Original paper

Migration of Ti and Zn from Nanoparticle Modified LDPE Films into Food Simulants

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Nanoparticle modified films (NMFs) were prepared by blending low-density polyethylene (LDPE) with nano-TiO₂ or nano-ZnO. Migration of Ti or Zn into four kinds of food simulants were performed under 40°C for 1, 4 and 7 d, as well as 70°C for 2 h. Furthermore, the effect of microwave or ultraviolet treatment on migration was investigated. Results showed that Ti or Zn migration increased with time, and the highest migration occurred in acid simulant, whereas the least occurred in fatty simulant. Temperature promoted the migration process. The amounts of Ti migrated into food simulants ranged from 0.0046 mg kg⁻¹ to 0.61 mg kg⁻¹. For Zn, the amounts were from 0.52 mg kg⁻¹ to 14.17 mg kg⁻¹. Microwaves facilitated the migration of nanoparticles, while ultraviolet did not. These results indicated that nano-TiO₂ modified LDPE films might be safe commercial food packaging films, while nano-ZnO modified LDPE films might require further investigation.

Keywords: nanoparticles, migration; food simulants, LDPE, microwave, ultraviolet radiation

Introduction

Low-density polyethylene (LDPE) has been widely used in packaging due to the superior properties of its high flexibility, high impact strength and good chemical resistance. However, toughness, low thermal stability, medium gas barrier, low water resistance and antibacterial properties restricted application of LDPE for food packaging (Rhim *et al.*, 2009). It was reported that nanotechnology could improve properties of LDPE (Chaudhry *et al.*, 2008). Nowadays metallic nanoparticles (NPs) have attracted rising attention due to their novel properties (Majeed *et al.*, 2013). Several food package materials, containing NPs, have been investigated for their anti-microbial and anti-photochemical properties, which were greatly involved in food and cosmetic packaging (Marcous *et al.*, 2017; Bieberstein *et al.*, 2013). Luo *et al.* (2014 & 2015) have proved the excellent properties of nano-TiO₂ modified LDPE on suppressing microbiological and physicochemical decay of shrimp and strawberry packaging. Nano-

TiO₂ was often applied in packaging as a photo catalytic antibacterial agent (Xing *et al.*, 2012). Matsunaga *et al.* (1985) reported that nano-TiO₂ could kill E.coli through photo catalysis for the first time. Recently, research reports have also conducted on the estimation and probable application of photocatalytic bactericidal activity of nano-TiO₂ (He *et al.* 2011). Meanwhile, Li *et al.* (2011) suggested that nano-ZnO active packaging could be a viable alternative to common technologies for improving properties and extending shelf life of 'Fuji' apples. Chitra *et al.* (2013) have also proved of the antibacterial activity of ZnO nanoparticles against food borne pathogens such as E.coli.

However, as the potential toxic effects of NPs migration from NMFs have not been fully investigated, concerns over the possible harm to consumers remain (Lin *et al.*, 2014). Nanosilver was reported might not to migrate into food (Störmer *et al.*, 2017), however, it still needed more researches about other nanoparticles except nanosilver. It was obvious that under certain conditions,

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some NPs could migrate from the NMFs into the products and environment (Duncan, 2011). The European Food Safety Authority issued Commission Regulation (EU) No. 10/2011 and renewed it to 2016/1416, which stated the migration process should be imitate and the extent of migration could be measured by applications of analytical methods. It also restricted the field and type of NPs applied on foods. Moreover, several researches have raised concerns about potential toxic effect of nanoparticles migration from NMFs. According to Huang *et al.* (2011) and von Goetz *et al.* (2013), nano-silver from fresh food containers migrated into food simulants. Unlike the active silver cations, silver nanoparticles were found to be toxic (Asharani *et al.*, 2008). Lin *et al.* (2011) have also studied the migration of nano-TiO₂-polyethylene particles into food simulants.

Due to the application of NPs in polymer preparation and their potential toxicity, the specific migration rate of nano-TiO₂ and nano-ZnO in direct contact with food simulant was of particular importance. Several environmental influences can initiate nanoparticle migration, such as the humidity and acidity of contact interface, heat which leads to thermal degradation, light which leads to photooxidation reactions, mechanical action or UV and microwave treatments (Simon *et al.*, 2008). However, at present, only a few studies have investigated the relationship between NPs-migration and physical treatments such as microwave and ultraviolet. The objective of this study was to investigate the migration level of metals from nano-TiO₂ or nano-ZnO modified films in different food simulants under different temperatures and the effect of microwave and UV light treatments.

Materials and Methods

Reagents Distilled water, acetic acid, ethanol, nitric acid and 30% hydrogen peroxide, used as food simulants were purchased from Chinese Medicine Group Chemical, Reagent Co., Ltd, China.

Preparation of Films According to Luo *et al.* (2015), Nano-TiO₂ or nano-ZnO particles were modified using the titanate crosslink reagent NDZ-201 (Dao Ning Ltd., Nanjing, China), before mixed with LDPE for 10 min in a high-speed mixer (SHR-10A, SHIHUYUE Ltd., China). Next, the mixture was extruded by a twin-screw extruder (HAAKE PolyLab OS; Thermo Electron GmbH Ltd., Ulm, Germany) at 180°C after cooling, then cut into granules. Afterwards, they were added into LDPE and cut into granules again to ensure uniform distribution of nano-TiO₂ or nano-ZnO in LDPE. Finally, a single-screw extruder (KE 19; Brabender Instrument Ltd., Ulm, Germany) was applied to extrude the granules into film at 200°C. According to preliminary experiments, concentrations of nano-TiO₂ or nano-ZnO were tested at 0.5%, 1.0%, 1.5% and 2.0%. Results showed concentration of 1.0% was best for the properties. Therefore, 1.0% of nano-TiO₂ or nano-ZnO was added into the films. The thicknesses of nano-TiO₂ and nano-ZnO modified LDPE film were respectively $40 \pm 2 \mu\text{m}$ and $46 \pm 2 \mu\text{m}$, within the range of general thickness used in

polyethylene packaging film.

Film characterization by transmission electron microscope (TEM) Transmission electron microscopy (TEM) was used to evaluate the films' micromorphology. The film TEM analyses were performed using a transmission electron microscope (H-600, HITACHI Co., Japan) operated at a 75 kV acceleration voltage. The samples were prepared by depositing the aqueous solution-containing nanocapsules onto a carbon-coated copper grid. Before the microscopy observation and analysis, the samples were air-dried at room temperature without further modification.

Migration test According to (EU) NO. 10/2011, distilled water (pH=7.0), acetic acid (3 g/100 mL, pH=2.7), 95% ethanol (v/v, pH=7.0) and 10% ethanol (v/v, pH=7.0) were chosen as the neutral, acidic, fatty and alcoholic food simulants, respectively. 0.1 g of samples were cleaned by distilled water and cut down to $3.5 \text{ cm} \times 3.5 \text{ cm}$ (acreage as 12.25 cm^2), then placed into glass bottles with 50 mL food simulants, respectively. Bottles were set in thermostat water bath at 40°C for 1 d, 40°C for 4 d, 40°C for 7 d or 70°C for 2 h to conduct migration test, respectively. Then the materials were removed and the residues were measured by ICP-MS for Ti and Zn concentration.

Microwave treatment in migration test For the simulation of food contact, 0.1 g of sample were cut into $3.5 \text{ cm} \times 3.5 \text{ cm}$ pieces and placed in 50 mL neutral and acidic simulants by single contact. For the determination of the overall migration, two different migration conditions were realized in Treatment 1st as defrosting (250 W for 6 min) and Treatment 2nd as cooking (600 W for 6 min). As procedural blanks, the food simulant was filled into conical glass flasks with glass stoppers and stored under the same conditions as the samples under room temperature to check for contamination. After microwave treatment, all samples were placed under 40°C for 1 d, then the materials were removed and the residues were measured by ICP-MS for Ti and Zn concentration.

UV-treatment in migration test A low pressure steam UV sterilization lamp was used as UV source (tube diameter radio 2.4 cm, length 89 cm, power 30 W, wavelength intensified in 254 nm). 0.1 g of sample were cut into $3.5 \text{ cm} \times 3.5 \text{ cm}$ pieces and placed under UV source and the intensity was measured by hand-held ultraviolet ray intensity meter as 6 W/m^2 . The materials were exposed to UV radio in 40°C for 0, 8 or 40 h, respectively. After UV treatment, all samples were placed under 40°C for 1 d, then the materials were removed and the residues were measured by ICP-MS for Ti and Zn concentration.

Degradation methods Nano-TiO₂ or nano-ZnO NMs were cut into fragments ($1 \text{ cm} \times 1 \text{ cm}$). For degradation, 0.1 g fragments of sample were placed in a PTFE microwave degradation tank, where 6 mL 5% (v/v) HNO₃ and 2 mL 30% (v/v) H₂O₂ were then added to the tank. Afterwards, the tank was settled in the vessel microwave degradation system (Ethos One, Milestone, Italy) for degradation.

The degradation was performed under 1000 W microwave and 3.5 MPa pressure. The temperature was raised to 150°C in 10 min,

then to 210°C in 10 min, and kept for 10 min. The degradation solvent was cooled for 1 h, and then heated to remove the redundant acid. The solvent was transferred to 100 mL colorimetric tube with distilled water. The initial concentration of Ti and Zn was then determined by ICP-MS.

ICP-MS analysis procedure ICP-MS analysis was carried out with the NexIon 300XX (Perkin Elmer, Waltham, MA, USA). Details on the instrumentation and the operating conditions were executed as in Bass and Jones (2010). Triplicate determinations of each sample were carried out. All results were blank subtracted. Ti^{47} was applied as the isotope of Ti and Zn^{66} was for Zn.

Statistical analysis Experiments were performed according to a completely randomized design. All statistical analyses were carried out using the Origin statistical software (Originlab Inc., Hampton, MA, USA). Data were expressed as the mean values $\pm$ standard deviation, and analyzed by one-way analysis of variance (ANOVA). The overall least significant difference (LSD) at $P = 0.05$ was calculated and used to detect significant differences among treatments.

Results and Discussion

Size and distribution condition of NPs in NMFs The nanoparticles were relatively distributed homogeneously in NMFs, and the size of nano- TiO_2 and nano-ZnO was observed to be about 100 nm in TEM image (Fig. 1). These indicated that particles in these NMFs still possessed nano-sizes. Emamifar *et al.* (2010) investigated nanocomposite LDPE films containing Ag and ZnO for food packaging applications, and results showed that with the increase of each nanocomposite content, the films showed lower elongation.

Specificity and linearity of ICP-MS ICP-MS was used to measure the concentration of metal migration in food simulants. The linearity of response in ICP-MS was assessed by plotting the intensity values (y axis) to standard solutions, containing 1, 5, 10, 50, 100, 200 ppb (x axis) of Ti and Zn, respectively. The regression equation obtained was $y = 845.73x + 702.19$ (Ti) and $y = 905.11x + 6751.36$ (Zn) with regression coefficient of 0.9994 and 0.9976, respectively, which illustrated a linear relationship between intensity and individual Ti contents. As described in the experimental methods, the concentration was converted from $\mu g L^{-1}$ to $mg kg^{-1}$. Unit conversion was conducted according to the following formula: $Y \text{ mg kg}^{-1} = \frac{y \times 50 \times 10^{-3}}{0.1}$

All the concentrations below were expressed as $mg kg^{-1}$.

Migration test at 40°C In accordance to European Commission (2011) Regulation No. 10/2011, to assess the migration potential of NMFs under non-cooking condition, migration experiments were set at 40°C. Prior to migration tests, the concentrations of Ti in control LDPE film and NMFs were 44.49 and 5013.80 $mg kg^{-1}$ respectively. While Zn concentrations in control LDPE film and NMFs were 45.53 and 8254.40 $mg kg^{-1}$. It was obvious that NMFs had relatively higher Ti and Zn content

Fig. 1. TEM images of normal LDPE films (a for 15000 times), nano- TiO_2 -LDPE films (b for 20000 times) and nano-ZnO-LDPE films (c for 15000 times).

Fig. 2. Migration of Ti and Zn from normal LDPE films and NMFs into fatty (A and a), neutral (B and b), acidic (C and c) and alcoholic (D and d) food simulants in 40°C for 1, 4 and 7 d. Values are the means $\pm$ SD of triplicate assays

compared to the control in all food simulants (Fig. 2). This indicated higher migration of metals from NMFs might be attributed to NPs. Research also showed that for silver, migration from nanocomposites was influenced mostly by the percentage of filled nanoparticles (Cushen *et al.*, 2013).

For NMFs, when in acid simulants, the concentrations of Ti and Zn were 0.61 mg kg^{-1} and 14.17 mg kg^{-1} in 40°C for 7 d, respectively, which were higher than those in 40°C for 1 d by 26% and 31%, respectively. In neutral simulants, the concentrations of Ti and Zn in 40°C for 7 d increased by 8% and 9% compared to those in 40°C for 1 d, respectively. While in fatty and alcoholic simulants, the concentrations of Zn in 40°C for 7 d increased by 10% and 4% in comparison to those in 40°C for 1 d, respectively. However, no significant change of Ti concentration was observed in fatty or alcoholic simulants, which indicated that the Ti migration reached equilibrium within one day in fatty or alcoholic simulants. It might be due to the non-polar ethanol, forming a barrier around the films, preventing solvent from coming into contact with nanoparticles directly on the film's surface, thus the migration process was significantly hindered (Addo *et al.*, 2015). Interestingly, it was discovered that for NPs migration, only $9.6 \times 10^{-5}\%$ to $1.2 \times 10^{-2}\%$ of Ti migrated into the simulant; whereas it was found to be $6.2 \times 10^{-3}\%$ to $1.7 \times 10^{-1}\%$ for Zn. This indicated that substantially most metals of NPs were still in the films. The concentration of both Ti and Zn in the simulant increased with time. Acidic simulants led to the highest migration, neutral simulants came second, followed by alcoholic simulants, while, fatty simulants resulted in the lowest migration. Acidic solution might permeate into the films and increase the intermolecular space, leading to higher diffusion coefficient (Garde *et al.*, 1998). These results might also attribute to the solubility of Ti and Zn in different simulants. Fatty simulants led to the lowest migration might due to low solubility of Ti and Zn in organic solvent. A similar result was observed from the study on migration content of nano-silver in acidic simulant, in which it was found to be higher than that in neutral simulant (Busolo *et al.*, 2010), but the migration concentration was still below European Food Safety Agency (EFSA)'s limitation. Extremely low migration content in fatty simulant was reported in nano-silver modified food contact materials (Addo *et al.*, 2015). Echegoyen & Nerin (2013) also found that at normal temperatures, silver migration in 3% acid simulation was higher than that in 50% ethanol.

In acidic simulant, concentrations of both Ti and Zn in 40°C for 7 d were higher than those in 40°C for 1 d. The percent increases were 26% for Ti and 31% for Zn. While in neutral simulant, the increases were 8% for Ti and 9% for Zn. The differences in percent increase between these two kinds of simulants suggest that acidity contributes to the continuous migration of Ti and Zn. These results were consistent with the previous studies (Bott *et al.*, 2014; Lin *et al.*, 2014), as the metal ion release rates increased with increasing acidity and polarity.

Fig. 3. Migration of Ti (A) and Zn (B) from NMFs into different food simulants in 70°C for 2 h, 40°C for 2 h and 40°C for 1 d.

Migration test in 70°C For NMFs, the migration concentration of Ti and Zn in 70°C for 2 h, 40°C for 2 h or 40°C for 1 d was shown in Fig. 3. For Ti and Zn, migration in 70°C for 2 h was higher than that in 40°C for 2 h. Migration in 70°C for 2 h could almost achieve level of 1 d in 40°C , however, there were still some differences. It was observed that the overall migration of Ti in 70°C for 2 h was lower than that in 40°C for 1 d, on the contrary, overall migration of Zn in 70°C for 2 h was higher than that in 40°C for 1 d. The ratio of Ti migration in 70°C for 2 h and 40°C for 1 d was 75% and 85%, respectively, in acidic and neutral simulant, however, that ratio of Zn migration was 114% and 132%, respectively, in acidic and neutral simulant. Interestingly, in fatty simulant, the migration concentration changed slightly for Ti and Zn in 40 or 70°C , while in alcoholic simulant, migration of Ti in 70°C for 2 h was 36% lower than that in 40°C for 1 d and migration of Zn in 70°C for 2 h was 62% higher of that in 40°C for 1 d. The difference between Ti and Zn migration in 70°C for 2 h and 40°C for 1 d indicated different physiochemical characteristics of TiO_2 and ZnO nanoparticles. In research of Lin *et al.* (2014), after 8 h, migration of Ti into 3% (w/v) aqueous acetic acid were $1.4 \mu\text{g kg}^{-1}$ in 25°C and $6.3 \mu\text{g kg}^{-1}$ in 70°C , while into 50% (v/v) aqueous ethanol, the maximum migration amounts were 0.5 ± 0.1 , 0.6 ± 0.03 and $2.1 \pm 0.1 \mu\text{g kg}^{-1}$ in 25, 70 and 100°C , respectively, which indicated higher temperature increased the migration process.

Migration under microwave conditions Results of migration under microwave conditions were shown in Fig. 4. In acidic

Fig. 4. Migration of Ti (A) and Zn (B) from NMFs into acidic and neutral food simulants in 40°C for 1 d with microwave treatment.

simulants, microwave treatment increased Ti migration by 8% and 21% compared to the control, respectively, at 250 W and 600 W, however, no significant increase of Ti migration in neutral simulants was observed ($P > 0.05$). For Zn, microwave treatment facilitated Zn migration in acidic and neutral simulants in both levels, and the concentration of Zn migration in acid simulants after 600 W for 6 min was 19.16 mg kg⁻¹. These values might be attributed to the degradation of films caused by microwave heating in combination with stronger packaging-solvent interactions (Alin & Hakkarainen, 2012). Microwave heating increased the

Fig. 5. Migration of Ti (A) and Zn (B) from NMFs into acidic food simulant in 40°C for 1 d with ultraviolet treatment.

temperature of films, resulting in higher migration coefficient of nano-particles. Microwave heating might also destroy combination between nano-particles and films, which enhanced the migration. Similar results were reported that nano-silver migration into acidic and neutral simulants was increased after microwave treatment at 700 W and 1000 W for 2 min (Echegoyen & Nerin, 2013; Hannon *et al.*, 2015).

Migration under ultraviolet conditions Ultraviolet treatment promoted the migration of Zn and Ti in acidic simulant compared to the control, while this effect was slight (Fig. 5). This result might be due to the degradation effect of ultraviolet light. However, nano-particles absorbed and scattered the light, weakening the degradation effect. The significant increasing effect of UV irradiation on the migration of organic plasticizers from food packaging films into foods has been reported (Funk *et al.*, 2016). However, such an effect on metal migration into foods has not been reported yet. Enhanced migration of plasticizers from the films under UV treatment might result from the accelerated degradation process of the films (Funk *et al.*, 2016). However, both nano-TiO₂ and nano-ZnO had great ability of absorbing and scattering ultraviolet (Mahmoudifard *et al.*, 2012). Therefore, the effect of UV treatment on migration was slight.

Conclusion

The present study showed that low concentrations of Ti or Zn migrated from LDPE films modified with TiO₂ or ZnO

nanoparticles when in contact with different food simulants. In 40°C conditions of migration test, the contribution to migration of the food simulants from highest to lowest were acidic, neutral, alcoholic, and finally, fatty simulants. Results of auxiliary migration tests showed that microwave was an effectively contributive factor to Ti and Zn migration, while ultraviolet was not. In addition, based on present results of our research, it can be deduced that nano-TiO₂ modified LDPE films can be used as a safe commercial food packaging material, while nano-ZnO modified LDPE films still need further investigation.

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