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Research Article
Migration and Characterization of Nano-zinc Oxide from Polypropylene Food Containers

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Abstract

Background and Objective: Zinc oxide has achieved increasing attention in an extensive range of areas, due to its strong antimicrobial effect and generally recognized as safe material listed by FDA. However, the possibility of migration from commercial products is always an issue of mutual concern when its application is food packaging. This study evaluated the migration of nano-zinc oxide from polypropylene food containers to the food-simulating solutions based on the Chinese standard. **Methodology:** Several experimental factors influenced zinc oxide release: Food simulant, temperature and storage time. **Results:** Results revealed a significant nano-zinc oxide migration into oily, acidic and aqueous simulants. The amount of zinc oxide migrated increased with storage time and temperature although, zinc oxide showed a low tendency to migrate into food simulants. **Conclusion:** The Zn^{2+} substance was quantified by inductively coupled plasma mass spectroscopy (ICP-MS) and migration was found to occur within a range of 0.15-0.56 μg L^{-1}. Meanwhile, Scanning Electron Microscopy/Energy Dispersive Spectrometer (SEM/EDS) and Malvern Zetasizer Nano were applied to identify the existence and the morphology of nano-zinc oxide.

Key words: Nano-zinc oxide, migration, polypropylene, food safety, food container

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

For the food industry, where competition is fierce and innovation is crucial, the emergence of nanotechnology have aid advancements in food production, packaging and shelf life of foods. Nanoparticles are easily incorporated into polymers to produce functional materials[1], which make food packaging materials achieved antimicrobial effects, improved tensile properties, oxygen scavenging, extended shelf life and some novel features[2-6].

Metals and metal oxides with nanosized particle size such as nano-Ag, nano-TiO_2 and nano-ZnO have emerged as a promising substance in a wide range of applications, including food packaging, due to their antibacterial properties and thermal stability[7,8]. Among them, zinc oxide have attracted increasing attention because its features are low cost of production, high performance of particle size and morphology and degradation by human body. The ZnO nanoparticles have strong bacteriostatic activity against *E. coli* and *Staphylococcus aureus*[9] and the antibacterial activity increases with increasing nanoparticle concentration and decreasing nano particle diameter.

The US Food and Drug Administration Center[10] has been classified zinc oxide as one of the generally recognized as safe, five kinds of zinc compounds[11]. Zinc oxide can be degraded by the body, unlike silver or titanium dioxide which will accumulate in human body chronically and cause hazard.

However, compared with the macroscopic material, nanomaterial have smaller particle size and larger surface area which may cause the nanoparticles penetrate through the network structure of packaging materials and diffused into food more easily. After entering into body, nanoparticles may transfer to the surrounding tissues or organs, break through the blood brain barrier and cause potential food safety issues[12]. According to the domestic and foreign studies, the toxicity of nano-zinc oxide to human bronchial epithelial cells[13], human lung epithelial cells[14] and human kidney cells[15] has been demonstrated. While, at the same time some studies indicated that ZnO nanoparticles would not enter into the normal cells or do harm to human or animal skin[16]. However, *in vivo* toxicological studies concerning nano-zinc oxide are still deficient in the literature and their conclusions are sometimes contradictory[17,18].

The main pathway nanoparticles in packaging materials entering into human body is through the digestive tract and for the nano-zinc oxide in food packaging materials, primarily this study should confirm whether the ZnO nanoparticles would migrate from food packaging materials into food. If the migration exists, there is need to explore further the potential toxicity after ZnO nanoparticles migrated into food.

The aim of this study was to evaluate the presence and possible migration of ZnO nanoparticles from the commercially available polypropylene antibacterial food containers to food simulating solutions. A wide range of analytical techniques are required for detection and characterisation of nanoparticles, because no single technique can provide all relevant information[19]. Migration experiments were carried out according to the Chinese standard[20]. The amount of nano-zinc oxide in the obtained food-simulating solutions were inspected by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). In addition, further confirmation of the presence and morphology of ZnO nanoparticles were performed by Scanning Electron Microscopy Energy-Dispersive X-ray (SEM/EDX) and the Malvern Zetasizer Nano analysis.

MATERIALS AND METHODS

Materials: Commercially available nano zinc oxide antibacterial food containers composed of polypropylene (pp) plastic (Nano center, Ltd., Shanghai, China) were used as the original material and all chemical reagents this experiment used were of analytical grade. Solutions were prepared with distilled water (A.S. Watson Group (Hong Kong) Ltd., Hong Kong, China). The food-simulating solutions this study selected were as follows: Distilled water-simulating solution A, 4% acetic acid (v/v)-simulating solution B, hexane-simulating solution C.

The simulating solution A (distilled water), simulating solution B [4% acetic acid (v/v)] and simulating solution C (hexane) represent water, acid and fatty foods, respectively, according to the Chinese standard GB/T 5009.60-2003.

The antibacterial containers were washed with pure water and dried under natural conditions for sample preparation.

Determination of zinc oxide in polypropylene antibacterial nanocomposite: A microwave digestion method was carried out to pre-process the polypropylene (pp) food container. A precise mass of 0.15 g polypropylene sample was placed in a digestion tube within a mixed solution of 4 mL of distilled nitric acid and 3 mL of hydrogen peroxide as digestion reagent. Then the tube was sent into the microwave digestion oven (CEM MARS, Matthews, NC, USA). After the microwave digestion procedure, the digested solution was cooled and diluted with distilled water to 50 mL. The samples were quantified in triplicate by ICP-MS.

Migration experiments and analysis by ICP-MS: The antibacterial food containers cut into a certain size of 2×2 cm

and weighted accurately were placed in contact with food simulants and sealed in clean wide-mouth bottles at the certain conditions of temperature and contact time. The full migration immersion method of US Food and Drug Administration (FDA) stipulates that every 24 g sample should be immersed in 200 mL food-simulating solutions. In this study, samples were kept in the dark at tem peratures of 30, 45 and 60°C for 3, 5, 7 and 10 days. The storage time and temperature for this study were chosen according to the reasonable circumstances of the real and worse conditions, which would be beneficial to study the migration laws[19].

Due to the migrated ZnO nanoparticles present in metal oxide form in the food-simulating solutions, microwave digestion was carried out to digest ZnO molecular to Zn^{2+} under the action of high temperature, high pressure and adding acid. Then an ICP-MS (NexION 300X, PerkinElmer, USA) was employed to quantify the migrated Zn^{2+} concentration, so that the migration of nano-ZnO particles content would be infered. The ICP-MS analysis is a quantitative technique which combines a high temperature ICP source with a mass spectrometer. It is commonly used to detect ultra trace metals in complex matrices such as foods[21].

Scanning electron microscopy/energy dispersive spectrometer analysis: Scanning electron microscopy (Hitachi SU8010 FE-SEM, Hitachi, Tokyo, Japan; TEAM Apollo XL EDS EDAX, USA) was applied to detect the existence and the morphology of ZnO nanoparticles in pp antibacterial food container and in the migration extracts. The EDS detector was equipped to get further confirmation of the atomic composition of the samples. The food containers were converted into ash under 600°C to collect some original powder of the containers. The three types of food-simulating solutions were, separately, gathered and concentrated to gain migration substances, in which there existed ZnO nanoparticles along with some other food additives.

RESULTS AND DISCUSSION

Test of nano-ZnO particles in pp antibacterial food containers: The ICP-MS analysis of the solution after microwave-assisted digestion indexed that the total quantity of ZnO nanoparticles in pp antibacterial nanocomposite was 200 μg (ZnO)/g. The SEM-EDS testing results identified the existence of nano-ZnO particles in pp food containers and confirmed the morphology of the nano-ZnO content. Figure 1a shows SEM image of nano-ZnO particles in the ashes. The nano-ZnO particles in columnar forms with sizes between 30-400 nm could be demonstrated. Figure 1b shows a typical EDS spectrum analysis of points within the columnar nano-ZnO particles and determines a majority of nano-ZnO particles. Columnar nano-ZnO particles perform good characteristics of more surface photocatalytic activity points, more easily absorbed and deposited in the bacterial body and more effectively killing bacteria, therefore, columnar nano-ZnO particles possess better antibacterial properties[12].

Characterization of nano-ZnO particles in the migration content: The SEM-EDS images show that nano-ZnO were confirmed in the migration content from food-simulating solutions. Figure 2 were SEM and EDS images of nano-ZnO particles. Figure 2 shows the SEM image, indicated that the nano-ZnO particles migrated out from the pp food containers to distilled water presented in columnar forms and the particles size ranged from 50-300 nm.

In conclusion, the nano-zinc oxide added in polypropylene food containers indeed migrated into the food simulant solutions. The migrated particles presented in columnar forms within 500 nm in size. However, the nano-ZnO particles are with size distribution nonuniform and easy agglomeration. Therefore, the situation of nanoparticles adding into products should not be only considered, the virtually migrated nanoparticles, should also be evaluated correctly in later toxicology studies and safety evaluation of this kind of nanotech products.

Migration amount of ZnO into food-simulating solutions: The ZnO content that migrated from polypropylene food containers to each kind of food-simulating solutions at varying storage time and temperature conditions was quantified by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and migration was found to occur.

Figure 3 demonstrated a significant ZnO nanoparticles migration into food simulants. Several experimental factors influenced zinc oxide release: Food simulant, temperature and storage time.

Results revealed a significant nano-zinc oxide migration into oily, acidic and aqueous simulants. The amount of zinc oxide migrated increased with storage time and temperature although, in general, zinc oxide showed a low tendency to migrate into food simulants. The Zn^{2+} substance was quantified by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and migration was found to occur within a range of 0.15-0.56 μg L^{-1}. Compared with aqueous stimulant, zinc oxide got higher concentration of migration to 4% acetic acid and hexane simulants.

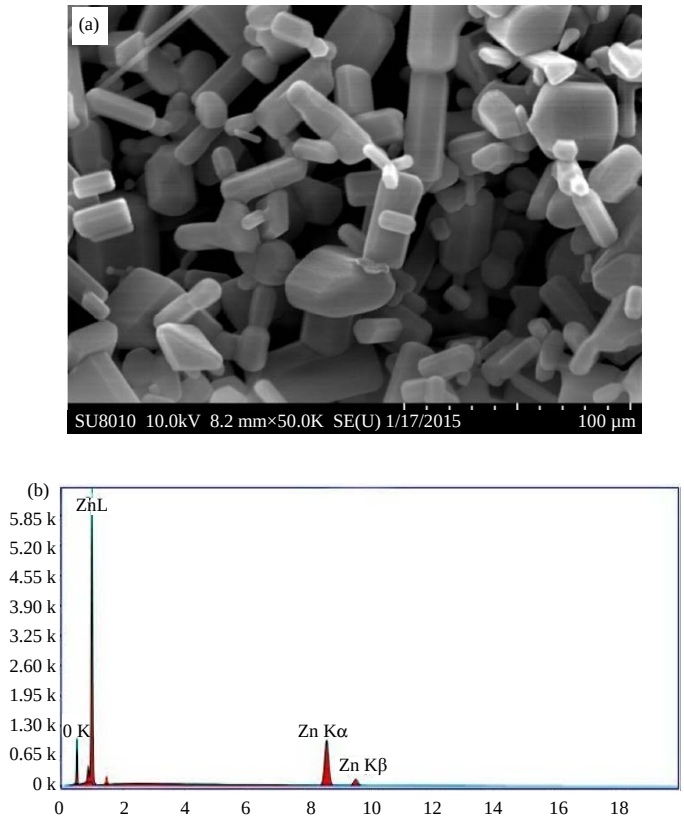

Fig. 1(a-b): (a) SEM image of nano-ZnO particles in the ashes, the nanoparticles are in columnar forms with sizes between 30-400 nm and (b) Corresponding EDS analysis confirming a majority of nano-ZnO particles

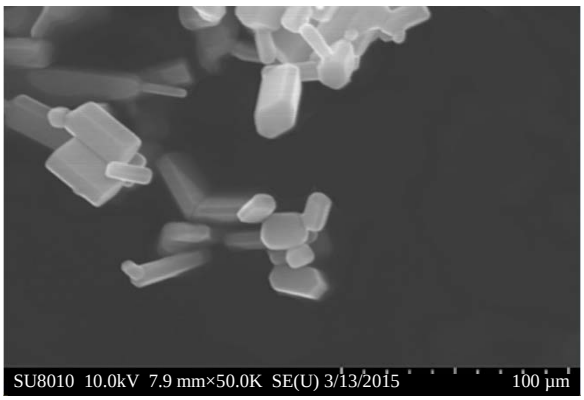

Fig. 2: SEM image of migration content from the distilled water food-simulating solution under 60 and 15 days

The reason may be that the ZnO nanoparticles encapsulated within the surface layers of the samples released firstly, then, the succeeding release of ZnO nanoparticles were from the inner part of the samples which had to cross the diffusion barrier constituted by many crystalline lamellae[22]. In plastics, the water and organic molecules in the interlamellar regions can change the overall crystalline state[23].

According to the analysis of ICP-MS, the polypropylene food containers released ZnO nanoparticles to 4% acetic acid and hexane food simulants more easily. Organic food-simulating solutions have a swelling effect for polypropylene which may cause a high migration concentration of ZnO nanoparticles, secondly, the ZnO can be dissolved by acetic acid and released into the food-simulating solution in the form of Zn^{2+} [24].

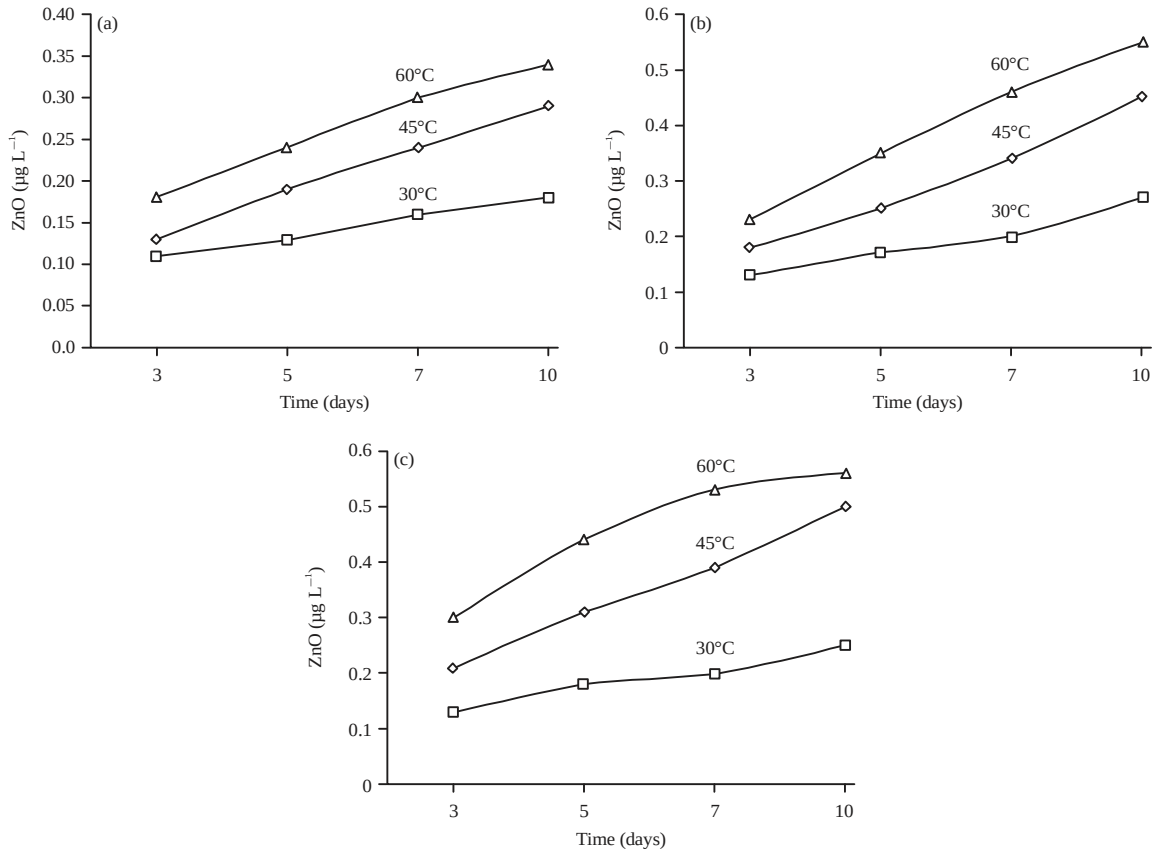

Fig. 3(a-c): Concentration of zinc oxide migrated into (a) Distilled water, (b) 4% acetic acid and (c) Hexane at 30, 45, 60°C for 3, 5, 7 and 10 days

CONCLUSIONS

This study evaluated the migration of ZnO nanoparticles from polypropylene food containers to each kind of food-simulating solutions, which based on the Chinese standard under a variety of time intervals and temperature conditions. Results obtained confirmed the presence that polypropylene food containers released ZnO into the three kinds of food-simulating solutions. The migrated ZnO nanoparticles presented in columnar forms within 500 nm in size, besides easily agglomerated. The amount of ZnO migrated was discovered as increasing with storage time and temperature. The migration was found to occur within a range of 0.15-0.56 μg L^{-1}. Compared with aqueous stimulant, zinc oxide got higher concentration of migration to 4% acetic acid and hexane simulants.

The addition of ZnO nanoparticles brings excellent performance for products but , at the same time security risks exsit. Consequently, both performance and safety aspects should be considered seriously to make the products safe and efficient.

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