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State of Nano technology in novel food packaging and new application opportunities

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ABSTRACT: Nanostructure materials have attracted special attention in recent years due to their phenomenal properties that makes them suitable to be applied for food packaging as they enhance the mechanical, thermal and gas barriers properties, with no threat able to become non-toxic and biodegradable. In this article, different types of polymers including natural, synthetic and semi-synthesis polymers as well as various types of nanocomposites and bio-composites have been discussed. Moreover, several applications of nanocomposites in food packaging and food safety are reviewed in which nanomaterials are employed as potent antimicrobial agents, as well as the detection of food-relevant analytes in smart food packaging [1-5].

Keywords: *Active packaging, Food packaging, Nanocomposite, Nanocomposite, Nano sensor*

INTRODUCTION

A package provides protection/ tampering resistance and special physical, chemical or biological needs.

Importance of food packaging

The importance of food packaging is further supported by the final choice of the consumers because it directly involves demand, accessibility, branding and information. The food industry and the food packaging industry are reinventing the food service channel. Food packaging is able to fulfill several requirements including Protection, Containment, Label information, Marketing, Safety, Convenience, Portion control. In this review, the focus is on protection part. The food inside the packages, require to be protected from different factors like vibration, shock, compression, temperature, etc. Moreover, barrier protection is strongly needed to avoid oxygen, dust, water vapor, etc. from penetrating into the package [6-9].

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History of Packaging

Packaging has launched with natural materials such as leaves. Serial production was later done with products such as woven materials and pots. It is estimated that glass and wood packaging are being employed for around 5000 years.

Primary/secondary and tertiary packaging

There are three levels of packaging regarding a specific purpose including Primary, secondary and tertiary packaging. It is essential to distinguish among the three levels because it is proposed for different packaging circumstances.

Primary packaging:

Primary packaging the main purpose of primary packaging is to protect, preserve contain and inform the consumer. A common example for the primary packaging of a liquid material could be a bottle [1-5].

Secondary packaging:

This packaging mostly involves cardboard boxes, although they can also be a kind of plastic. A common instance is in the case of milk, a separate carton would be primary packaging, while the cardboard box containing the pack of cartons would account for secondary packaging.

Tertiary packaging:

Tertiary packaging can also play a significant role relative to the brand's perspective. This is especially true for e-commerce logistics, where the box or packaging employed in transportation is tertiary and can include visual brand elements. Tertiary packaging is applied for protection in transporting and warehousing the product and is not commonly displayed on the retail shelf. Again, printing, if relevant, is for identification.

Material of packaging

In 1823 British man Peter Durand obtained the patent for the first metal packaging made from sheet metal "canister". Double stitched three peace started to be used in 1900. Paper and cardboard have become important packaging materials in 1900s. With the invention of plastic, it started replacing paper as a packaging material. General use of plastics in packaging applications has begun after World War 2. Polyethylene was produced in abundance during the war years and became an available material in the market right after the war. In the beginning it replaced the wax paper used in bread packaging. The growth in plastic packaging has speed up since 1970s. With new technology and conditions, these previous materials have been replaced by more suitable and economic materials such as glass, metal, plastic, paper and cardboard [10-13]. Plastic is a word that originally meant "pliable and easily shaped." It only recently became a name for a category of materials called polymers

Polymer

Polymers are a group of materials that have been widely used for packaging since last century and a half. During this time, humans have learned how to make synthetic polymers, sometimes using natural substances like cellulose, but more often using the plenty of hydrocarbon molecules provided by petroleum and other fossil fuels. The word polymer means "of many parts," and polymers are made of long chains of molecules. Polymers exist in nature. Cellulose, the material that makes up the cell walls of plants, is a very common example of natural polymer [14-16].

Classification of Polymers

Polymers cannot be classified under one category because of their complex structures, different behaviors and vast applications. Depending on the source of availability, polymers are classified to three types including natural polymers, synthetic polymers and semisynthetic polymers.

Natural Polymers

In natural polymers, the polymerization process occurs naturally and the polymers are found in plants and animals. Famous examples are proteins, starch, cellulose, and rubber. To add up, we also have biodegradable polymers which are called biopolymers.

Natural biodegradable polymers

Biopolymers are polymers formed in nature during the growth cycles of all organisms; hence, they are also referred to as natural polymers. Their synthesis generally involves enzyme-catalyzed, chain growth polymerization reactions of activated monomers, which are typically formed within cells by complex metabolic processes (8). An overview of these categories is given in Fig. 1.

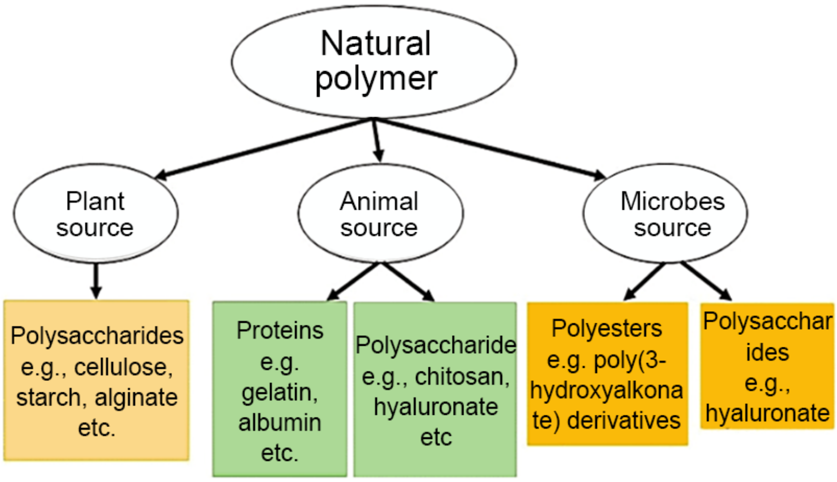

Fig. 1. Scheme of natural polymers [9].

Synthetic Polymers

These are man-made polymers. Plastic is the most common and widely used synthetic polymer. It is used in various industrial productions such as nylon-6, 6, polyether's etc. [17-19].

Semi-synthetic Polymers

They have originated from natural polymers and undergo further chemical modification. For example, cellulose nitrate, cellulose acetate.

Application of nano technology in food industry

The application of nanotechnology in food industry can be divided into two major groups: food packaging and food processing (Fig. 2) [20].

In the case of food processing, nanomaterials can be applied as: (a) carrier and food additives for smart delivery of nutrients, to expand nutritional value of food, (b) anticaking agents, to improve the consistency of food and preventing the lump formation, (c) gelating agents, to develop the food texture and (d) nanocapsules and nanocarriers, to protect aroma, flavor and other ingredients in food. While, in the case of food nano-packaging, improved packaging, active packaging, smart packaging and bio-based packaging are considered. In this review, the role of bionanotechnology in food science with emphasis on application of (bio) nanomaterial in the field of packaging is summarized and also some negative acts associated with application of nanotechnology in the field of food ap-

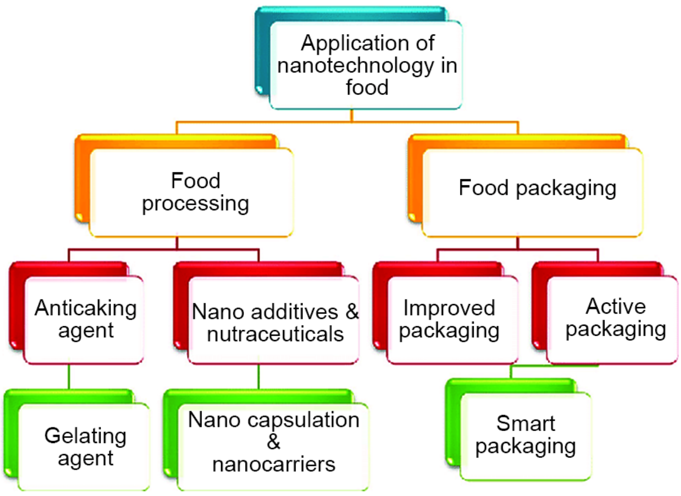

Fig. 2. Classification of food packaging [20].

plication are discussed. Future perspective and aspects of nanotechnology in food industry are included.

Food Packaging

Food packaging is one of the most critical steps in terms of food safety. The purpose of food packaging is predominantly to prevent spoilage and contamination, increasing sensitivity by enabling enzyme activity, and reducing weight loss [21-23].

Advanced nanocomposite and nanobiocomposite packaging

Advanced packaging is based on Nanocomposite and nanobiocomposite materials which are appropriate for food packaging. The nanocomposite packaging materials are biodegradable films that could be applied for food packaging to control the transfer of moisture or gas exchange increasing shelf-life, safety and maintaining the nutritional ingredients and sensory quality (Siracusa *et al.* 2008). The bio-based packaging materials serve to be more eco-friendly comparing the plastic packaging through providing a protection between a food and its surrounding environment, therefore avoiding food from deterioration, such as microorganisms, gas conditions and relative ambient humidity.

Nanocomposite and biocomposite material

Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometre range (1 nm = 10-9 m). Nanocomposite materials have emerged as a suitable alternative to overcome limitations of microcomposites and monolithics, while posing preparation challenges related to the control of elemental composition and stoichiometry in the nanocluster phase. They are reported to be the materials of 21st century in the view of possessing design uniqueness and property combinations that are not found in conventional composites. The general understanding of these properties is yet to be reached2, even though the first inference on them was reported as early as 1992. Properties of Polymer Nanocomposites For the packaging applications of polymer nanocomposites, the performance properties such as mechanical, barrier, optical, thermal, biodegradation, antimicrobial, and other functional properties ought to be evaluated. The properties of polymer nanocomposites are closely related to their microstructure. Substantial improvements in the properties were found with various polymer/nanofillers nanocomposites, which are mainly attributed to the high interfacial area between nanofillers and polymer matrices [22-25].

Classification of nanocomposite based on different type of support materials

As in the case of microcomposites, nanocomposite materials can be classified, regarding their support materials, in three different categories as shown in Ta-

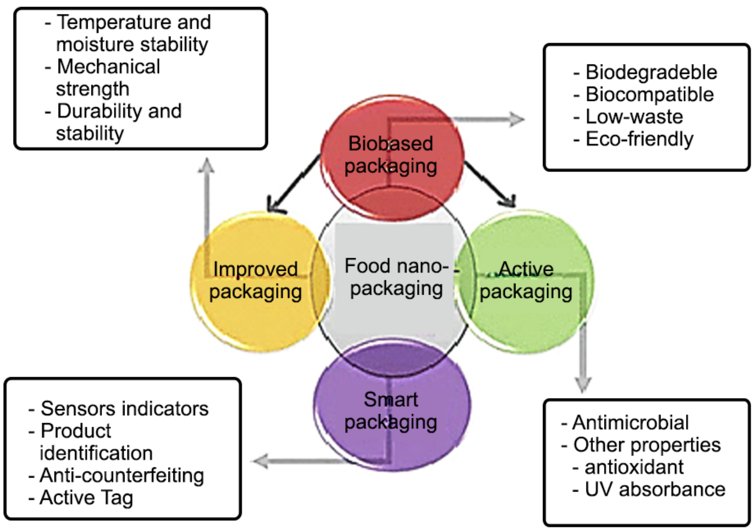

Fig. 3. Food nano-packaging, classification, functions and features [21].

ble 1. Ceramic is as support Nanocomposites (CSNC), Metal as Support Nanocomposites (MSNC) and Polymer as Support Nanocomposites (PSNC).

a) Ceramic as Support in Nanocomposites (CSNC)
Ceramics are usually brittle and easily fractured as consequence of crack propagation. There have been attempts to make ceramics suitable for engineering applications through the incorporation of a ductile metal phase or another ceramic into the matrix.

b) Metal as Support Nanocomposites (MSNC)
The most common techniques for the processing of metal support nanocomposites are 113-150 Spray pyrolysis, Liquid metal infiltration, Rapid solidification, Vapor techniques (PVD, CVD) Electrodeposition.

c) Polymer as Support Nanocomposites (PSNC)
Polymer nanocomposites (PSNC) are the combination of polymer continuous phase and nanoparticles as discontinuous phase that show several advantages in mechanical, electric, and optical properties as compared with individual components. Many methods have been described for the preparation of polymer nanocomposites, including layered materials and those containing CNTs [26-28].

Nano biocomposite food packaging
Various types of nanocomposite food packaging are improved using biopolymers and nanomaterial. For example, the nanofillers from renewable resources have been applied to increase the water vapor barrier property. Reinforcement of chitin nanofibrils in carrageenan biopolymer improved the mechanical property and decreased the water vapor permeability of nanocomposite [19]. The water vapor permeability of carrageenan biopolymer also decreased when it was reinforced with paper mulberry pulp nanocellulose [11]. Rhim and Wang [33] reinforced (embedded) clay into carrageenan biopolymer to increase the water vapor barrier property and mechanical properties of nanocomposite. Kanmani and Rhim [34] mixed nanoclay into gelatin matrix to improve the mechanical and water vapor barrier properties.

Nanocomposite Active packaging
Nanocomposites composed of inorganic nanoparticles and the polymer matrixes for optical and magnetic applications have been employed in active packaging. Optical or magnetic characteristics could be changed upon the decrease of particle sizes to very small dimensions, which have attracted a lot of attention in the area of nanocomposite materials. The use of inorganic nanoparticles into the polymer matrix can provide high-performance novel materials that find applications in many industrial fields. With this respect, frequently considered features are optical properties such as light absorption (UV and color), and the extent of light scattering or, in the case of metal particles, photoluminescence, dichroism, and so on. Food packaging applying an antimicrobial agent is a type of active packaging in which antimicrobial substances embedded into packaging material in order to ensure and extend microbial safety of food products. The technology has many advantages comparing conventional packaging (Lotfi *et al.* 2018). In this case, nanomaterial as antimicrobial agents can be coated, laminated, incorporated or immobilized onto a natural or synthetic polymer in order to reduce or inhibit the growth of the microorganism on packaged food.

Smart materials have phenomenal properties based on nanotechnology. Carbon and boron nitride nano-

Table 1. Type of nanocomposite polymer [26].

Class	Examples
Metal	Fe-Cr/Al_2O_3, Ni/Al_2O_3, Co/Cr, Fe/MgO, Al/CNT, Me/CNT
Ceramic	Al_2O_3/SiO_2, SiO_2/Ni, Al_2O_3/TiO_2, Al_2O_3/SiC, Al_2O_3/CNT
Polymer	Thermoplastic/thermoset polymer/layered silicates, polyester/TiO_2, polymer/CNT, polymer/layered double hydroxides.

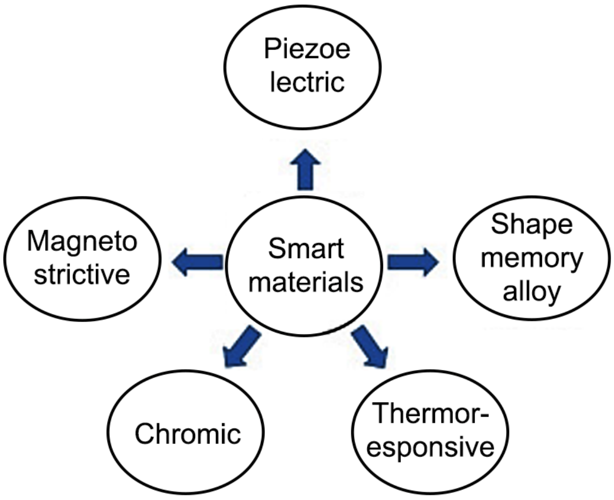

Fig. 4. Smart material [27]

tubes in theory can be used to manufacture fibers that have piezoelectric, pyroelectric, piezoresistive, and electrochemical field properties. Smart nanocomposites designed using these fibers will sense and respond to elastic, thermal, and chemical fields in a positive human-like way to improve the performance of structures, devices, and possibly humans. Remarkable strength, morphing, cooling, energy harvesting, strain and temperature sensing, chemical sensing and filtering, and high natural frequencies or damping will be the properties of these new materials [27-30] Type of smart packaging:

Smart packaging materials are the substances by which the condition of packed food or surroundings of the food could be monitored. Smart packaging could also be defended as inexpensive labels attached to primary packaging such as pouches, trays and bottle or to the shipping container, which can help to be linked throughout the supply chain. Edible coating or film can be described as a thin layer of edible nano material present on the surface of food, which acts as a barrier to mass transfer. These edible coatings can provide a barrier to oxygen, moisture, gas, etc.

Anti-microbial nanocomposite packaging

Nanocomposites are polymeric matrices in which nanoparticles can be incorporated to provide a material with specific functions such as high barrier, improved mechanical performance, antioxidant capacity, or antimicrobial activity. Different nanoparticles have been considered due to their strong antibacterial and/ or antifungal capacity such as nanoclays, silver, titanium dioxide or zinc oxide nanoparticles [31-32].

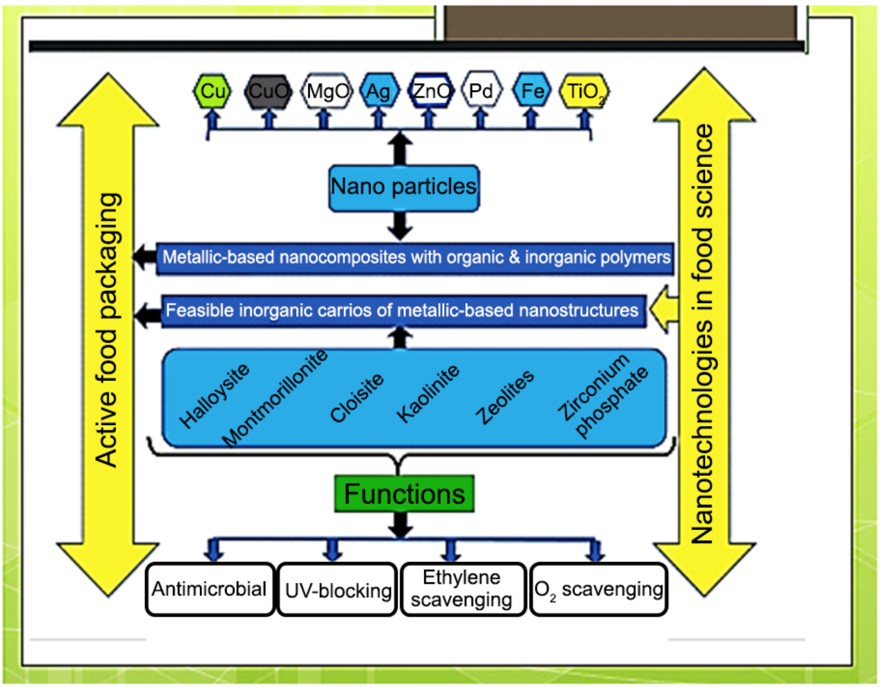

Fig. 5. Active food nano packaging [32].

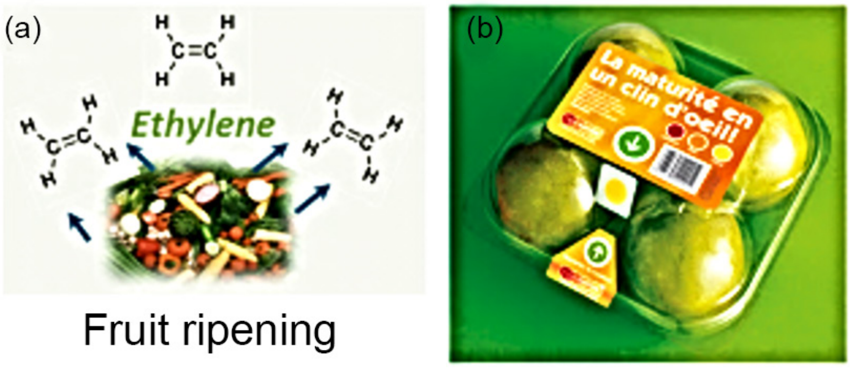

Fig. 6. Gas nano sensor packaging [40].

Smart nano sensor in food packaging

One of the main challenges in this field is the complexity of food samples and the difficulty in measuring markers of degradation directly in closed packaging without prior sample treatment. Most successful examples of sensors to date are related to the detection of volatile compounds, such as amines and ethylene. In the current development status, most food biosensors still need food-sample pretreatment. Future developments should be focused on reducing the detection limit and growing the possibility of measuring markers upon simple contact with the sample [33-37].

Classification Nanosensors in food packaging

Nanosensors may be designed for controlling both the internal and ex¬ternal conditions of food products. On this base, nanosensors could be classified in two groups, one for detection of atmospheric impacts (external conditions) and the other for detecting microorganisms and chemical detection inside the package (internal condition) [38-39].

Nanosensors in food safety

Modified environment inside the package can also be observed by measuring the increase of O_2/CO_2, microbial or moisture content, indicating changes in freshness status or conditions leading to degradation. Therefore, developing sensors and labels to evaluate changes in the pH, O_2, CO_2, RH, CH_2CH_2 and the presence of degradation compounds will enable technologies that can provide direct information to the consumer, farmer or retailer considering the food quality.

Humidity sensing nanosensor

In the past decade, humidity measurements have attracted lots of attentions in the wide range of applications such as industrial food packaging, agriculture, climate monitoring, healthcare, and semiconductor industries. Accurate humidity measurements fabrication processes for nanosensors with flexible form factors are essential to meet the stringent performance requirements of the emerging application areas [40-43].

Gas sensing nanosensor in food packaging

The conservation of food quality in the traditional packaging systems is challenging because of the respiration of fresh products, the changes in gas concentration, and the gas leakage inside or some metabolites, such as H_2S, CO_2, O_2, and ethylene, and volatile compounds such as amines, ammonia, and ethanol, are formed in the headspace of packaging during the storage time.

Developments on biocomposite sensors (i.e., sensors that are using compounds obtained from natural products and using biopolymers) to be used as smart packaging for food products, mainly focus on freshness indicators. The indicators have the function to provide information about changes occurring in a food product or in the surrounding environment, providing more accurate information about the status of a food product for the consumers [45-46].

CONCLUSIONS

In the present review, we have concentrated on the novel nanopackaging materials such as active, smart and bioactive packaging material, which develops the shelf-life of food. Furthermore, the international status of nanopackaging materials has been discussed, which has greatly increased in the last two decades, because of enormous applications of nanomaterials in the packaging of minimally processed food. Therefore, the safety and regulatory issues concerning the application of nanomaterials in food packaging have been discussed herein. Nanosensors provide a technologically advanced solution to detect food contaminants addressing a critical component of a complex public health issue of food safety.

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