

Research Article

Migration of Nanosilver into Food-simulating Solutions from Polypropylene Disposable Spoons

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Abstract: The aim of this study was to investigate the possible migration of nanosilver from the commercially available nanosilver antibacterial disposable spoons to food simulating solutions and find out a relationship between migration and conformance with the external conditions. Migration experiments were carried out according to the Chinese standard (GB/T 5009.60-2003), to cover a variety of food simulants and use conditions. Several experimental factors influenced nanosilver release: food simulant, temperature and storage time. An Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) was employed to quantify the total and migrated silver concentration and results demonstrated an increasing migration of nanosilver with storage time and temperature conditions. Meanwhile, Scanning Electron Microscopy/Energy Dispersive Spectrometer (SEM/EDS) was applied to identify the existence and the morphology of nanosilver.

Keywords: Food safety, migration, nanosilver, nanocomposite, polypropylene

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 (Althues *et al.*, 2007), which make food packaging materials achieved novel features of antimicrobial effects, improved tensile properties, oxygen scavenging, extended shelf life (Avella *et al.*, 2005; Bouwmeester *et al.*, 2007; Rhim and Ng, 2007; Song *et al.*, 2011; Xiao-e *et al.*, 2004).

In recent years, nanosilver have emerged as a promising substance with a rapidly increasing use in surprisingly many products, especially in food packaging, due to their antibacterial properties and thermal stability (Simoncicb and Tomsic, 2010; Chaudhry *et al.*, 2008). The antimicrobial action is thought to be exhibited by the migration of silver cations from the particles (Busolo *et al.*, 2010; Kumar and Münstedt, 2005). However, in toxicological studies, nanosilver is of great concern to regulatory bodies, Federal Drug Agency and European Environment

Protection Agencies. Silver nanoparticles are confirmed to be cytotoxic, genotoxic, antiproliferative and possibly carcinogenic (AshaRani *et al.*, 2009).

“Migration” represents a diffusion process, which may be strongly influenced by an interaction of the packaging material with the food (Arvanitoyannis and Bosnea, 2004). Migration testing is an important procedure in the food packaging industry. When introducing a new packaging material, no matter it contains nanomaterials or not, the migration detection is a necessary procedure for checking compliance of a food packaging material against specific migration limits (SMLs), as set out by Commission Regulation (EU) No 10/2011 (EU 10/2011, 2011) on plastic materials and articles intended to come into contact with food (Cushen *et al.*, 2014; García *et al.*, 2006). Nanomaterials in food containers can diffuse or dissolve into the stored food (Benn *et al.*, 2010) and cause food safety problems. Recently, the motivation and tendency of nanoparticles migration from food containers to food and its impact on human health have been preliminary confirmed (Lagarón *et al.*, 2005; Duncan, 2011). In the diffusing process, secondary nanoparticles might be formed, their properties and

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effects may differ from the primary particles (Schluesener and Schluesener, 2013). It has been shown that clumps of nanosilver can break through the colon mucosa and accumulate causing potential toxicity (Gatti, 2004). The nanosilver from certain food containers is known to bind to DNA and interfere with fidelity of replication (Yang *et al.*, 2009b).

The aim of this study was to investigate the possible migration of nanosilver from the commercially available nanosilver antibacterial disposable spoons to food simulating solutions and find out a relationship between migration and conformance with the external conditions. Migration experiments were carried out according to the Chinese standard (GB/T 5009.60-2003), to cover a variety of food simulants and use conditions. The presence of nanosilver in the obtained food-simulating solutions was inspected by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). In addition, further confirmation of the presence and morphology of nanosilver particles was performed by scanning electron microscopy and energy-dispersive X-ray (SEM/EDX).

MATERIALS AND METHODS

Instrumentation: A microwave oven (CEM MARS, Matthews, NC, USA) equipped with polytetrafluoroethylene (PTFE) vessels was carried out for nanosilver-polypropylene disposable spoons digestion.

An ICP-MS (NexION 300X, PerkinElmer, USA) was employed to quantify the total and migrated silver concentration.

An SEM (Hitachi SU8010 FE-SEM, Hitachi, Tokyo, Japan; TEAM Apollo XL EDS EDAX, USA), was applied to detect the presence and morphology of nanosilver in the pp spoons and in the extracts obtained after the different migration assays. An EDX detector was equipped to get further confirmation of the atomic composition of the samples.

An ultrasonic bath ((Kun Shan Ultrasonic Instruments Co., Ltd, Jiangsu, China) with an ultrasonic micro-homogeniser were employed to avoid nanoparticles aggregation before the testing analysis.

Reagents and samples: Commercially available nanosilver antibacterial disposable spoons composed of polypropylene (pp) plastic (Nano center, Ltd, Shanghai, China) were considered as the original material for the study.

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). Distilled water A, 4% acetic acid (v/v) B and hexane C solutions were prepared for the food-simulating solutions: water, acid and fatty foods,

respectively, according to the Chinese standard (GB/T 5009.60-2003).

Silver in Water (Aladdin Industrial Corporation, 16050 Kaplan Ave, U.S.A) 1000 ug/mL and 5% HNO₃ (Guaranteed reagent) were used to prepared daily the stock standard solution of silver 10 ug/mL and kept in the dark.

Determination of silver in polypropylene disposable spoon: The disposable spoons of 2*2 cm each in dimension were washed with pure water and dried under natural conditions for sample preparation.

A microwave digestion method was carried out to pre-process the samples. A precise mass of 0.15 g samples were 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 send into the microwave digestion oven. 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:

Experiment at different temperature: The polypropylene disposable spoon samples weighted accurately intended to come into contact with food simulant-4% acetic acid (v/v) and fully dipped in the food simulant at temperatures of 25, 40, 60, 70, 100°C for 2 and 6h.

Experiment at different storage time: The polypropylene disposable spoon samples weighted accurately were placed in contact with food simulant-4% acetic acid (v/v) and fully dipped in the food simulant. Then, the samples were kept in the dark for 0.5h, 1h, 2h, 4h, 6h, 1d, 2d, 3d, 5d, 7d and 10d at temperatures of 40 and 70°C.

Experiment in different food simulants: The polypropylene disposable spoon samples weighted accurately were placed in contact with food simulants: distilled water A, 4% acetic acid (v/v) B and hexane C and sealed in clean wide-mouth bottles at temperatures of 40 and 70°C for h and 6h.

In these experiments above, samples were all kept in the dark. And the contrast experiments were settled in order to avoid excessive error and influence of other factors.

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.

Then an ICP-MS (NexION 300X, PerkinElmer, USA) was employed to quantify the migrated nanosilver concentration. 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 (Cushen *et al.*, 2013).

Scanning electron microscopy/energy dispersive spectrometer analysis: An Scanning Electron Microscopy (SEM) was applied to detect the existence and the morphology of nanosilver in pp spoons and in the migration solutions. An Energy Dispersive Spectrometer (EDS) detector was employed for the atomic composition confirmation of the samples. The pp spoons were converted into ash under 600°C to collect some original powder of the nanocomposite. The three types of food-simulating solutions were, separately, gathered and concentrated to gain migration substances, in which existed nanosilver along with some other food additives.

RESULTS AND DISCUSSION

Characterisation of nanosilver by SEM-EDS: The SEM-EDS tests, confirming the atomic composition of the samples, indicated the presence and the morphology of nanosilver in pp spoons and in the migration solutions. Figure 1A shows a SEM image of nanosilver in the ashes, in which nanosilver existed in spherical forms with size between 40-400nm. Figure 1B shows a

typical EDS spectrum analysis of points within the spherical nanoparticles, which made a further

confirmation of a majority of nanosilver particles. Figure 2 shows an SEM image obtained from migration substances in which the nanosilver particles were aggregated.

The large differences in diameter may transform into an even larger differences in surface area, which extremely impacts its biological properties. The surface charge is known to influence toxicity (El Badawy *et al.*, 2011). In the industrial processes and quantity production, the size of nanosilver particles might vary and is often not given. Further, the nanosilver particles have a tendency to agglomerate and might be difficult to disperse properly (Schluesener and Schluesener, 2013).

Tests of nanosilver by ICP-MS: The ICP-MS analysis of the solution after microwave-assisted digestion indexed that the total quantity of silver in polypropylene disposable spoon was 30 µg (ZnO)/g.

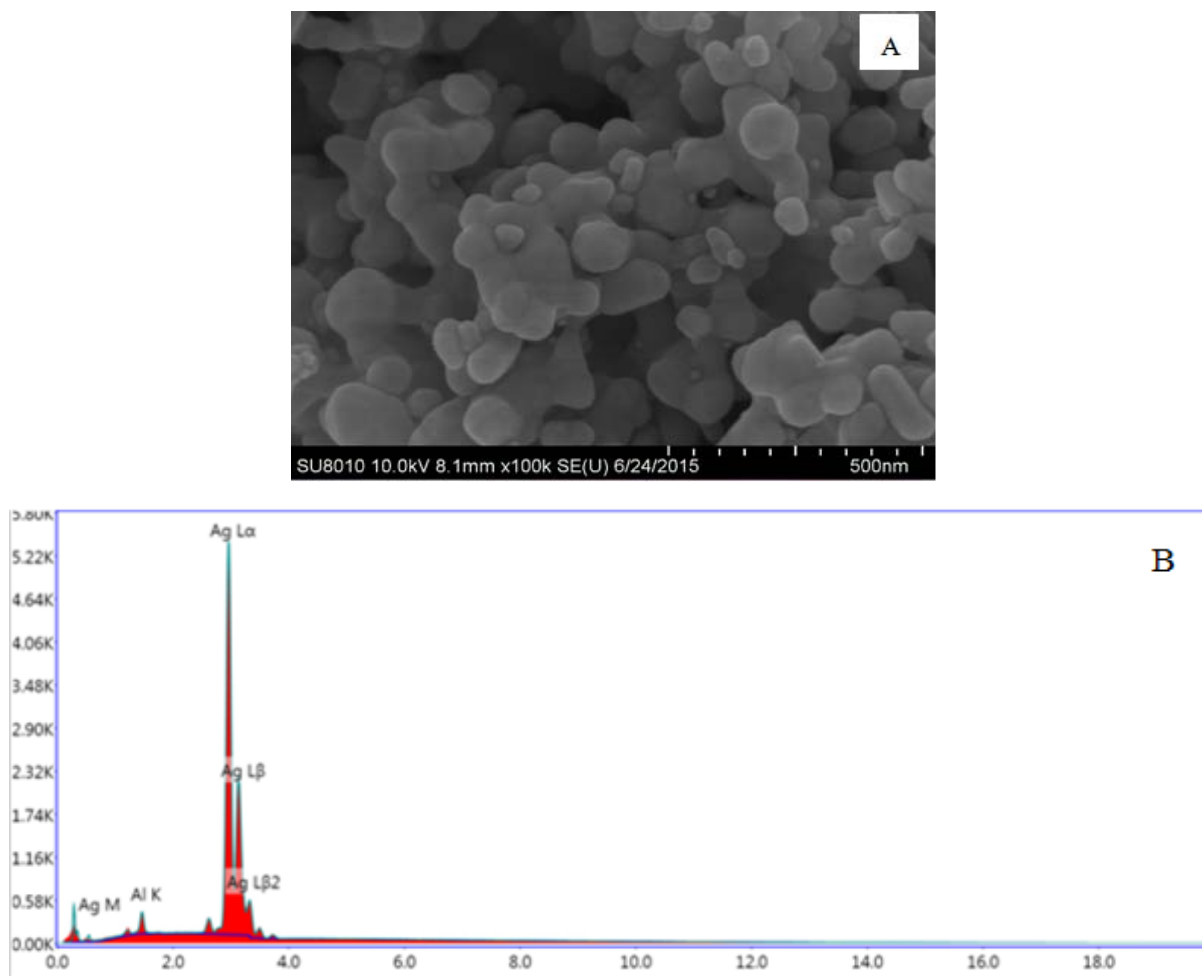


Fig. 1: A: SEM image of nanosilver in the ashes. The nanoparticles are in spherical forms with size between 40 nm-400 nm; B: The corresponding EDS analysis confirming a majority of nanosilver particles

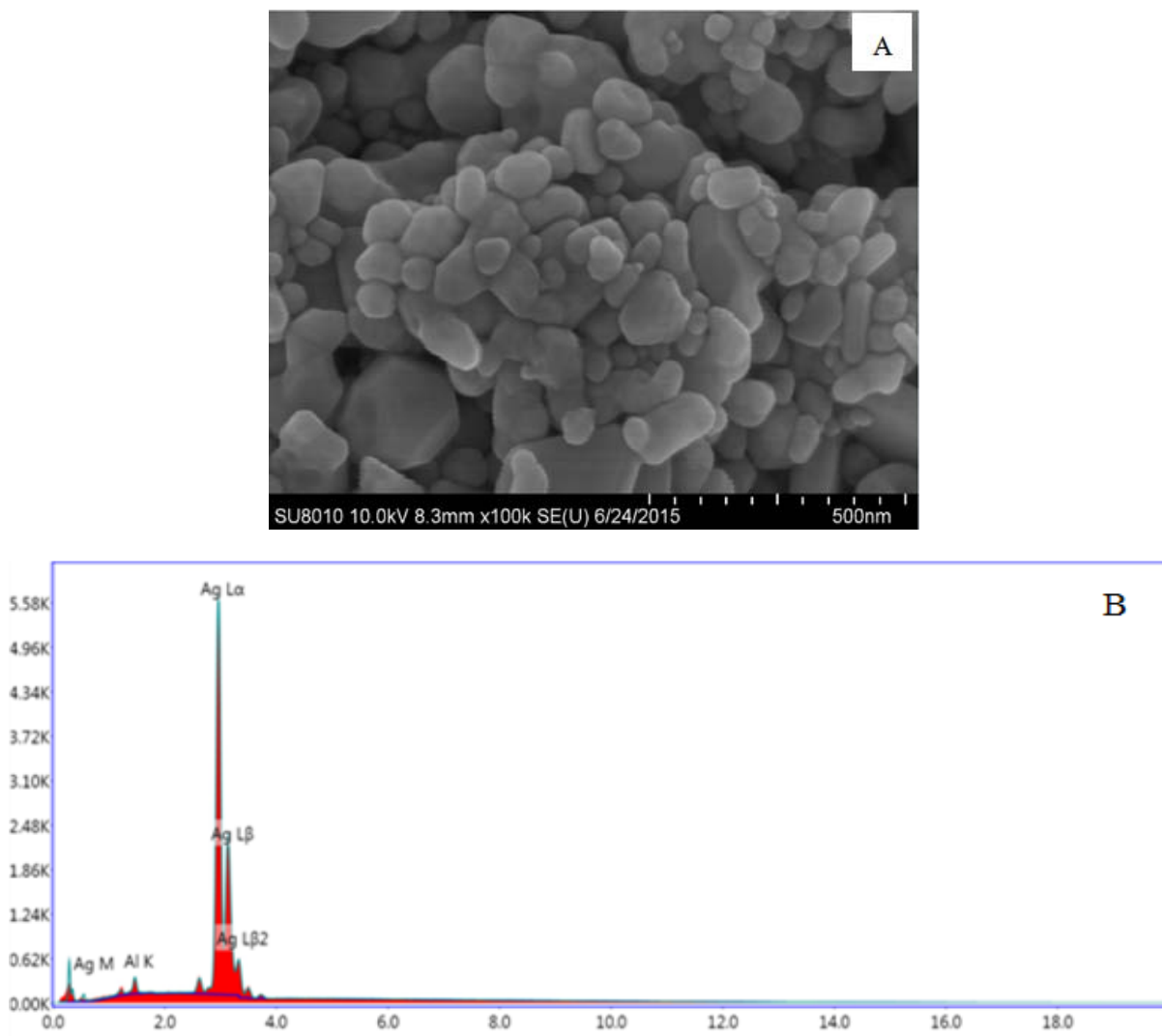
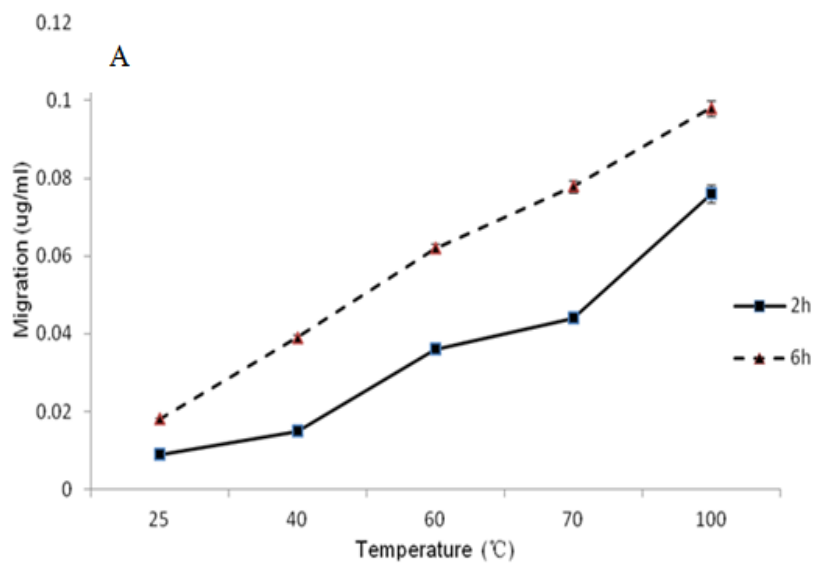


Fig. 2: A: An SEM image obtained from migration substances; B: The EDS analysis of points within the spherical nanoparticles, confirming a majority of nanosilver



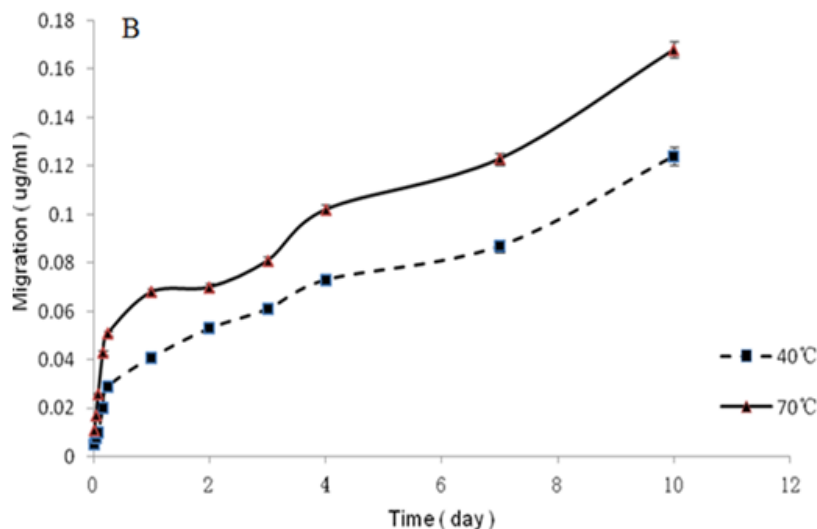


Fig. 3: A: Concentration of silver migrated into 4% acetic acid at a series of temperature for 2h and 6h separately; B: Concentration of silver migrated into 4% acetic acid at different storage time

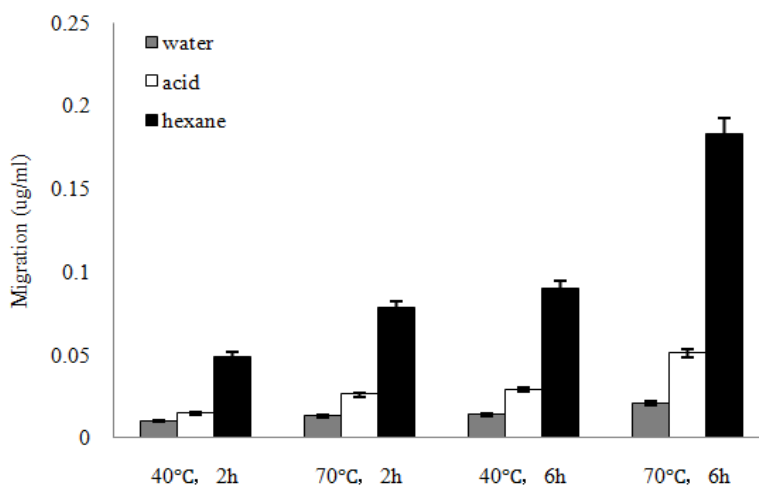


Fig. 4: Concentration of silver migrated into distilled water (A), 4% acetic acid (B) and hexane (C) at 40°C and 70°C for 2 h and 6 h

Migration amount of silver into food-simulating solutions:

The silver content that migrated from polypropylene disposable spoon 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 1 demonstrated a significant nanosilver migration into the acid food simulant at a range of temperatures. Figure 2 demonstrated a significant nanosilver migration into the acid food simulant at varying storage time. The amount of silver migration is discovered as increasing with storage time and temperature. Figure 3 demonstrated a significant nanosilver migration into the three food simulants: distilled water A, 4% acetic acid (v/v) B and hexane C at temperatures of 40 and 70°C for 2 and 6h. According

to the ICP-MS analysis, the disposable spoons detectably diffused silver into the three food simulans and obviously, the amount of silver migrated into hexane is much higher than the other two food simulans.

And the reason may be that the nanosilver encapsulated within the surface layers of the samples released firstly, then, the succeeding release of nanosilver were from the inner part of the samples which had to cross the diffusion barrier constituted by many crystalline lamellae (Murthy *et al.*, 1989). In plastics, the water and organic molecules in the interlamellar regions can change the overall crystalline state (Alt *et al.*, 2004).

According to the analysis of ICP-MS, nanosilver got a higher concentration of migration to the hexane food simulans. Organic food-simulating solutions have

a swelling effect for polypropylene which may cause the high released concentration of nanosilver (Fig. 4).

CONCLUSION

This study investigate the possible migration of nanosilver from the commercially available nanosilver antibacterial disposable spoons to food simulating solutions, which based on the Chinese standard (GB/T 5009.60-2003) under a variety of time intervals and temperature conditions.

The ICP-MS analysis confirmed the presence that polypropylene disposable spoons released silver into the three kinds of food-simulating solutions, meanwhile, the amount of silver migrated into hexane is much more than the other two food simulans. Results demonstrated an increasing migration of nanosilver with storage time and temperature conditions. The combined use of SEM/EDS technical analysis suggested the atomic composition in pp spoons and in the migration solutions. The nanosilver particles existed in spherical forms with size between 40-400 nm and easily agglomerated.

During the migration process, nanosilver particles may suffer some transformations and secondary nanoparticles could be formed, their properties and effects may differ from the primary particles. Therefore, both performance and safety aspects should be considered seriously to make the products safe and efficient.

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