Journal of Advancements in Food Technology
Volume 1 | Issue 1

Review Article Open Access

TiO_2/Polymer Nanocomposites for Antibacterial Packaging Applications

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Citation: Rehim MHA, Alhamidi J (2018) Tio_2/Polymer Nanocomposites for Antibacterial Packaging Applications. J Adv Food Technol 1(1): 101. doi: 10.15744/2639-3328.1.101

Received Date: June 28, 2018 **Accepted Date:** July 11, 2018 **Published Date:** July 13, 2018

Abstract

Packaging material should meet many requirements for safe preservation of food and extend shelf life. Utilization of nanoparticles to prepare active packaging films has been widely investigated. This review deals with food packaging films modified with nanotitania to enhance mechanical, barrier and antibacterial properties of the packages. The photocatalytic activity of TiO_2 nanoparticles extended its application to antimicrobial food packaging, photocatalytic paper and toxin passivation and deodorizing. Different TiO_2 morphologies are favorable in many potential applications such as in environmental purification. Finally, this review will also discuss safety assessment of nanomaterials used in food packaging and migration mechanism into food staff.

Keywords: nanoparticles; antibacterial; active packaging; nanocomposite; Food-safety

Introduction

A nanocomposite is the product of coupling of at least two dissimilar substances having a distinct interface, even if one of them at least one dimension in the nanometer size range (1-100 nm). Polymer-inorganic hybrids offer promise for engineering new composites in the automotive, packaging, and aerospace industries as well as materials exhibiting excellent thermal, gas spacing, and other valuable properties. This is due to they combine both the advantages of organic polymer (flexibility, lightweight, good impact resistance, good processability) and inorganic materials (high mechanical strength, good chemical resistance, thermal stability, optical properties [1]. However, the choice of inorganic material and polymeric matrix depend on the application and the required properties. Combination of polymers and metal oxides nanoparticle can enhance thermal, optical, electronic and mechanical properties of the obtained nanocomposites [2,3].

Recently, much attention has been paid to nanosize transition metal oxide such as Titanium dioxide (TiO_2) and Zinc oxide (ZnO) because of their versatile properties. Hence, they found applications in energy storage, catalysis, sensors and biological fields [4-7]. Titanium dioxide is a naturally occurring mineral, that exists in different crystalline structures among them anatase, rutile and brookite [8-11]. Under standard conditions, rutile form is the most thermodynamically stable phase [10,12]. However, anatase is transformed to rutile phase by annealing at appropriate temperatures [13,14]. Moreover, photocatalytic activity of anatase structure is higher compared to other phases of TiO_2 [15]. Moreover, TiO_2 is characterized by its high refractive index, durability, dispersion, tinting, strength, chemically inert nature, low cost, and nontoxicity [10,16].

To date, the majority of TiO_2 used industrially is not nanoscale and considered chemically inert and safe for human health and ecosystems. However, with the development of nanotechnology, titania nanoparticles have been produced more extensively and found wider applications owing to their unique physicochemical properties when compared to the bulk [8]. Incorporation of TiO_2 nanoparticles in polymeric films leads to significant improvement in surface hardness. Moreover, other properties such as antibacterial and self-cleaning can be introduced to the formed film based on the photocatalytic effect of the TiO_2 nanoparticles [17]. In fact, TiO_2 is considered the best available photocatalyst due to its high photoactivity and photodurability [18] A high surface-to-volume ratio is very significant for photocatalytic reaction since it takes place on the surface of the catalyst. Therefore, reducing the size of TiO_2 powder to the nanoscale is of great significant in increasing the decomposition reaction [19]. However, utilization of other morphologies of TiO_2 such as nanofibers or nanotubes as photocatalysts has been reported [20,21]. The results confirmed that the large surface area of the nanofibers enhanced the photocatalytic efficiency of the photocatalyst. Moreover, the good shape retention favorable the potential application in environmental purification.

This work is concerned with synthesis of antibacterial packaging films based on TiO_2/ polymer composites. A special attention will be given to the stat-of-the-Art food packaging films and their properties such as gas and vapor barrier, extending food shelf life and quality assurance.

Properties for Food Packaging Material

Food packaging is the largest growing manufacturing sector in the world. The main role of the packaging material is to protect food from heat, oxygen, moisture, dust, microorganisms and insects. General properties of packaging materials are mechanical properties, optical properties, gas, water vapor and aroma barrier, antimicrobial and environmentally friendly. Nowadays, there is a demand to extend shelf life of the food by controlling bacterial and enzymatic reactions within the packages. Number of strategies have been described such as controlled release of oxygen, removal of oxygen and addition of antimicrobial agents within the packaging film.

Tio_2 as Antibacterial Agent

The substance that can kill or inhibit the growth of microorganisms is known to be antibacterial material [22]. Many industrial applications require presence of antibacterial agents such as food, health care, packaging and textiles. TiO_2, among other metal oxides nanoparticles, is characterized by its antimicrobial property beside its nontoxicity [23] So that, TiO_2 is used in many industries such as sunscreens, cosmetics and pharmaceutical products. Pişkin *et al.* investigated the antimicrobial properties of TiO_2 nanoparticles against Esherichia coli, Stapyloccus aureus, Pseudomonas aeruginosa, Candida albicans and Bacillus subtilis (ATCC 6633) [24]. Well diffusion method and minimum inhibitory concentration (MIC) were used to investigate the antimicrobial activity of the nanoparticles. While MIC observed were 9.7 μg /ml for E. coli, 19.5 μg /ml for S.aureus., 19.0 μg / ml, P.aeruginosa, 9.7 μg /ml for C.albicans and 19.5 μg/ml for B.subtilis. Researchers also investigated the antibacterial activity of TiO_2 nanoparticles against *E. coli* in the solid state [25]. Study of the growth curve of *E-coli* against different concentrations of TiO_2 nanoparticles revealed the inhibitory effect of the nanoparticles. The reason for this might be due to the inactivation of cellular enzyme and DNA by the nanoparticles causing little pores in the bacterial cell wall that leads to increase of permeability and cell death. Evaluation of antibacterial activity of TiO_2 nanoparticles in combination with cell wall active antibiotics–ceftazidime against Pseudomonas aeroginosa is reported [26]. The drug resistant-Pseudomonas aeroginosa isolated from pus and commercial P25 TiO_2 nanoparticles were used. The nanoparticles exposed to UV light for an hour during the study showed enhanced antibacterial activity. It was suggested that generation of electron hole pair on the surface of the nanoparticles due to irradiation of UV light have been occurred. Reaction of the holes in the valence band with H_2O or hydroxide ions on the surface leads to formation of hydroxyl radical, while, electron in the conduction band reacts with O= to yield superoxide ion (O_2•–). Scheme 1 shows different reactions of electrons and holes on irradiated TiO_2. Both hydroxyl ions and (O_2•–) are reactive to phospholipid components in the cell membrane of the microorganism. As a result, deterioration of the cell membrane occurs and finally inactivates the bacteria [27,28].

$$TiO_2 + h\nu \rightarrow TiO_2\ (e^-; h^+)$$
$$h^+ + H_2O \rightarrow H^+ + \bullet OH$$
$$h^+ + OH^- \rightarrow \bullet OH$$
$$e^- + O_2 \rightarrow O_2\bullet^-$$
$$O_2\bullet^- + H^+ \rightarrow HO_2$$
$$\bullet OH + \bullet OH \rightarrow H_2O_2$$
$$e^- + H_2O_2 \rightarrow \bullet OH + OH^-$$

Scheme 1: Reaction products of photo-activated TiO_2 and water.

Tio_2 Based Antibacterial Packaging Materials

In today's state-of-the-art nanocomposites antibacterial materials, making several improvements regarding used nanoparticels and preparation of antibacterial packaging films is essential. Antibacterial packaging materials are very attractive and promising nanocomposites as food-packaging films that can protect food staff from microorganisms. Moreover, extending shelf life and increasing safety assurance can be achieved. Preparation of polymer hybrids either as coatings or incorporated in the polymer matrices using nanotitania antibacterial agent is the most attractive [29-36]. Recently, these kinds of polymer hybrids have gained considerable attention due to the cheap cost of nanotitania, nontoxicity and hence their approval from FDA to be used in food industry [37]. Many TiO_2/ polymer nanocomposites based on conventional linear polymers have been prepared and characterized so far [38]. High impact polystyrene/TiO_2 nanocomposite have been prepared by melt compounding technique [39]. The testing bars were fabricated from the nanocomposites' pellets using an injection molding machine. The antibacterial properties of the prepared samples showed remarkably enhancement with increasing contacting time. On the other hand, presence of the nanofiller did not affect much rheological and mechanical properties of the obtained nanocomposites. Recently, an article was published describing the preparation of bio-nanocomposite packaging film through incorporation of TiO_2 nanoparticles in poly(butylene adipate-co-terephthalate) [40]. The films prepared by solution casting technique showed increase in the mechanical and oxygen barrier properties by increasing concentration of TiO_2 nanoparticles. Moreover, the antibacterial activity of the obtained films against both Gram-positive and Gram-negative pathogenic bacteria, have been investigated. The results revealed the utility of the bionanocomposite films in food packaging application. Incorporation of TiO_2 anatase and rutile nanoparticles into a low density polyethylene (LDPE) polymeric matrix has been reported [31]. The photocatalytic antimicrobial effects the prepared nanocomposite food packaging film has been evaluated by in vitro and in vivo tests. For the later test, covering of fresh pear with the TiO_2 nanocomposite film and illumination with by a fluorescent light lamp for 17 days at 5°C revealed that the number of mesophilic bacteria and yeast cells decreased significantly compared to samples stored in unmodified LDPE film. Nanocomposites based on biocompatable polycaprolactone and TiO_2 nanoparticles were prepared via straight forward melt processing [41]. Testing of the antibacterial activity of the prepared nanocomposites was carried out in UV and visible light against Gram-negative *Escherichia coli* bacteria and Gram-positive *Staphylococcus aureus*. The larger effect is to the homogenizing distribution and no aggregation at large scale. It should be pointed out that, TiO_2 works as surface-to-near surface contact unlike other antibacterial agents such as Ag that is typically released to the media [42].

The obtained results for control or elimination of E-coli the prepared nanocomposites are better when compared to other work using TiO_2 powders or immobilized on polymer support [43-47]. These results might be attributed to the fact that the biocidal capability is better in the UV region than in the visible light.

Fonseca *et al.* studied another example for TiO_2 nanocomposite based on a biopolymer [48]. In this work, polylactic acid (PLA) is used as a matrix for TiO_2 nanoparticles that were prepared by sol-gel method. The study evidenced that no end conclusion can be made concerning the optimum concentration of TiO_2 nanoparticles in the nanocomposite. Increasing dispersion of TiO_2 nanoparticles in the polymer matrix can be attained through surface modification of the nanoparticles [49,50]. It was found that inclusion of TiO_2 in the PLA matrix increased polymer crystallinity beside improving its mechanical properties. The rheometric properties of the prepared nanocomposites showed pseudoplastic behavior and decreasing in the viscosity especially at low shear rate. The low viscosity can be attributed to the lubricant effect of the nanoparticles that improves the mobility of polymer chains. Moreover, reduction of the frictional coefficient and improvement in the wear resistance was observed [51]. surface modification of TiO_2 nanoparticles with stearic acid significantly reduced the shear values of the prepared nanocomposite [52].

Different morphologies of TiO_2 in the nanoscale have been exploited as filler in a polymer matrix. Nanowires and nanobelts are among these morphologies. The idea is increasing surface area of the 1D prepared nano-titania and hence better dispersion in the polymer matrix could be reached. Preparation of TiO_2 nanowires (NWs) using hydrothermal method is successfully used to get NWs of different diameters and thickness up to nanobelts. This change in the NWs dimensions is due to change in the hydrothermal reaction conditions. Preparation of composites from hyperbranched polyester and TiO_2 nanowires has been reported as photocatalyst for removal of organic compounds from wastewater [53]. In this work, the NWs used without previous modification, showed good dispersion in the hyperbranched polymer due to presence of hydroxyl groups on the surface of titania nanowires and also as terminal groups in the polymer. Youssef *et al.* described synthesis of TiO_2 NWs/polystyrene nanocomposites through inclusion of the nanowires in the polymer matrix [54]. Abdel Rehim *et al.* described a novel technique for surface tuning of sodium titanate ($Na_2Ti_3O_7$) nanobelts to more hydrophobic one through exchanging crystal lattice cations [55]. This interfacial modification have been carried out through nanoblending of NBs into the poly(vinyl benzyl chloride) or p(VBC) and the sulfonated form of pVBC's [or sp(VBC)] matrixes. This successful method led to tailoring the surface character from being hydrophilic to being hydrophobic by design. The hydrophobic NB's were used to prepare nanocomposites through blending with commercial polystyrene [56]. The novel surface modification technique allowed better dispersion and compatibility of the modified NBs in the hydrophobic polystyrene matrix. Investigation of the antimicrobial properties of the obtained nanocomposites against different microorganisms namely, Gram-positive (S. aureus) and Gram-negative bacteria (P. aerugenosa), fungi (A. niger) and yeast (C. albicans) have been carried out. The results suggested that this method can be generalized in low cost industrial mass production. Several articles have described preparation of nanocomposites based on TiO_2 nanowires with other linear polymers such as polymethylmethacrylate and polyvinyl pyrrolidone for packaging application [57,58].

Doped Tio_2 in Antibacterial Packaging Materials

Recently, researchers gave particular interest to improvement of antibacterial properties of TiO_2 through its combination with other active antimicrobial agents [59]. Combination of TiO_2 with Ag nanoparticles is reported to prepare packages for agricultural products and rice storage [58-64]. Ag nanoparticles are characterized by its high thermal and electrical conductivity. Moreover, silver is considered a promising material for doping of titania due to its ability to prevent recombination of electrons and holes generated during the photoreaction [65-68]. So that, enhancement in the decontamination is attained and TiO_2/Ag based nanocomposites are considered efficient antimicrobials for food packaging [67-76]. Other materials such as chitosan have been used as matrix for TiO_2 nanoparticles. Films prepared from TiO_2/chitosan showed high antibacterial properties against various pathogenic microrganisms [77]. Red grapes packed in the prepared biofilms and stored for a week showed low microbial infection beside extended shelf life.

Incorporation of TiO_2/chitosan in PVA to prepare films for white cheese packaging has been carried out [78]. The soft white cheese wrapped in the composite film was stored at 7oC for 30 days. The tested wrapping films proved themselves as antimicrobial packaging films after evaluation of the cheese color, rheological and chemical properties beside the behavior against gram-positive and gram-negative bacteria. Starch as a biopolymer was also used as a matrix for TiO_2 nanoparticles in order to prepare bionanocomposite for food packaging [79]. Films of low water-vapor permeability and increased elongation at break and tensile energy, were obtained these, also considered as UV-protecting packaging films.

Photocatalytic and Antibacterial Paper

Paper is an important packaging material but recently utilization of nanotechnology enabled researchers to prepare specialty paper such as photocatalytic and antimicrobial paper. This type of modified paper can find applications in food packaging beside hygienic and medicinal fields. Production of such paper is started 10 years ago by Mitsubishi paper that produced paper coated with light catalyst (TiO_2) and commercialized as air purifiers. Also, Fushimi Inc. commercialized Titernal photocatalyst which composed of TiO_2 nanoparticles of size 10 nm and can be applied on paper, walls or ceilings.

Modification of paper sheets with antimicrobial nanoparticles can be performed either by coating the sheets with the modifier or addition of the nanoparticles during making sheets [80-82]. Combination of TiO_2 nanoparticle and a synthetic polymer in order to prepare a formulation for paper coating, has been also described [83]. A new approach for preparing photocatalytic and antimictobial paper has been reported by Abdel Rehim *et al.* [84]. The method is based on preparation of TiO_2 modified by sodium alginate, then addition different amounts during making sheets. Sodium alginate has two major tasks, the first is stabilization of the nanoparticles and aggregation and secondly increased adhesion of the nanoparticles to paper fibers and prevent harmful effect of the photocatalyst on them.

An interesting study dealing with investigation of antibacterial and preservation efficiency of packaging paper coated with TiO_2/chitosan on nanguo pears [85]. Measuring of the sensory of the nanguo pears showed that the weight loss of the fruits packed in antibacterial paper is less than those packed in normal paper. By 30 days storage, the decay index of the nanguo pears is minimum. On the other hand, for the physiological index, the nanguo pears coated with antibacterial paper showed superior results concerning the peel aerobic bacterial count compared to the base paper. Moreover, the content of titratable acid of nanguo pear packed in the antibacterial paper is higher than of the control group packed in normal paper, i.e. the antibacterial paper preserved that taste of the nanguo pear.

Preparation of photocatalytic paper for antimicrobial passivation using Zeolite based TiO_2 nanoparticles for packaging is investigated [86]. Cationic starch and cationic polyacrylamide, are used for nanoparticle retention during papermaking process. The modified paper sheets showed superior photocactlytic activity compared to unmodified paper. Such photocactlytic paper can find further application in wrapping paper for fresh meat and fish, napkins, uncooked food and fruits [87,91].

Food Shelf Life and Safety

Conventional plastic or paper packaging materials are not sufficient to fulfill the today's needs. Packaging materials required to preserve food or vegetables for long times must meet important requirements. Thanks to nanotechnology, a great improvement in the food packaging materials is attained through addition of nanoparticles that add new properties to the packaging. Properties such as oxygen and water vapor barrier is essential since water and oxygen facilitate the environment for pathogenic microorganisms. So that addition of oxygen scavenger such as TiO_2 as a photocatalyst reduces amount of oxygen in the oxygen-sensitive food staff [92]. On the other hand, addition of the antibacterial agent to the food might cause instant inhibition in the food microorganisms. However, the survive population will grow again upon depletion of the antibacterial material causing reduction of food shelf life [93,94]. Since the main goals of a packaging material are extending shelf life, safety assurance of the food and maintaining food quality, the novel antibacterial packaging should be designed to fulfill these goals.

Great interest of scientists in food antimicrobial packaging led to numerous research articles. However, the lab scale work is much less complicated than real case since food contains more salt, water and nutrients that can interact with bacteria [95-97]. Moreover, considerable effect of transportation and storage of food has been found. Microbiologists and chemists have revealed that achieving the same results in real life is difficult. It was found that on testing of antimicrobial properties for food packaging contains oils as antimicrobial agent, much oil is required than used on the lab scale to get the same effect [91,98,99].

Another important issue should be considered while manufacturing a packaging material contains nanoparticles that is, *safety* and an important question might rise: *Does presence of such nanoparticles near our food is safe?*

Actually, it is difficult to answer this question since understanding of potential exposure via migration into food is required for correct assessment of nanomaterials in food packaging. However, there are several issues complicate the explanation of the migration of nanomaterials into food staff through polymer packaging. Among these issues uncertainty of the analytical techniques to determine and detect nanoparticles also, limited description of sample preparation method beside uncertainty about the influence of the used method. Factors affecting migration of nanoparticles into food are many such as temperature, position of nanoparticles in the packaging material, nature of food and interaction of the nanoparticles with the food stuff [100-102]. Migration of silver from nano-Ag/nano-TiO_2 containing packaging materials contains fruits, white cheese or fresh carrot was studied [103]. Samples were stored for 7 days at 40 °C then the processed food samples were analyzed to detect Ag and TiO_2 using SEM-EDX and XRD. The results showed that no significant amounts of Ag or Ti were found in the food. The level of Ag nanoparticles in orange juice was 5.7 ± 0.02 μg/L vs. 0.16 ± 0.01 μg/L in controls while the level of Ti was found to be 2.5 ± 0.03 μg/L. Another study for Panea *et al.* [104] to detect Ag and Zn in (5% and 10% w/w) LDPE blend using ICP-MS revealed that the nanoparticles level is lower than detection limit. Although TiO_2 is approved to be added to food as coloring agent (E171), the nano-TiO_2 is not [105]. Migration tests of TiO_2 have been carried out by Lin *et al*. for Ti-PE packaging films using ICP-MS analysis [106]. Particle size determination by laser particle size analysis confirmed the nanosize of Ti while SEM imaging revealed presence of some aggregates. The results showed that migration of Ti increases by increasing its concentration in the film, time of exposure and acidity of food.

Recently, the *European Commission* has published a list of authorized substance to be in direct contact with food among these substances titanium nitride in PET plastic up to 20 mg/kg. Nevertheless, migration experiments concerning TiO_2 suggested that potential exposure of consumers and public health issue because of incorporation of the nanoparticles in the polymer packaging materials is likely to be very low. As a conclusion, the previous question is still opened for arguments and more migration studies should be made by establishing multidisciplinary approach through bringing experts of different fields such as food technology microbiology and material science. In this way, creation of a promising future of antibacterial food packaging industry is achievable.

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