

Preparation of Organic and Inorganic Nanoparticles and their Subsequent Application in Nanocomposites for Food Packaging Systems: A Review

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Abstract

Objectives: To review the methods involved in the preparation of organic and inorganic nanoparticles important for the food packaging sector and their applications thereafter. **Findings:** Nanotechnology has come up with its contribution in food packaging technology by providing various kinds of packaging materials, films, coatings etc. Different nanoparticles and biopolymers could be coupled resulting in biodegradable films that not only provides mechanical strength, barrier properties, increased shelf life but also provides antimicrobial properties that helps in keeping the food safe and fit for human consumption. Among these nanoparticles there come the metal oxides (inorganic) such as TiO₂, ZnO and Ag, also organic nanoparticles such as chitosan and starch nanoparticles which are safe for human consumption. The inorganic nanoparticles were effectively prepared in the previous studies by sol-gel method, mechano-chemical processing and physical vapor synthesis whereas entirely different methods were effective for organic nanoparticles viz. acid hydrolysis, ultrasonication, ionic gelation and reverse micellar method. **Application/Improvements:** The review reflects the information available on nanoparticles' synthesis and their application; it could further be used to conduct studies on thrust areas such as nanoparticle aggregation and migration of nanoparticles into the food.

Keywords: Food Packaging, Inorganic Nanoparticles, Nanocomposites, Nanoparticles, Organic Nanoparticles

1. Introduction

Food safety and shelf life have become an irresistible topic of concern for the food industry, researchers as well as the consumers. The use of protective, antimicrobial and suitable packaging films for food is desirable. By means of the correct selection of materials and packaging technologies, it is possible to keep the product quality and freshness

during the time required for its commercialization and for consumption^{1,2}.

The new trends in nanotechnology has shown us the path for development of food packaging films using nanoparticles, incorporated in biopolymer matrices offering a variety of advantages over the conventional packaging methods. Nanotechnology offers its advantages because it involves the manufacture and use of materials with size of

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up to about 100 nm in one or more dimensions and this increases the surface area and thereby activity³.

To improve the properties of biopolymers used in film manufacturing, nanofillers are added which apart from improving the barrier and mechanical properties also offer other functions such as antimicrobial agent depending upon the nanoparticle used. Nanoparticles can be either incorporated on the surface of a polymer or embedded into the matrix. However, the best methodology or technology is far to be solved, as it will depend on both the final application and the polymer matrix used. A range of nanoparticles are available and among the metal oxides, ZnO, TiO₂ have received particular interest because they are safe for animals and human^{4,5}.

The efforts have been taken in the present review to discuss some of the biopolymer packaging films utilizing nanoparticles; possessing characteristic properties thus facilitating new advances in food packaging.

2. Organic Nanoparticles

Organic nanoparticles can be commonly described as solid particles composed of organic compounds (mainly lipids or polymeric). The main advantages of fillers extracted from renewable sources in comparison with inorganic fillers are their reinforcing capability, low energy consumption, high specific mechanical performance, abundance, low density, and biodegradability⁶. Starch and chitosan are the most studied organic nanoparticles in context to food applications.

2.1 Starch

Starch is a renewable source of nanoparticles thus facilitating its use as reinforcing material in films. Because of the nano-metric size effect, nano-scale fillers typically have greater surface area per mass, leading to higher likelihood self-interaction, which enable mechanical enhancement at lower filler contents than with traditional filler⁷.

2.2 Chitosan

Chitosan is a biopolymer obtained by N-deacetylation of chitin, which is the second most abundant polysaccharide on nature after cellulose. Chitosan forms clean, tough and flexible films with good oxygen barrier, antimicrobial properties against variety of microorganisms. Chitosan is an excellent choice for use as edible films or coatings, enhancing shelf life of a diversity of food products.

3. Inorganic Nanoparticles

3.1 Titanium Dioxide

Titanium dioxide (TiO₂) is an inert, nontoxic, and inexpensive material with potential activity against a wide variety of microbes due to its photocatalytic activity. Incorporation of TiO₂ into polymer matrix provides protection against foodborne microorganisms on the presence of radiation of relatively low wavelength near the ultraviolet region also it leads to improved mechanical properties. In the visible and near-infrared region thin TiO₂ films exhibit excellent mechanical and chemical durability^{8,9}.

3.2 Zinc Oxide

ZnO in nanoscale has shown antimicrobial properties and potential applications in food preservation¹⁰. ZnO nanoparticles have been incorporated in polymeric matrices in order to provide antimicrobial activity to the packaging material. In addition, ZnO nanoparticles allow for the improvement of packaging properties such as mechanical, barrier properties and thermal stability. ZnO is currently listed as a generally recognized as safe (GRAS) material by the Food and Drug Administration.

ZnO nanoparticles has been tested against some gram-positive and gram negative bacteria. Gram positive bacteria such as *Bacillus subtilis* and *Staphylococcus aureus*, were found to be sensitive to ZnO nanopar-

ticles^{11,12}. The study on gram negative bacteria such as *Pseudomonas aeruginosa*, *Campylobacter jejuni* and *Escherichia coli* also revealed antimicrobial action of ZnO nanoparticles^{13,14}.

3. Preparation Methods of Organic and Inorganic Nanoparticles

The micro scale particles could be transformed into nanoparticles by using “top-down” or “bottom-up” approach of synthesis. In “top-down” process, nanoparticles can be produced from structure and size refinement

through a breakdown of larger particles. In “bottom-up” process, nanoparticles can be prepared from a buildup of atoms or molecules in a controlled manner that is regulated by thermodynamic means such as self-assembly¹⁵.

4.1 Preparation of Inorganic Nanoparticles

4.1.1 Sol-gel Method

Figure 1 represents Sol-gel method. In order to obtain crystalline nanoparticles of titanium dioxide, titanium hydroxide gel is prepared by the sol-gel method and then dried at 80°C. After drying it is calcined at a high temperature around 450°C.

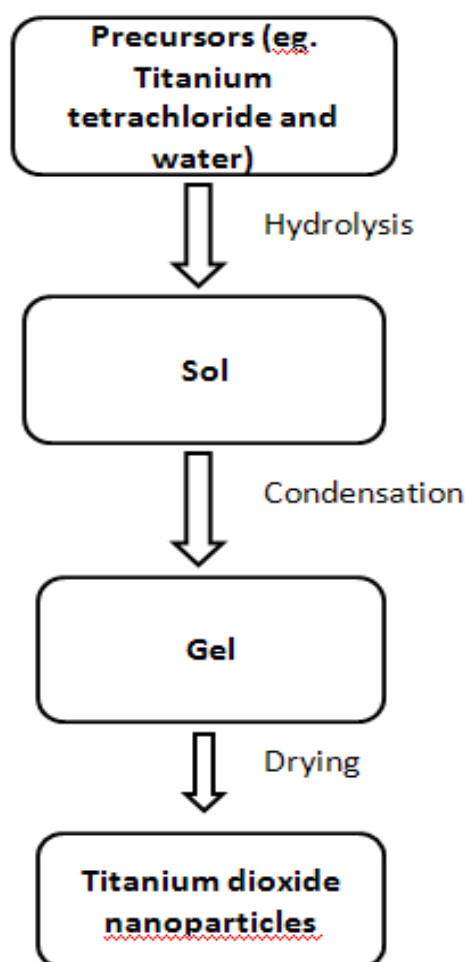


Figure 1. Sol-gel method of nanoparticles synthesis.

4.1.2 Mechanochemical Processing Method

MCP method **Figure 2** combines size reduction by ball mill coupled with chemical reactions activated at nanoscale during grinding.

4.1.2.1 Physical Vapor Synthesis

This method involves addition of reactant gas to the vapor, which is then cooled at a controlled rate and condensed to form nanoparticles. This method typically produces particles with average sizes ranging from 8 to 75 nm.

4.2 Preparation of Organic Nanoparticles

Organic nanoparticles could be prepared by different techniques depending upon the source.

4.2.1 Preparation of Chitosan Nanoparticles

There are mainly two methods of synthesis: a) Ionic gelation method b) Reverse micellar method¹⁶.

4.2.2 Ionic Gelation Method

In this method chitosan interacts with oppositely charged macromolecules for eg. TPP (Tri-polyphosphate). The extent of interaction between these two depends upon charge density which in turn varies with pH of solution. The concentration of chitosan and TPP is directly proportional to size of nanoparticle formed.

4.2.3 Reverse Micellar Method

Another method of synthesizing chitosan nanoparticles is to add enough surfactant and aqueous salt solution to

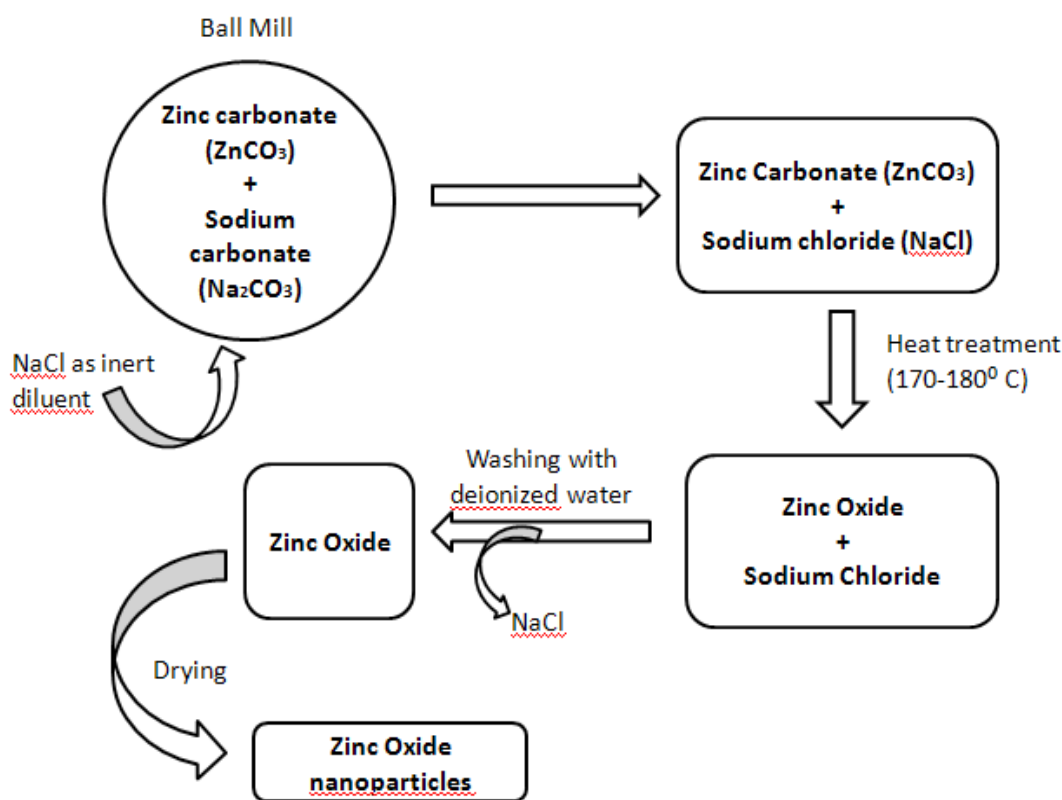


Figure 2. Mechanochemical processing method.

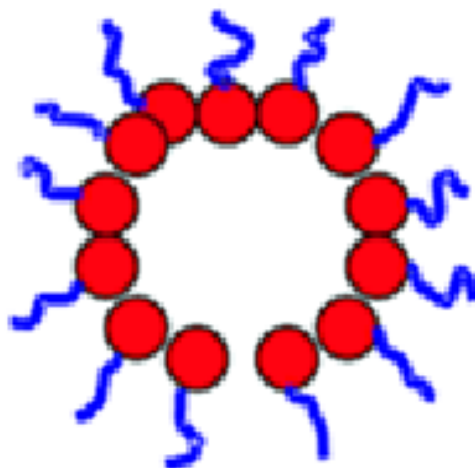


Figure 3. Inverted micelle.

a nonpolar organic solvent to produce spherical inverted micellar structures **Figure 3** around the target size of the nanoparticles. An aqueous solution of chitosan is added with constant agitation to avoid any turbidity. More water should be added if nanoparticles of a larger size are to be prepared. After the reaction, the surfactant remains adsorbed to the surface of the nanoparticles stabilizing them against aggregation and oxidation¹⁷.

4.2.4 Preparation of Starch Nanoparticles

Starch consists of two components: amylose and amylopectin. Amylose is defined as linear molecules of anhydrous glucose units that are linked mainly by α -(1-4)-d-glycoside bonds, with average molecular weights less than a million^{18,19}. Amylopectin, however, extensively branched with α -(1-6) linkages, has average molar mass up to hundreds of millions²⁰⁻²². More is the amylose content more crystallinity will be there in the nanoparticles.

4.2.4.1 Acid Hydrolysis

Starch is found in semi-crystalline state and aqueous acids could be used to hydrolyze the amorphous amylose regions so as to release the crystalline sections of amylopectin from the polysaccharide. Acid hydrolysis facilitates nanoparticles formation because the crystalline portions of starch are usually more resistant to hydrolysis than the amorphous one. Therefore, because of the difference in acid susceptibility crystalline nanoparticles could be prepared by selective acid hydrolysis of the amorphous regions²³. The initial stage of acid hydrolysis is thought to be the hydrolysis of the amorphous parts within starch granules, whereas the slow stage is attributed to the erosion of the crystalline regions^{24,25}. Two hypotheses have been proposed to account for the slow hydrolysis of the crystalline domains in starch granules. The first one is that the dense packing in the crystalline regions retards the

penetration of H_3O^+ . The second one is that the hydrolysis of the glucosidic bonds in crystalline domains requires a change from chair to half chair conformation.

4.2.4.2 Ultrasonication

Ultrasound are the sound waves above the frequency of normal human hearing range (>15-20 kHz). Piezoelectric or magneto strictive transducers are used to create high energy vibrations. These vibrations are amplified and transferred to a sonotrode or probe, which is in direct contact with the fluid. Sonication power, frequency, temperature and time of the effect of ultrasound on starch depends on many parameters such as sonication power and frequency, temperature and time of the treatment, and properties of starch dispersion (e.g. solid concentration and botanical origin). Recently, ultrasonication of starch suspension was introduced as a process for the preparation of SNPs²⁶. Compared with the common acid hydrolysis, this process offers the advantages of being rapid and easy to implement without the need to undertake repeated washing treatment because no chemical reagent is used.

4.2.4.3 Gamma Irradiation

Gamma irradiation can generate free radicals which are capable of hydrolyzing chemical bonds, thereby producing smaller fragments of starch called dextrin²⁷. According to the study by Lamanna et al. (2013)²⁸, SNPs that have a size of approximately 20 and 30 nm were obtained by applying a dose of 20 kGy from cassava and waxy maize starches (with an irradiation rate of 14 kGy/h), respectively.

5. Nanocomposites

Nanocomposite is a multiphase solid material in which one of the phase has one, two or three dimensions of nanometer scale. Generally nanocomposites are composed of two components: one is the matrix whose role is to support and protect the filler materials, other

component is the filler which is at nanoscale i.e. nanoparticles. Nanocomposites were established to improve the mechanical, thermal, and barrier properties of biopolymers and to extend the application field.

As per the previous studies the nano-sized fillers or the nanoparticles play an important structural role while acting as a reinforcement to improve the mechanical and barrier properties of the matrix. The matrix tension is transferred to nanofillers through the boundary between them^{29,30}. The incorporation of nanoparticles such as silicate, clay, and titanium dioxide (TiO_2) to biopolymers not only improved their mechanical and barrier properties but also added antimicrobial, biosensor, and oxygen-scavenging properties.

Apart from these nano-fillers, starch nanoparticles have been used as fillers in different polymer matrices. Spray dried and vacuum freeze dried starch nanoparticles have been incorporated in corn starch based films; the films obtained were denser and with improved mechanical properties. Kristo and Biliaderis studied the addition of starch nano-crystals on the properties of pullulan film. The water uptake of pullulan-starch nano-composites decreased with increasing filler content whereas water vapor permeability remained constant up to 20% (w/w)³¹.

6. Conclusion

All the above methods of nanoparticles synthesis whether it be organic or inorganic, encounters the problem of particle aggregation and thus control over the size and shape of nanoparticles become difficult. Much control and care over the concentration and parameters of every process is needed which is difficult to achieve. More work need to be done to overcome the problem of nanoparticles aggregation. Compatibility between the filler nanoparticles and the matrix polymer is most important criteria which decide the safety of food as well as effectiveness of reinforcement and barrier properties of the nanocomposites formed.

7. References

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