period of time to break down. In the small intestine, the nanoparticles may penetrate through the epithelial lining and reach the blood circulation and therefore translocate to the different vital organs of the body such as the brain, kidney and liver [100-102]. Recently, the migration of silver nanoparticles in Nanosilver-containing food containers have been investigated by von Goetz et. al. and Artiaga et. al. and they have reported the possibility of the migration of Ag ions into the food products [103,104]. Silver nanoparticles have been found to have toxic effects on human fibroblast and carcinoma cells [105] and may cause damage to the DNA and mitochondria and lead to anti-proliferative activity [106,107]. 6.25 µg/mL concentration has been reported to be the safety threshold for silver nanoparticles by Duncan et. al [108]. Hence, toxicity serves as a major concern related to nanopackaging of food.

Figure 6: Accumulation of nanoparticles in the GI tract [111]



PUBLIC CONCERNS: The commercial success of a product launched in the market is solely dependent on the acceptance of the product by the consumers and the perceptions and views instilled in the minds of the public. A major drawback of nanotechnology is the lack of knowledge and awareness amongst people. In fact, a survey among 1500 people was carried out in the United States, and it was found out that more than 60% of the participants had never heard of the term 'nanotechnology' [109]. Due to the unfamiliarity of the technology, people find it extremely difficult to accept this technology and its related products. Hence, it is the consumers' views that play a crucial role in using nanoparticles in food packaging [110].

REGULATORY ISSUES: The Institute of Food Science and Technology (IFST) has made it compulsory that food particles containing nanomaterials must be labelled with a subscript "n" [71]. The regulatory bodies are constantly monitoring the development and applications of nanomaterials in the food industry and assessing the potential risks and threats that are associated with them. For instance, a Food Standards Agency in the UK, Advertising Standards Authority (ASA), has drafted certain regulatory guidelines related to the applications of nanoparticles in food products [111]. An in-depth study and analysis is of prime importance as this technology is still at a nascent stage and eventually, proper regulations must be put up by the authorities to maintain the safety of the people.

CONCLUSION

Nanotechnology has clearly shown promising results in the food preservation and packaging arena, which is beneficial to both the food industry and the consumers. The technology offers numerous innovative and overwhelming opportunities for better storage, preservation and consumption of food products. Nanomaterials can serve as excellent active packaging materials as they demonstrate a wide spectrum of antimicrobial, mechanical and barrier properties, thereby increasing the shelf life of food. Additionally, the smallest concentration of adulterants and contaminants can be detected and the condition of the food can be prominently monitored with the help of nanosensors and hence, smart nanopackaging materials are additional assets to the industry and the people. Nanomaterials furthermore, come with effective benefits like biodegradability, renewability and affordability. Hence, the major problem of food spoilage can be eminently combated and the issue of global food crisis can be effectively dealt with. However, certain fundamental studies pertaining to the associated risks of nanoparticles need to be conducted and the results must be clearly stated by the regulatory authorities so that mankind can enjoy the benefits of this emerging technology.

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