



# Effect of organic additives on silver release from nanosilver–polyethylene composite films to acidic food simulant



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## ABSTRACT

The effects of organic additives (Irgafos 168, Irganox 1076, Tinuvin 622, Chimassorb 944, UV-P, and UV-531) on silver release from nanosilver–polyethylene composite films into an acidic food simulant (3% acetic acid) were investigated using inductively coupled plasma mass spectrometry. The limits of detection and quantification, coefficient of determination, and recoveries of the method used were 3.7 ng L<sup>-1</sup>, 12.4 ng L<sup>-1</sup>, 0.999, and 89–113%, respectively. The results indicated that additives can affect silver release via two simultaneous processes: (i) reactions between organic additives and silver that promote silver release from the composite film to the acidic food simulant; and (ii) the promotion or inhibition of silver release by affecting silver oxidation. High temperature and humidity treatment of the composite films was found to significantly increase silver release by promoting silver oxidation.

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## 1. Introduction

The small size and unique physicochemical characteristics of nanomaterials have attracted attention in various fields of science and technology, including medicine, colloids, diagnostics, drug delivery, personal care (Ranjan et al., 2014), food (Cushen, Kerry, Morris, Cruz-Romero, & Cummins, 2012), and food packaging (Chaudhry et al., 2008).

As shown in reviews (Hannon, Kerry, Cruz-Romero, Morris, & Cummins, 2015; Huang, Li, & Zhou, 2015; Youssef, 2013), nanomaterials, such as Ag, clay, zinc oxide, titanium dioxide, copper, copper oxide, and carbon nanotubes, have been incorporated, coated, and exfoliated into different polymer or biopolymer matrices to form different nanocomposites. Polymer and biopolymer matrices used include polyethylene (PE), high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC), polylactic acid (PLA), polyethylene terephthalate (PET), starch, and wheat gluten. Nanomaterials can increase the mechanical barrier properties of polymers and biopolymers, and act as oxygen, humidity, and freshness indicators. Furthermore, nanoma-

terials in food packaging can also have antimicrobial, oxygen scavenging, and shelf-life extending functions (Mihindukulasuriya & Lim, 2014). Despite the many suggested benefits of using nanomaterials in food packaging, the risk of possible nanomaterial migration into foodstuffs could negatively impact human health, marketing, and consumer confidence (Kuorwel, Cran, Orbell, Buddhadasa, & Bigger, 2015). Furthermore, the disposal of nanocomposite materials could damage the environment and harm wildlife.

Nanosilver (silver nanoparticles), which shows broad-spectrum antibacterial activity, high temperature stability, and low volatility, has been suggested for incorporation into food packaging (Echegoyen & Nerín, 2013). Food packaging containing nanomaterials is already available in some countries (Bumbudsanpharoke & Ko, 2015). However, food packaging containing nanosilver could release silver nanoparticles and toxic Ag<sup>+</sup> ions (oxidation product from reaction with O<sub>2</sub> and other molecules on the nanosilver surface) into foodstuffs through direct contact. Although nanosilver and Ag<sup>+</sup> might have antibacterial effects on foodstuff, they could also have toxic effects on human health. Furthermore, the cytotoxic activities of nanosilver and Ag<sup>+</sup> are much higher than their antibacterial activities (Guo, Yuan, Lu, & Li, 2013). Research on the toxic effects of nanosilver is ongoing. McShan, Ray, and Yu (2014) stated that nanosilver is often a source of Ag<sup>+</sup> inside cells, potentially causing DNA damage, antioxidant enzyme activation, antioxidant depletion, protein binding and disabling, and cell

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membrane damage. Therefore, the inhalation of nanosilver and/or Ag<sup>+</sup> could harm humans and wildlife.

Migration tests are crucial during the introduction of nanopackaging (Cushen, Kerry, Morris, Cruz-Romero, & Cummins, 2013). Šimon, Chaudhry, and Bakoš (2008) predicted that, theoretically, only small nanoparticles (radius of approx. 1 nm) would migrate into food from polymers with low dynamic viscosities, and would not interact with nanoparticles. However, the release of Ag from different polymers (PE, LDPE, PLA, PP, and PVC) containing silver nanoparticles has recently been reported. Factors affecting the release of Ag from food contact materials have been investigated, including temperature, food simulants, exposure time (Huang et al., 2011; Song, Li, Lin, Wu, & Chen, 2011), real food (Cushen, Kerry, Morris, Cruz-Romero, & Cummins, 2014; Metak, Nabhani, & Connolly, 2015), sampled bag area (Artiaga, Ramos, Ramos, Cámara, & Gómez-Gómez, 2015), film formation procedure, and the presence of cations in the contacting media (Fernández, Soriano, Hernández-Muñoz, & Gavara, 2010).

In general, different kinds of organic additives, such as plasticizers, antioxidants, and light stabilizers, are essential for obtaining polymers with improved mechanical properties and an extended service life. These organic additives can interact with nanomaterials within nanoparticle–plastic composite food packaging and affect their release, or that of corresponding ions, into food. To our knowledge, research on this topic is limited. Xia, Rubino, and Auras (2014) found that the presence of nanoclay affected surfactant release from nanocomposite materials.

This study aimed to investigate the effects of different antioxidants and light stabilizers on the release of silver from nanosilver–polyethylene composite films. The effects of high temperature and humidity treatment were also investigated. Previously, we found that a four-additive combination (containing antioxidants Irgafos 168 and Irganox 1076, and hindered amine light stabilizers Tinuvin 622 and Chimassorb 944) hindered the release of Ag from nanosilver composite film, possibly by affecting silver oxidation (Su et al., 2015). Herein, the effects of plastic additives on the release of Ag were further investigated using both individual and combined additives.

## 2. Materials and methods

### 2.1. Instruments

An electronic analytical balance with 0.1-mg resolution (AG 204; Mettler Toledo, Zurich, Switzerland) was used to weigh samples for determining total Ag contents. Film thicknesses were measured in five replicates using a thickness gauge (DRK203B; Drick, Jinan, Shandong, China). Film colors were described using the CIE-LAB model (a color-opponent space with dimensions L\* for lightness and a\* and b\* for the color-opponent) and directly measured using a spectrophotometer (X-Rite SP64; Michigan, USA). A microcontroller digital electric heating plate (DB-3; Xinrui, Jintan, Jiangsu, China) was employed to digest plastic films after adding moderate mixed acid. After digestion, inductively coupled plasma atomic emission spectrometry (ICP-AES; iCAP 6500; Thermo, California, USA) was used to determine total Ag content in the plastic films. ICP-AES was operated under the following conditions: Plasma power, 1150 W; cool gas flow, 14 L/min; auxiliary gas flow, 0.6 L/min; nebulizer gas flow, 0.5 L/min; plasma view, axial; and analytical wave length, 328.68 nm.

Two incubators (DHG 9140A; Jinghong, Shanghai, China) were used to conduct migration tests. The acceleration test was carried out in a temperature humidity chamber (GDJS-101; Zhongya, Huaian, Jiangsu, China). Ag determination in the food simulant (3% acetic acid) was carried out using inductively coupled plasma

mass spectrometry (ICP-MS; iCAP Qc; Thermo, California, USA), equipped with a polytetrafluoroethylene (PTFE) nebulizer, a quartz spray chamber, and a Peltier-cooled cyclonic chamber. ICP-MS was operated under the following conditions: Plasma power, 1548.6 W; cool gas flow, 13.9 L/min; auxiliary gas flow, 0.8 L/min; nebulizer gas flow, 1.06 L/min; dwell time, 0.2 s; measurement mode, kinetic energy discrimination (KED).

Chemical reaction equations were drawn using ChemDraw Ultra (7.0, Cambridge Soft Corporation, Cambridge, MA, USA).

### 2.2. Reagents

Silver nanoparticle powder (20 nm) was purchased from Shanghai Chaowei Nanotechnology Co., Ltd (Shanghai, China). Pure polyethylene granules were purchased from China Petroleum & Chemical Corporation (2420H; Maoming, Guangdong, China). Antioxidants Irgafos 168 (denoted as 168) and Irganox 1076 (denoted as 1076), hinder amine light stabilizers Tinuvin 622 (denoted as 622), Chimassorb 944 (denoted as 944), UV-P, and UV-531, were all industrial grade and obtained from Rianlon Corporation (Tianjin, China) (see Table 1 for details). Nitric acid (HNO<sub>3</sub>), perchloric acid (HClO<sub>4</sub>) and acetic acid (CH<sub>3</sub>COOH) were all analytical grade and provided by Guangzhou Chemical Reagent Factory (Guangzhou, China). Solutions were prepared using distilled water obtained from a Milli-Q water purification system (Advantage A10; Millipore, Boston, USA). Stock 1000 µg mL<sup>-1</sup> standard solutions of silver (Ag) and rhodium (Rh; internal standard) were obtained from the National Nonferrous Metals and Electronic Materials Analysis and Testing Center (Beijing, China). Working Ag solutions for ICP-AES and ICP-MS were prepared using 5% nitric acid and 3% acetic acid, respectively.

### 2.3. Samples

Silver nanoparticles, pure polyethylene pellets, and additives (formulations shown in Table 2) were added to a twin screw granulator (MEDU-22/40; Potop, Guangzhou, China) to obtain corresponding granules. To achieve more homogenous granules, the granulation process was performed twice for each formulation. The prepared granules were then added to a lab-scale blowing machine (FYC-25; Jinzhong, Guangzhou, China) to manufacture the corresponding nanosilver–polyethylene composite films.

### 2.4. Characterization of nanosilver powders and nanosilver–polyethylene composites

Nanosilver powders and nanosilver–polyethylene films were characterized by scanning electron microscopy (SEM; Ultra 55; Zeiss, Goettingen, Germany) to determine the original morphology of the silver nanoparticles and their presence in the composite films. Before analysis, the nanosilver–polyethylene composite films were cut into small pieces (25 mm<sup>2</sup>), placed on carbon tape, and gold coated.

### 2.5. Determination of initial silver content in film samples

From the samples prepared for the migration test, 18 pieces of film (1 cm × 1 cm, approx. 0.1 g) were picked randomly and weighted into an Erlenmeyer flask. This ensured that the uniformity of total silver content in films was reflected in the migration test. The prepared film samples were carbonized on the microcontroller digital electric heating plate at 400 °C. The carbonized samples were cooled for about 30 s at room temperature, then mixed acid (15 mL, HNO<sub>3</sub>/HClO<sub>4</sub> = 3:1, v/v) was added. The mixture was heated on the heating plate at 250 °C until all films were digested. After cooling the vessels for 2 h, the digested solutions were

**Table 1**  
detail information of the studied organic additives.

Type of additives	Commercial Name	Chemical name	CAS number	Formulas
Antioxidant	Irgafos 168	Tris (2,4-di- <i>tert</i> butyl phenyl) phosphite	31570-04-4	C <sub>42</sub> H <sub>63</sub> O <sub>3</sub> P
	Irganox 1076	Octadecyl 3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl) propionate	2082-79-3	C <sub>35</sub> H <sub>62</sub> O <sub>3</sub>
Light stabilizer	Tinuvin 622	Poly(4-hydroxy-2,2,6,6-tetraMethyl-1-piperidine ethanol- <i>alt</i> -1,4-butanedioic acid)	65447-77-0	H[C <sub>15</sub> H <sub>25</sub> O <sub>4</sub> N] <sub>n</sub> OCH <sub>3</sub>
	Chimassorb 944	Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl]][(2,2,6,6-tetramethyl-4-piperidiny)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidiny)imino]]	71878-19-8	(C <sub>35</sub> H <sub>68</sub> N <sub>8</sub> ) <sub>n</sub>
	UV-P	2-(2H-Benzotriazol-2-yl)-p-cresol	2440-22-4	C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> O
	UV-531	Octabenzene	1843-05-6	C <sub>21</sub> H <sub>26</sub> O <sub>3</sub>

**Table 2**  
Detailed information of 10 studied films (n = 3 except for thickness).

Code name of film	Silver content (mg/kg ± SD)	Added additives	Thickness (μm ± SD, n = 5)	CIELAB		
				L* ± SD	a* ± SD	b* ± SD
Blank	373.4 ± 0.7	–	64 ± 4	66.6 ± 1.0	1.2 ± 0.3	10.0 ± 0.2
168	365.7 ± 0.3	0.12% Irgafos 168	56 ± 6	68.8 ± 1.0	0.7 ± 0.1	9.6 ± 0.3
1076	361.7 ± 3.7	0.03% Irganox 1076	60 ± 8	68.9 ± 0.9	0.1 ± 0.1	8.6 ± 0.4
622	306.0 ± 4.3	0.05% Tinuvin 622	59 ± 5	67.1 ± 1.8	1.0 ± 0.2	9.5 ± 0.1
944	288.0 ± 6.7	0.05% Chimassorb 944	58 ± 4	66.2 ± 1.7	0.3 ± 0.1	8.2 ± 0.1
168 + 1076	343.8 ± 10.2	0.12% Irgafos 168 + 0.03% Irganox 1076	51 ± 7	66.5 ± 0.9	0.5 ± 0.2	9.3 ± 0.3
622 + 944	285.6 ± 0.8	0.05% Tinuvin 622 + 0.05% Chimassorb 944	60 ± 8	71.0 ± 1.4	0.4 ± 0.1	7.5 ± 0.2
UV-P	559.5 ± 19.7	0.5% UV-P	63 ± 7	58.9 ± 2.1	1.4 ± 0.1	8.7 ± 0.1
UV-531	425.0 ± 3.8	0.5% UV-531	55 ± 4	66.1 ± 2.1	0.4 ± 0.1	8.7 ± 0.3
B900 + 783	297.5 ± 0.9	0.12% Irgafos 168 + 0.03% Irganox 1076 + 0.05% Tinuvin 622 + 0.05% Chimassorb 944	54 ± 2	69.1 ± 1.3	2.3 ± 0.1	13.6 ± 0.2

Note:

- The films were named according to additives added in the films, where “–” means no additive was added;
- +L\* means white, –L\* means black; +a\* means red, –a\* means green; +b\* means yellow, –b\* means blue.

diluted to 50 mL with distilled water and analyzed by ICP-AES. Unless otherwise specified, all measurements were carried out in triplicate.

## 2.6. Migration tests and ICP-MS analysis

Film samples were cleaned with deionized water and cut into small pieces (1 cm × 1 cm). After mixing evenly, 18 film pieces were picked at random and placed into a plastic centrifuge. Finally, 3% acetic acid (30 mL) was added to conduct the migration test. Acetic acid (3%) was chosen as the only food simulant due to its higher extractability compared with that of 50% ethanol, as shown in our previous study (Su et al., 2015). The following conditions were selected for the migration tests: 70 °C for 2 h, 70 °C for 12 h, 20 °C for 10 days, and 40 °C for 10 days.

## 2.7. Method validation

To determine the initial silver contents in the composite films, linearity and correlation coefficients were obtained for six Ag standard solutions diluted with 5% HNO<sub>3</sub> to concentrations of 0.01, 0.05, 0.1, 0.2, 0.5, and 1 μg mL<sup>–1</sup> using ICP-AES analysis. Limits of detection (LOD) and quantitation (LOQ) for Ag determination in the plastic films by ICP-AES were the corresponding concentrations of the blank response plus 3 and 10 times the standard deviation of 11 blank (5% HNO<sub>3</sub>) measurements, respectively.

All obtained migration solutions were analyzed by ICP-MS at concentrations of 0.02, 0.2, 0.5, 1, 2.5, 5 ng mL<sup>–1</sup>. A 1 ng mL<sup>–1</sup> standard solution (diluted with 3% acetic acid) was prepared daily and used to correct the standard curve every 15 samples. The LOD and LOQ for Ag determination in food simulant by ICP-MS were the corresponding concentrations of the blank response plus 3 and 10 times the standard deviation of 11 blank (5% HNO<sub>3</sub>) measurements, respectively.

To check the accuracy of the migration test, a spiked recovery study of the food simulant (30 mL, 3% acetic acid) was performed

at three silver concentration levels (0.02, 0.5, and 2 ng mL<sup>–1</sup>) with six replicates.

## 2.8. Statistical analysis

Statistical analysis was carried out using Minitab 15.0 (Minitab Inc., State College, PA, USA) and statistical product and service solutions (SPSS) 13.0 (IBM SPSS Inc., New York, USA) analytical software. A value of P < 0.05 was identified as being statistically significant at the 95% confidence level.

## 3. Results and discussions

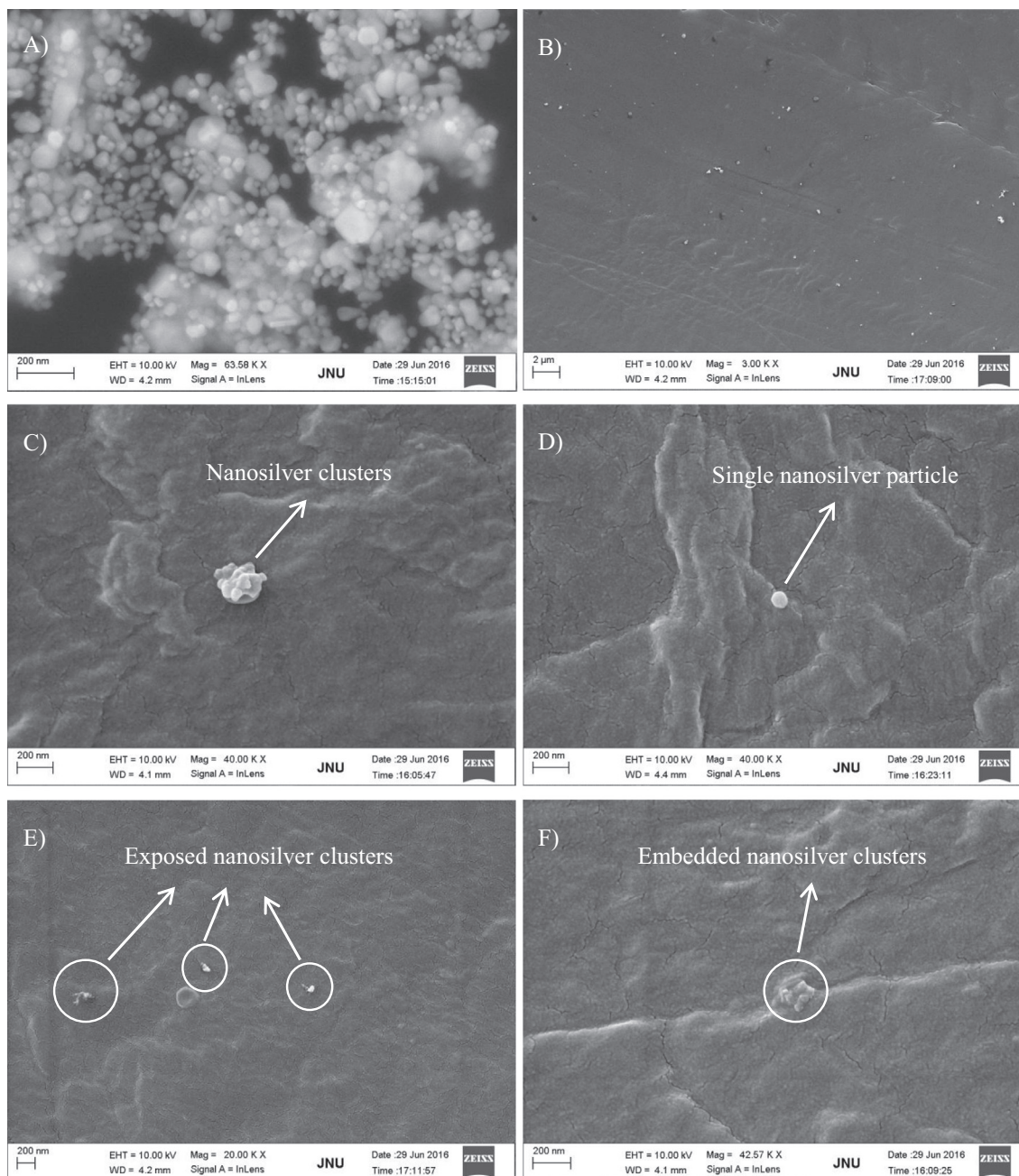
### 3.1. Characterization of nanosilver powder and composite films by SEM

Characterization of the nanosilver powder and nanosilver–polyethylene composite films was conducted using SEM. As shown in Fig. 1A (nanosilver powder), most nanosilver particles were consistent with the labelled diameter (20 nm). In the composite films studied, no significant homogeneous distribution of nanosilver was found (Fig. 1B), with both nanosilver clusters (Fig. 1C) and single nanoparticles (Fig. 1D) present in the composite films. Furthermore, partially/totally exposed nanosilver clusters were discovered (see Fig. 1E), which can easily detach, as shown by previous studies (Echegoyen & Nerín, 2013; Artiaga et al., 2015; Echegoyen, Rodriguez, & Nerín, 2016). The release of embedded nanosilver clusters (Fig. 1F) would be more difficult due to the wrapping effect of the polymer.

### 3.2. Method validation

ICP-AES analysis of initial silver content in the composite films gave an LOD and LOQ of 1.3 × 10<sup>–3</sup> and 3.2 × 10<sup>–3</sup> μg mL<sup>–1</sup>, respectively. The linear equation for 0.01–1 μg mL<sup>–1</sup> was y = 34000.2x





**Fig. 1.** SEM images of (A) nanosilver powder and (B–F) nanosilver–polyethylene composite films.

+ 22.3, with a correlation coefficient ( $R$ ) of 0.9999. ICP-MS analysis of silver migrated into the food simulant gave an LOD and LOQ of  $3.7 \times 10^{-3}$  and  $12.4 \times 10^{-3}$  ng mL $^{-1}$ , respectively. The linear equation for 0.02–5 ng mL $^{-1}$  was  $y = 23715.2x + 282.3$ , with a coefficient of determination ( $R^2$ ) of 0.999. In the above linear equations,  $x$  represents the concentration ( $\mu\text{g mL}^{-1}$  for ICP-AES and ng mL $^{-1}$  for ICP-MS) and  $y$  represents the silver signal intensity. The spiked recoveries in 3% (w/v) aqueous acetic acid ranged from 89 to 113%, with RSDs of 3.4–7.8%. In summary, the method achieved good linearity, repeatability, recoveries, and LOD and LOQ values.

### 3.3. Nanosilver–polyethylene composite films

Detailed information regarding the studied nanosilver–polyethylene composite films is shown in Table 2. Although

500 mg kg $^{-1}$  nanosilver was added to each film, the actual silver contents of most films were lower due to nanosilver loss during the film manufacturing process. However, errors during the film blowing process resulted in the composite film containing UV-P having a higher silver content (559 mg/kg) than the set value, because added nanosilver powder gathered in the film. This higher silver content was also evidenced by the lower  $L^*$  value (blackier).

### 3.4. Migration test

Although the distribution of silver nanoparticles in composite films was not particularly homogeneous, using 18 pieces of evenly mixed composite film (1 cm  $\times$  1 cm) instead of one piece to perform migration tests improved the comparison of silver release from different composite films. Furthermore, the release ratio (% $_{\text{e}}$ , released silver content to total silver content in polymer)

was used to express the silver release to make the results more comparable.

Migration test results are shown in Fig. 2, showing that silver release under the chosen conditions was in the following order: 70 °C, 2 h < 20 °C, 10 d < 40 °C, 10 d < 70 °C, 12 h. The four-additive combination, comprising antioxidants 168 and 1076 and hindered amine light stabilizers 622 and 944, was found to hinder silver release, as reported in our previous study (Su et al., 2015). However, additives added individually or as partial combinations (168 and 1076, or 622 and 944) were found to promote silver release.

We speculated that additives affect silver release from nanosilver–polyethylene composite films into food simulants via two mechanisms. First, silver release might be related to interactions with additives. These interactions might result from the relatively high surface energy of the nanoparticles, such that small silver nanoparticles inside the film or attached to the film surface are released together with additives, or from interactions with silver ions. In both cases, silver could be released along with the additives, resulting in increased silver release compared with films containing no additives (as shown in Fig. 2, except for the four-additive combination). The interaction between additives and nanoparticles correlated with both the additive chemical structure and the form of silver. Furthermore, the oxidation of silver within the polymer could also affect silver release. Easily oxidizable silver would be oxidized and subsequently released from the polymer into foodstuff if conditions were appropriate. Theoretically, every factor influencing silver oxidation could impact silver release. Therefore, additives could also promote or inhibit silver release by affecting silver oxidation.

Silver release from the film containing four additives (168, 1076, 622, and 944) was lower than for the blank film (Fig. 2). This effect could be partially due to the antagonistic effect of the four additives on interactions with silver, and partially due to the synergistic effect of the four additives in preventing silver oxidation. This interpretation was also evidenced by the film color analysis. As shown in Table 2, the film with four combined additives has a significantly different color to the other films, with a  $b^*$  value of 13.6 (more yellow). This phenomenon might be explained by interactions among the four additives. Furthermore, Peña's group found that hindered amine light stabilizers and antioxidants have an antagonistic effect on LDPE photodegradation (Peña, Allen, Edge, Liauw, & Valange, 2001a), but a synergistic effect on LDPE thermal oxidation (Peña, Allen, Edge, Liauw, & Valange, 2001b).

In contrast, the same four-additive combination was found to promote the release of Ti from TiO<sub>2</sub>–polyethylene composite film in our previous study (Lin et al., 2014). These different phenomena

suggest that titanium and silver might have different mechanisms for release from nanocomposite films, because Ag is more easily oxidized than TiO<sub>2</sub> (inertia). The detailed functional mechanism could be an interesting topic for future research.

### 3.5. Acceleration test

The migration of nanoparticles embedded in the polymer was unlikely, except for small silver nanoparticles. However, ionic silver formed by oxidation in the polymer could react or interact with additives. This process would affect the migration process of ionic silver. To further investigate the effect of additives on silver release caused by silver oxidation, composite films were exposed to high temperature and humidity (70 °C and 90% relative humidity) for 35 days in an attempt to accelerate silver oxidation. These severe conditions replicated long-term film storage at high humidity and temperature. Afterwards, the treated films were used to perform migration tests under the following conditions: 70 °C for 2 h and 40 °C for 10 days. The results are displayed in Fig. 3. After the acceleration test, silver release in the blank nanosilver–polyethylene film (with no additives) had significantly increased, perhaps due to nanosilver oxidation under these conditions. However, no statistically significant increase in silver release was observed for films containing 1076, 622, 944, 622+944, UV-P, or 168 + 1076 + 622 + 944. The results indicated that the presence of 1076, UV-P, 622, and 944 (also efficient thermal antioxidants) inhibited silver oxidation. However, while these additives were designed to prevent polymer oxidation, which has a different mechanism to silver oxidation, their presence could still affect silver oxidation, because of their reactivity with protons or dissolving oxygen. For example, 1076 and UV-P contain reactive hydroxyl groups, while 622 and 944 can quench singlet oxygen.

To our surprise, there was a significant increase in silver release from films containing additive 168 or UV-531 after the acceleration test. These phenomena could result from the coordination of 168 and UV-531 with Ag<sup>+</sup> under accelerating test conditions. The structure of 168 is shown in Fig. 4. Layered two-coordination compounds could be formed as follows: Ag<sup>+</sup> is trapped between two 168 ligands, forming a relatively stable structure due to the benzene rings. As for UV-531, the possible coordination process is shown in Fig. 5. UV-531 and Ag<sup>+</sup> can coordinate to form a relatively stable structure with a six-membered ring. Furthermore, the contents of additives 168 and UV-P in the studied films were relatively high, which would also contribute to increased silver release. As for 168 + 1076, both inhibition (1076) and promotion effects (168) were present, resulting in a small increase in silver release.

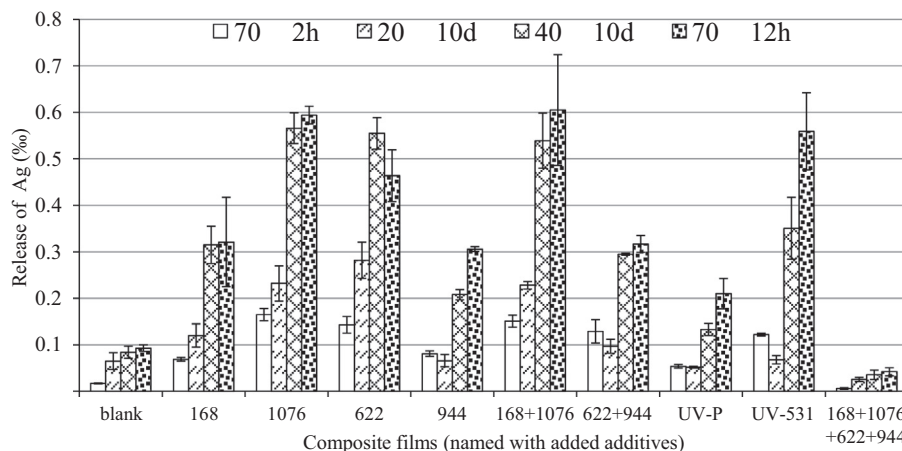


Fig. 2. Silver release from composite films before acceleration test.

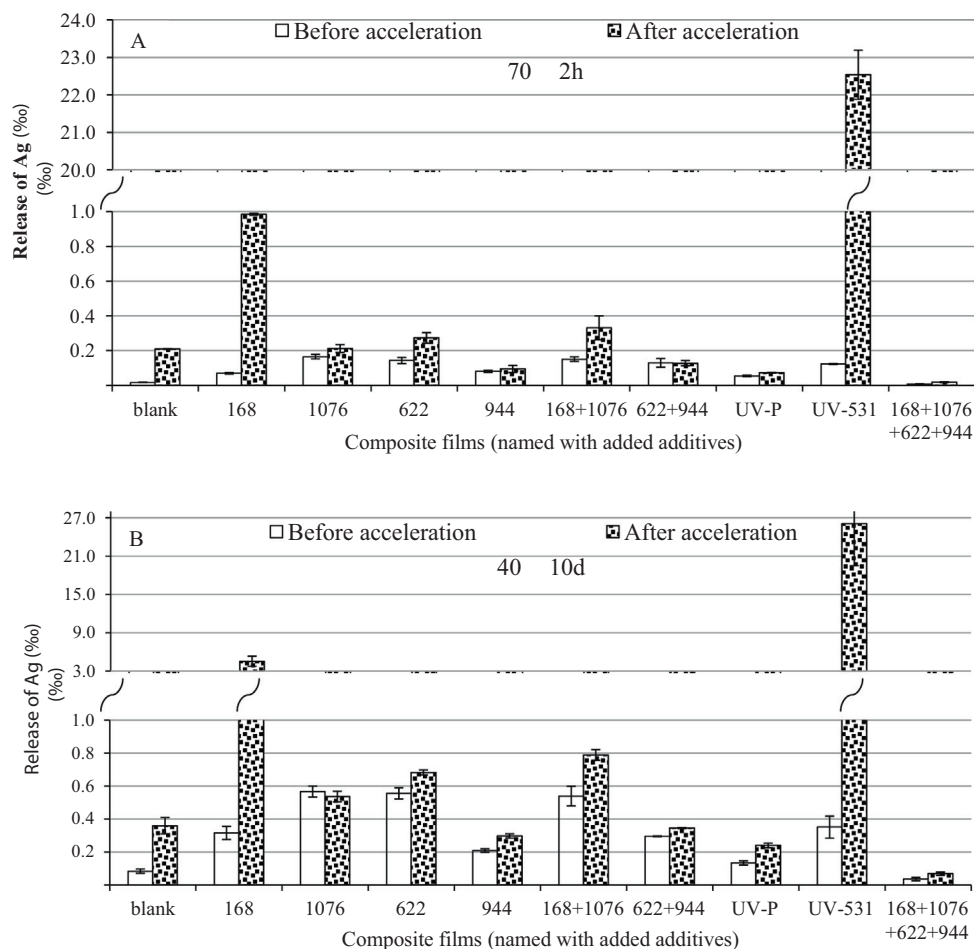


Fig. 3. Comparison of silver release from composite films before and after acceleration test at (A) 70 °C for 2 h and (B) 40 °C for 10 d.

#### 4. Conclusion

Antioxidants and light stabilizers were found to greatly affect the silver release from nanosilver–PE composite films into acidic food simulant. This effect has two possible causes: (i) reactions between organic additives and silver promoting silver release, and (ii) additives promoting or inhibiting silver release by affecting silver oxidation. Without exposing composite films to high temperature and humidity, silver release from most films (using additives 168, 1076, 622, 944, 168 + 1076, 622 + 944, UV-P, or UV-531) was significantly higher than from film without any additive, possibly due to additive–silver interactions. After exposure to high temperature and humidity, silver release from the film without additive increased sharply, due to increased silver oxidation. In contrast, silver release from most films with additives (additives 1076, 622, 944, 622 + 944, UV-P, or 168 + 1076 + 622 + 944) did not increase significantly under these conditions, due to the antioxidant effects of the additives.

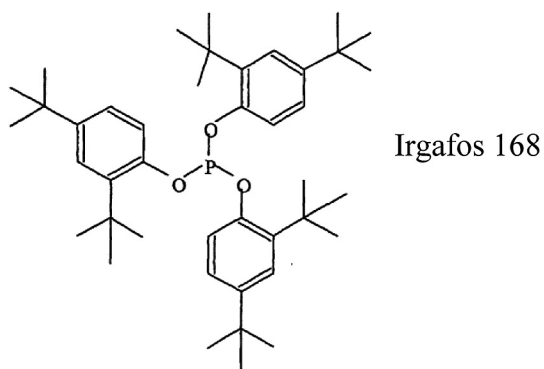


Fig. 4. Structure of antioxidant Irgafos 168.

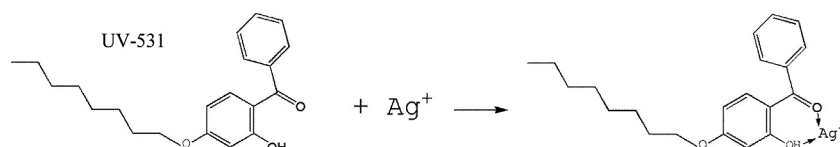


Fig. 5. Coordination of UV-531 with Ag<sup>+</sup>.



## Conflict of interest

The authors have declared no conflict of interest.

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## References

- Artiaga, G., Ramos, K., Ramos, L., Cámara, C., & Gómez-Gómez, M. (2015). Migration and characterisation of nanosilver from food containers by AF(4)-ICP-MS. *Food Chemistry*, 166, 76–85.
- Bumbudsanpharoke, N., & Ko, S. (2015). Nano-food packaging: An overview of market, migration research, and safety regulations. *Journal of Food Science*, 80(5), R910–R923.
- Chaudhry, Q., Scotter, M., Blackburn, J., Ross, B., Boxall, A., Castle, L., ... Watkins, R. (2008). Applications and implications of nanotechnologies for the food sector. *Food Additives and Contaminants Part A*, 25(3), 241–258.
- Cushen, M., Kerry, J., Morris, M., Cruz-Romero, M., & Cummins, E. (2012). Nanotechnologies in the food industry – Recent developments, risks and regulation. *Trends in Food Science & Technology*, 24(1), 30–46.
- Cushen, M., Kerry, J., Morris, M., Cruz-Romero, M., & Cummins, E. (2013). Migration and exposure assessment of silver from a PVC nanocomposite. *Food Chemistry*, 139(1), 389–397.
- Cushen, M., Kerry, J., Morris, M., Cruz-Romero, M., & Cummins, E. (2014). Evaluation and simulation of silver and copper nanoparticle migration from polyethylene nanocomposites to food and an associated exposure assessment. *Journal of Agricultural and Food Chemistry*, 62(6), 1403–1411.
- Echegoyen, Y., & Nerín, C. (2013). Nanoparticle release from nano-silver antimicrobial food containers. *Food and Chemical Toxicology*, 62, 16–22.
- Echegoyen, Y., Rodriguez, S., & Nerín, C. (2016). Nanoclay migration from food packaging materials. *Food Additives and Contaminants Part A*, 33(3), 530–539.
- Fernández, A., Soriano, E., Hernández-Muñoz, P., & Gavara, R. (2010). Migration of antimicrobial silver from composites of polylactide with silver zeolites. *Journal of Food Science*, 75(3), 186–193.
- Guo, L., Yuan, W., Lu, Z., & Li, C. M. (2013). Polymer/nanosilver composite coatings for antibacterial applications. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, 439, 69–83.
- Hannon, J. C., Kerry, J., Cruz-Romero, M., Morris, M., & Cummins, E. (2015). Advances and challenges for the use of engineered nanoparticles in food contact materials. *Trends in Food Science & Technology*, 43(1), 43–62.
- Huang, Y., Chen, S., Bing, X., Gao, C., Wang, T., & Yuan, B. (2011). Nanosilver migrated into food-simulating solutions from commercially available food fresh containers. *Packaging Technology and Science*, 24(5), 291–297.
- Huang, J.-Y., Li, X., & Zhou, W. (2015). Safety assessment of nanocomposite for food packaging application. *Trends in Food Science & Technology*, 45(2), 187–199.
- Kuorwel, K. K., Cran, M. J., Orbell, J. D., Buddhadasa, S., & Bigger, S. W. (2015). Review of mechanical properties, migration, and potential applications in active food packaging systems containing nanoclays and nanosilver. *Comprehensive Reviews in Food Science and Food Safety*, 14(4), 411–430.
- Lin, Q. B., Li, H., Zhong, H. N., Zhao, Q., Xiao, D. H., & Wang, Z. W. (2014). Migration of Ti from nano-TiO<sub>2</sub>-polyethylene composite packaging into food simulants. *Food Additives and Contaminants Part A*, 31(7), 1284–1290.
- McShan, D., Ray, P. C., & Yu, H. T. (2014). Molecular toxicity mechanism of nanosilver. *Journal of Food and Drug Analysis*, 22(1), 116–127.
- Metak, A. M., Nabhani, F., & Connolly, S. N. (2015). Migration of engineered nanoparticles from packaging into food products. *LWT – Food Science and Technology*, 64(2), 781–787.
- Mihindukulasuriya, S. D. F., & Lim, L. T. (2014). Nanotechnology development in food packaging: A review. *Trends in Food Science & Technology*, 40(2), 149–167.
- Peña, J. M., Allen, N. S., Edge, M., Liauw, C. M., & Valange, B. (2001a). Interactions between carbon black and stabilisers in LDPE thermal oxidation. *Polymer Degradation and Stability*, 72(1), 163–174.
- Peña, J. M., Allen, N. S., Edge, M., Liauw, C. M., & Valange, B. (2001b). Studies of synergism between carbon black and stabilisers in LDPE photodegradation. *Polymer Degradation and Stability*, 72(2), 259–270.
- Ranjan, S., Dasgupta, N., Chakraborty, A. R., Melvin Samuel, S., Ramalingam, C., Shanker, R., & Kumar, A. (2014). Nanoscience and nanotechnologies in food industries: Opportunities and research trends. *Journal of Nanoparticle Research*, 16(6), 2464.
- Šimon, P., Chaudhry, Q., & Bakoš, D. (2008). Migration of engineered nanoparticles from polymer packaging to food – A physicochemical view. *Journal of Food and Nutrition Research*, 47(3), 105–113.
- Song, H., Li, B., Lin, Q. B., Wu, H. J., & Chen, Y. (2011). Migration of silver from nanosilver-polyethylene composite packaging into food simulants. *Food Additives and Contaminants Part A*, 28(12), 1758–1762.
- Su, Q. Z., Lin, Q. B., Chen, C. F., Wu, Y. M., Wu, L. B., Chen, X. Q., & Wang, Z. W. (2015). Effect of antioxidants and light stabilisers on silver migration from nanosilver-polyethylene composite packaging films into food simulants. *Food Additives Contaminants Part A*, 32(9), 1561–1566.
- Xia, Y., Rubino, M., & Auras, R. (2014). Release of nanoclay and surfactant from polymer-clay nanocomposites into a food simulant. *Environmental Science & Technology*, 48(23), 13617–13624.
- Youssef, A. M. (2013). Polymer nanocomposites as a new trend for packaging applications. *Polymer-Plastics Technology and Engineering*, 52(7), 635–660.