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Simulation of nanosilver migration from polystyrene nanocomposite into food simulants

Jaber Soleimani [*1], Babak Ghanbarzadeh [2], Jalal Dehgannya [2],
Sima Baheri Islami [3] and Saeed M. Sorouraddin [4]

[1] *Agricultural Engineering Research Department, East Azarbaijan Agricultural and Natural Resources Educational and Research Center, Agricultural Research, Educational and Extension Organization (AREEO), Tabriz, Iran*
[2] *Department of Food Science and Technology, Faculty of Agriculture, University of Tabriz, Tabriz, Iran*
[3] *Faculty of Mechanical Engineering, Department of Mechanical Engineering, University of Tabriz, Tabriz, Iran*
[4] *Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran*

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Abstract. Polystyrene granules were combined with nanosilver to form a nanocomposite film. One-side migration was conducted to test into three food simulants (3% acetic acid, 10% ethanol and 95% ethanol) at 40°C temperature on different period of time (2, 4, 6, 8 and 10 days). It was found that, among the simulants, the highest migration amount was obtained with 3% acetic acid, while the 95% ethanol revealed the least migration level. Diffusion coefficients of nanosilver particles into simulants were estimated by inverse simulation using experimental data of concentration variation in the simulants. The finite element method used to solve the mass transfer equation and the numerical results indicates the sameresponse with the experimental data. The numerical results confirmed that the highest diffusion coefficient for acetic acid 3% (1.82E-10 to 1.76E-9 $m^2 s^{-1}$) and the lowest diffusion coefficient for ethanol 95% from 2 to 10 days were obtained, respectively. Also, results of diffusion coefficient – concentration relation showed, the diffusion coefficient had in direct correlation with time and concentration. The results indicated that, in the 3% acetic acid, due to the increasing of diffusion coefficient of silver nanoparticles, they are released faster and distributed uniformly.

Keywords: migration; nanosilver; simulants; concentration; diffusion coefficient

1. Introduction

Nanoscience is one of the most fascinating technological research fields for many researchers and manufacturers and it involves several utilization in food technology including, packaging and encapsulation. Nanocomposite packaging is produced by incorporating nanoparticles of metal, metal oxide, semimetal or clay into polymer films (Chaudhry *et al.* 2008, Panea *et al.* 2014, Huang *et al.* 2015). Despite many benefits of using nanocomposite packaging, the most disadvantageous of using nanoparticles in packaging is the possibility of their migration into the packaged food that maybe harmful for human healthand ecosystem (de Azeredo 2013, Bumbudsanpharoke and Ko

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∗Corresponding author, Ph.D., E-mail: j.soleymani@areeo.ac.ir

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2015). Migration is a mass transfer process where low molecular mass compounds are released into the food or food simulants due to concentration gradient (Katan 1996, Fernández *et al*. 2010). Migration process can be affected by several factors such as package and contained food characteristics, time and temperature conditions. Mass transfer from a plastic material into foodstuffs is predictable and in most cases, the transfer obeys Fick's laws of diffusion (Franz 2005). The knowing of accurate mass transfer parameters is important to modeling the migration process. Diffusion coefficient is a useful parameter in characterizing mass flow across a nanocomposite-food interface. Understanding the diffusion coefficient during migration phenomena would allow accurate determination of concentration distribution and hence the kinetic calculation for optimum production of nanocomposite.

Since migration experiments are time consuming and costly, predictive modeling has been introduced as an interesting alternative (Brandsch *et al*. 2002, Petersen *et al*. 2005, Franz 2005, Huang *et al*. 2015). A number of studies have done on the nanoparticles migration such as titanium nitride (Bott *et al*. 2014), Zinc oxide (Tada-Oikawa *et al*. 2015), Zinc oxide and silver (Emamifar *et al*. 2010, Panea *et al*. 2014), Silver and Copper (Cushen *et al*. 2014), Titanium dioxide (Lin *et al*. 2014), Clay (Huang *et al*. 2015, Echegoyen *et al*. 2016), Copper (Liu *et al*. 2016), Carbon black (Bott *et al*. 2014) and Silver (Huang *et al*. 2011, Song *et al*. 2011, Cushen *et al*. 2013, Echegoyen and Nerín 2013, Azlin-Hasim *et al*. 2015, Artiaga *et al*. 2015).

Among the metal nano-particles, nanosilver has been the most frequently used item (Luoma 2008). The food contact materials contain nanosilver have been widely used specially in United States and Japan. Because of food contact materials containing nanosilver may release silver nanoparticles into foods, it is important to study the release of nanosilver from nanocomposite packaging to foods (Huang *et al*. 2011). Silver nano particles can rapidly diffuse, because, they have small size, a larger surface area to volume ratio (An *et al*. 2008, Marambio-Jones and Hoek 2010, Artiaga *et al*. 2015) and like other plastic additives silver is not covalently bound to the plastic matrix and can or is intended to be released during storage times (Chaudhry *et al*. 2008). In the EU, the use of silver nanoparticles in plastic food containers is not allowed (Art 9, Directive EU/10/201), although the presence of certain silver zeolites is authorized in plastic food containers and rubber seals (Art 7, Directive EU/10/2011). World Health Organization has estimated a human no observable adverse effect level of Ag to be 0.39 mg/day (WHO 2004). According to the rules of European Food Safety Authority (EFSA 2006), the allowable amount of silver migration from food contact materials is to 0.05 mg Ag/kg food.

Until now, a lot of work has been done on modelling the migration of substances which are used in the packaging materials, such as monomers (Hamdani *et al*. 1997, Bichara *et al*. 1999, Brandsch *et al*. 2002, Silva *et al*. 2007, Franz and Welle 2008), nanoparticles (Bott *et al*. 2014), antimicrobial agents (Cerisuelo *et al*. 2012), other components (Djilani *et al*. 2000, Stoffers *et al*. 2005, Torres *et al*. 2012). A theoretical model established by Crank (1979), useful for the prediction of migration from a packaging in isothermal contact with a finite amount of food, but this method is not always applicable to three dimensional complex geometries with different boundary conditions, thus, numerical study or simulation of migration has been introduced as a promising alternative.

The objective of this work is to study the migration of nanosilver from polystyrene based film into food simulants and modeling of this migration with calculation of diffusion coefficient. Diffusion coefficient is then assessed by using experimental data of concentration variation in the liquid phase for silver nanoparticles. Finally the distance dependence of nanoparticle behavior and relationship between diffusion coefficients with concentration are evaluated.

2. Materials and methods

All chemicals and reagents used were of analytical grade and high purity. Polystyrene (PS) granule prepared from Iran- Tabriz Petrochemical Company (T.P.C). Polystyrene grade GPPS 1540 with characteristics are MFI gr/10 min (5 Kg) 11 and vicat softening point is 50°C/h (1Kg) 91. Nanosilver was obtained the NANOSANY COPRPORATION^{TM} USA. The primary particle diameter is about 20 nm with purity 99.99%. Non-metallic certified Nitric acid (HNO3), hydrogen peroxide (H2O2), acetic acid, ethanol, buffer phosphate, 1,2-dibromoethane (1,2-DBE) were obtained from MERK, sodium diethyldithiocarbamate (SDTTC) was purchased from Fulka.

2.1 Nanocomposite film production

Food packaging films selected for the migration study included neat PS granules and nanosilver(0.3%). The melt compounding of all the blends were carried out in a laboratory batch internal mixer (Brabender W50 EHT, Germany) at 190°C with a rotor speed of 60 rpm. The chamber volume was 44.88 cc and the filling factor was selected 0.85. Therefore, the weights of the different constituents were measured based on their weight ratios in blend and their melt densities. All samples were then compression molded for preparing sheet (thickness of 0.05 cm) laboratory hot press (Dr. Collin, P200P; 25 MPa, Germany) at 190°C for 8 min under50 bar pressure.

2.2 Migration assays

Migration experiments were performed by exposing one side of the films with the food simulants. Fig. 1 shows the experimental set-up used to study migration of nanosilver. Films were produced as discs with dimensions thickness of 0.05 cm and diameter of 2.56 cm. A conical vessel of 50 cc was used as a migration cell. Each disc sample was placed in one vessel, and 15 cc of simulant was then added to the vessel. The vessels were capped and left in an oven at a constant temperature; 1 cc of simulant was collected from the migration cell after each predetermined time interval for further analysis by Grafite Furnace Atomic Absorption Spectroscopy (GFAAS) manufactured by Analytik Jena, Germany. Migration tests were performed at 40°C and time periods set at 2, 4, 6, 8 and10 days. The simulant removed from the cell during sampling and it was replaced by fresh liquid. The samples were gently shaken to obtain a uniform dispersion of migrating nanosilver in food simulants every 24 h as well as before every sampling for analysis.

2.3 Food simulants

Food simulants were prepared according to Council Directive 10/2011 (European Commission, 2011). Which has been established the basic procedures and a list of simulants for testing the migration of constituents of food contact plastics. According to these guidelines, 3% (v/v) aqueous acetic acid (3% AA), 10% (v/v) aqueous ethanol (10% EOH) and 95% (v/v) ethanol (95% EOH) were selected as food simulants. Acetic acid (3.0 ml) was accurately diluted with ultrapure water to 100 ml to prepare the 3% (v/v) aqueous acetic acid. The 10% (v/v) and 95% (v/v) ethanol were prepared by diluting 10 ml and 95 ml of ethanol (≥ 99.7%) with ultrapure water to 100 ml, respectively.

2.4 Extraction of nanosilver from nanocomposite film

A microwave digestion method was used to quantify the total amount of silver in the nanocomposite contain nanosilver. Samples were cleaned with ultrapure water and dried before use. Portions (0.2 g) of the films were weighed into PTFE tubes within a mixed solution of 5 ml of nitric acid and 2 ml of hydrogen peroxide. The tubes were sealed and the samples digested in the microwave oven. The microwave program for digestion was as follows Table 1. (Huang *et al.* 2011). After the microwave procedure, the digestion solution was cooled, filtered through a glass fiber filter and diluted to 50 ml. Silverwas quantified by GFAAS.

2.5 Extraction of nanosilver from simulant

The samples were incubated in sealed containers at 40°C and the migration measurements investigated in 2, 4, 6, 8 and 10 days of storage. Then, the packaged samples were removed from the incubator and left to cool for few minutes at room temperature, and 1 mL of each simulants (aceticacid 3%, ethanol 10% and ethanol 95%) was combined with sodium diethyldithiocarbamate (SDTTC, 0.1M) as a chelating agent. The volume was increased to 5 mL by buffer phosphate (pH ≈ 8). Then 120 μL 1, 2-dibromoethane (1, 2-DBE, extraction solvent) was mixed with 1.5 mL ethanol (dispersive solvent) and the resulted solution was dispersed into prenominated solution by a 5 mL syringe. A cloudy solution, resulting from the dispersion of the fine droplets of ethanol into the aqueous solution, was formed in the test tube. The final solution with speed 4000 rpm for 5 min centrifuged. In order to investigate the extraction amount, the settled phase was removed and injected into GFAAS.

2.6 Numerical – experimental inverse method

2.6.1 Governing equations and numerical model geometry

The phenomenon of mass transfer from a package material into foodstuffs or food simulants could be very complex. Mass transfer during migration was simulated and diffusion coefficient of nanosilver for the process was estimated using a commercial simulation package. Governing equation followed by

$$\frac{\partial C_i}{\partial t} = \nabla.(D_i \nabla C_i) + R_i \tag{1}$$

$$N_i = -D_i \nabla C_i \tag{2}$$

C_i is the concentration of nanosilver in the simulant and nanocomposite; D_i the diffusion coefficient, N_i the mass flux and R_i the source term due to reaction. *i* once used for simulant (s) and once used for nanocomposite (Nc).

Table 1 Set up of nanocomposite microwave digestion

Stage	Power	Temperature rise time (min)	Controlled temperature (°C)	Holding time (min)
1	1200	6	120	1
2	1200	7	190	30

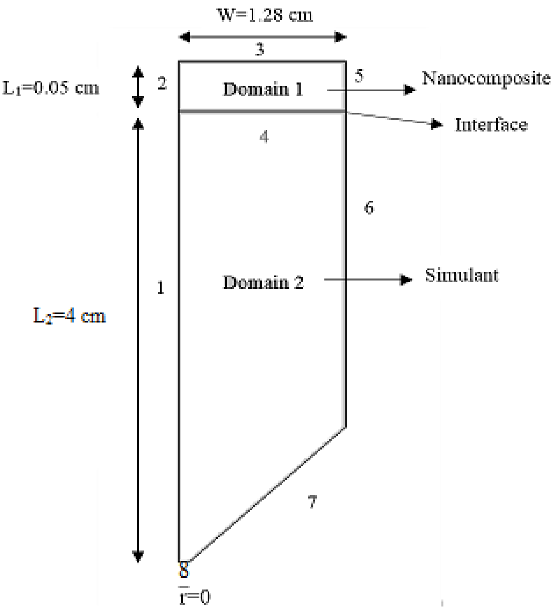

Fig. 1 Schematic of the set-up of migration experiment (no real scale)

The two dimentional axisymmetric geometry for numerical simulations is shown in Fig. 1.

Due to the symmetrical nature of the nanocomposite films and simulants container, the simulation was performed using 2-D axisymmetric assumption. To simplify the problem, the following assumptions were also considered:

1. Nanosilver initial concentration distribution in nanocomposite is homogeneous.
2. There is no chemical interaction between nanocomposite and simulants ($R_i = 0$).
3. No boundary resistance is considered to mass transfer between nanocomposite and simulants.

The following initial and boundary conditions were used to solve Eq. (1)

Initial condition

$t = 0$

$$C_{Nc} = C_0; \qquad \text{Domain 1} \tag{3}$$

$$C_s = 0; \qquad \text{Domain 2} \tag{4}$$

Boundary conditions

$$\text{No flux} \qquad -n.N_i = 0; \ \textit{boundaries}\ 3, 5, 6, 7, 8 \tag{5}$$

$$\text{Axial symmetry} \qquad \nabla N_i = 0; \ \textit{boundaries}\ 1, 2 \tag{6}$$

$$\text{Continuity} \qquad N_{domain1} = N_{domain2}; \ \textit{boundary}\ 4 \tag{7}$$

2.6.2 Numerical simulation

Eqs. (1) and (2) were solved using the COMSOL Multiphysics 4.4 (Chemical Engineering Module) software for nanocomposite films to quantify the extent of the migration process from films. The package is a partial differential equation (PDE) based on modeling and simulation tool that makes finite element method (FEM) useful. A guessed value for initial diffusion coefficient was then input in a time-defined interpolation form for the first time step 0–172800 s equal 2 day of storage and process was simulated. Nanosilver content profile was computed and compared with the corresponding data from the previously conducted experiments. Diffusion coefficient was adjusted appropriately for a best fit between the experimental concentration data and simulated ones. The simulation process is then repeated for the next time step of 172800–345600s equal 2-4 days of storage. This process was repeated for the other storage time steps 345600-518400s equal 4-6 days, 518400-691200s equal 6-8 days and 691200-864000s equal 8-10 days, each time comparing simulated and experimental data to reach an acceptable error. The relative error and root mean square have been defined according to Eqs. (8) and (9).

$$\delta = \frac{\left|C_{ex} - C_{sim}\right|}{C_{ex}} \tag{8}$$

$$RMSE = \sqrt{\sum_{j=1}^{m}(C_{ex} - C_{sim})^2} \tag{9}$$

For final simulated concentration values, the maximum δ and RMSE (Root mean square error) values were little than 1E-4 and 1E-9 respectively for each time step.

3. Results and discussions

3.1 Migration of nanosilver into food simulants

The migration kinetics of the nanosilver in contact with three aqueous simulants, 3% AA, 10% EOH and 95% EOH at 40°C are depicted in Fig. 2. The amount of migration increased with increasing of the storage time. The extent of migration of nanosilver from the film was obviously different in the three simulants. The highest migration levels were observed in 3% acetic acid solution 4.53e-5 mol m^{-3} to 5.5e-5 mol m^{-3} from 2 to 10 days, respectively and the 95% EOH solution showed the least migrated nanosilver (1.866e-5 mol m^{-3} to 2.377e-5 mol m^{-3}). So, the amount of nanosilver concentration in the 3% AA was about 1.43 and 2.36 fold higher than 10% EOH and 95% EOH, respectively. Also, nanosilver concentration in 10% EOH was about 1.65 fold higher than 95% EOH. It is clear that the nanosilver migration increases by time significantly in all food simulating solutions. These results are consistent with the results obtained by other researchers (Von Goetz *et al.* 2013, Huang *et al.* 2015, Artiaga *et al*, 2015). They found that the migrated nanosilver into 3% v/v acetic acid was higher than other simulants such as distilled water, 10% v/v ethanol and 95% v/v ethanol. The possible mechanism for this migration phenomenon consists of two steps. The initial release must be from the pented nanosilver particles which are on the film surface layers. Then, the subsequent release of nanosilver takes place by solvent embedding and diffusion. The simulant solvent molecules are firstly embedded in inter lamellar

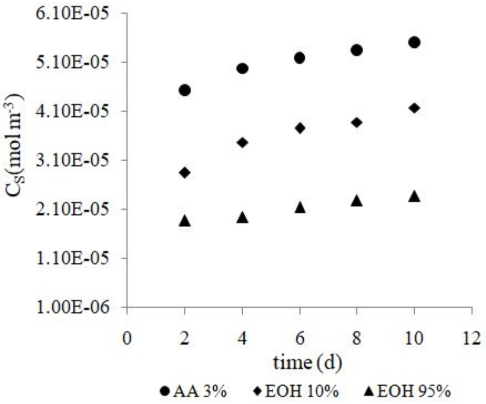

Fig. 2 Time variation of nanosilver concentration in three simulants at 40°C (experimental data)

areas and ultimately plasticize and widen the interspace between polymer chains. The sorption equilibrium induces the mobility of the macromolecular chains, in the amorphous polymer. This can facilitate the following diffusion of nanoparticles with simultaneous oxidation of nanosilver. Finally, the oxidized nanosilver can cross the diffusion barrier and migrate through the equilibrated specimen (Huang *et al*. 2011).

3.2 Diffusion coefficients kinetics

The diffusion coefficient kinetics of the silver nanoparticles in contact with three aqueous simulants, 3% AA, 10% EOH and 95% EOH at 40°C are shown in Fig. 3. As can be seen, the diffusion coefficient was not constant and with increase of contact time the diffusion coefficient also increased. The result showed that the highest diffusion coefficient was obtained for 3% AA (1.70E-10 to 8.4E-10 $m^2 s^{-1}$) from 2 to 10 days, respectively. As the same way, the lowest diffusion coefficient was observed for 95% EOH (4.6E-13 to 8.1E-12 $m^2 s^{-1}$). As a result, the amount of diffusion coefficient in the 3% AA was about 6.5 times higher than 10% EOH and 123 fold higher than 95% EOH. Also, diffusion coefficient in the 10% EOH 19 fold higher than 95% EOH. It can be concluded that, because the penetration rate and the depth of penetration of the 3% acetic acid in the film was major, leading to an increase in the diffusion coefficient nanoparticles.

The kinetics of nanosilver diffusion coefficient in the nanocomposite contacted with three aqueous simulants, 3% AA, 10% EOH and 95% EOH at 40°C has been shown in Fig. 4. The diffusion coefficient increment rate for nanocomposites contacted with 3% AA > 10% EOH > 95% EOH. Therefore, diffusion coefficient in the nanocomposite contacted with 95% EOH was about 7×10^{-3} lower than 3% AAand about 0.05 lower than 10% EOH. Generally, diffusivity of an additive describes by only one diffusion coefficient or constant diffusion coefficient. But, diffusion properties of polymer matrix changes widely, during contact with simulant, due to interaction between food or food simulants and packaging materials (Feigenbaum *et al*. 2000). To create Interactions between food and packaging may create polymer swelling and may accelerate the transfer of compounds. Polymers swell due to the absorption of organic compounds intensifies migration from the polymer material (Culter 1992). Also, evidences suggests that organic penetrants absorbed by organic polymers, leads to a gentle relaxation of polymer chains that accelerate the release (Halek 1988). Thus, by increasing the interaction between food and

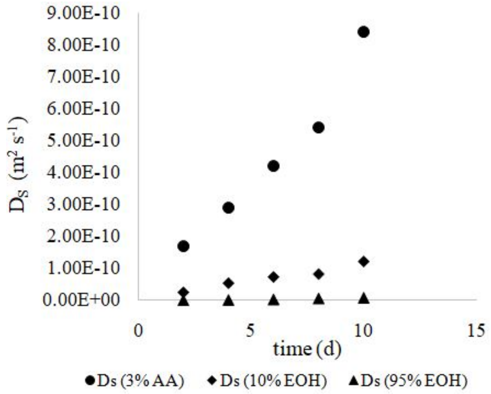

Fig. 3 Time variation of nanosilver diffusion coefficient in three simulants at 40°C

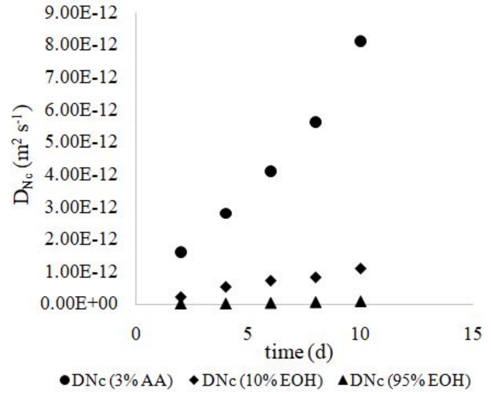

Fig. 4 Time variation of nanosilver diffusion coefficient in nanocomposite contacted with simulants at 40°C

packaging during the collision, the release process occur at higher rates due to increased diffusion coefficient of swollen polymer (Reynier *et al*. 2002, Huang *et al*. 2015). In fact, the diffusion coefficient should be changed frequently through simulant penetration into the polymer. As a result, reliable predictions of migration kinetics by using one or constant diffusion coefficient are not true (Huang *et al*. 2015).

3.3 The numerical determination of diffusion coefficient

As mentioned in Section 2.5, integral area average of nanosilver concentration was obtained by an acceptable error in comparison with experimental data at each time step. For three simulants, the variationof diffusion coefficient versus nanosilver concentration has been shown in Fig. 5(a) curve fitting using weighted least squares method has been done for diffusion coefficient of nanosilver in all simulants and the correlations are given in Table 2.

For all simulants, by increasing of diffusion coefficient, nanosilver concentration in the simulant increases (Figs. 5(a), (c) and (e)). Consequently, their concentration in the nanocomposite decreases (Figs. 5(b), (d) and (f)). As a result, the reduction rate of nanosilver concentration or the

Table 2 Nanosilver diffusion coefficient models in simulants and nanocomposite

Simulant	Diffusion coefficients					
	Model	R^2	σ	Model	R^2	σ
3% AA	$D_s = 2.477E - 14C^{188878.66}$	97.8	4.4E-11	$D_{nc} = 8.677E - 17C^{-1.4213}$	99.7	7.9E-15
10% EOH	$D_s = 5.864E - 8Ce^{93024.55C}$	99.8	1.9E-12	$D_{nc} = -1.283E - 8Ce^{-2156.14C}$	99.7	2.0E-14
95% EOH	$D_s = 1.3581E + 35C^{9.995}$	99.49	2.7E-11	$D_{nc} = 7.812E - 4Ce^{-6882.169C}$	99.4	2.5E-15

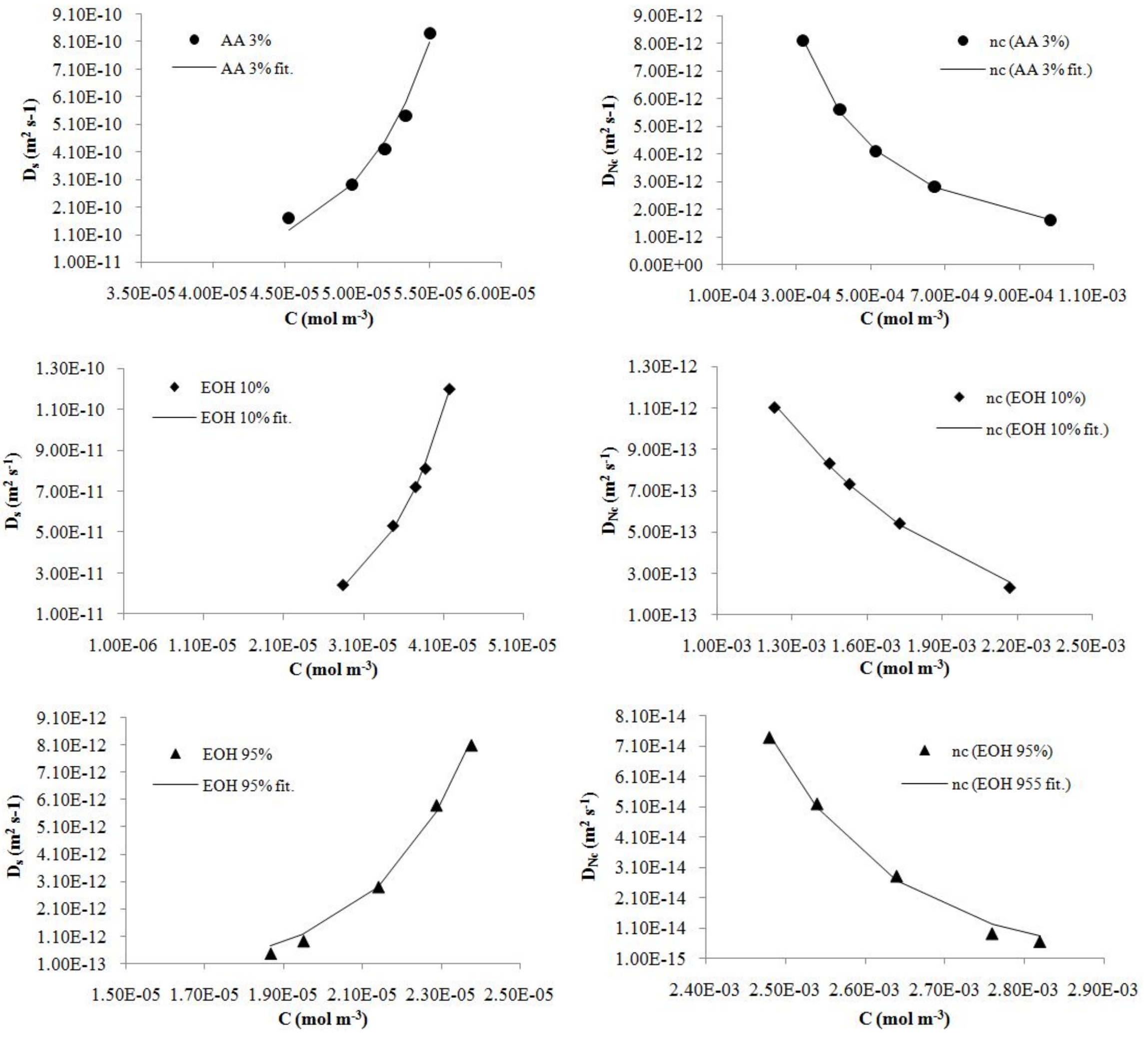

Fig. 5 Variation of nanosilver diffusion coefficient versus its concentration at 40 °C: (a) simulant 3% AA; (b) nanocomposite contacted with 3% AA; (c) simulant 10% EOH; (d) nanocomposite contacted with 10% EOH; (e) simulant 95% EOH; (f) nanocomposite contacted with 95% EOH

release rate of nanosilver in the nanocomposite contacted with 3%acetic acid is faster than the other 2 simulant. In the same way, the release rate of nanosilver from nanocomposite into 10%

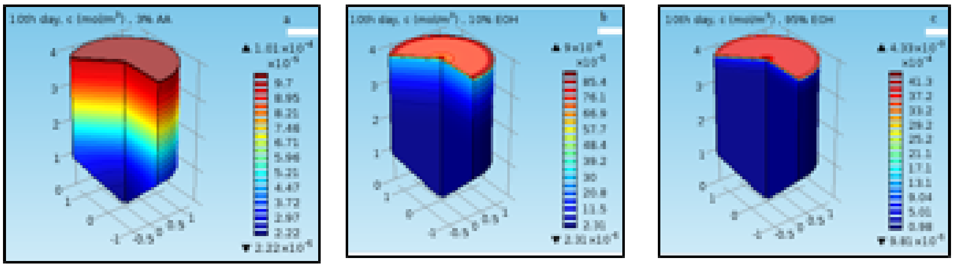

Fig. 6 The nanosilver concentration distribution after 10 days at 40 °C in the three simulant: (a) 3% AA; (b) 10% EOH; (c) 95% EOH. Note: for simplicity, only 10 days are shown here for illustration

ethanol was higher than 95% EOH.

According to Table 2, the obtained models are either power or exponential functions. For simulant 3% acetic acid, nancomposite contacted with it and simulant 95% ethanol power function is obtained. For Simulant 10% ethanol and nanocomposite in confronting with it, also nanocomposite contacted with simulant 95% ethanol an exponential function is obtained.

According to Fig. 6 nanosilver particles were distributed, well, uniformly and highly in the 3% AA. Here, Diffusion coefficient showed the importance of its role.

4. Conclusions

This paper describes an experimental-numerical method to evaluate the migration from a nanosilver/polystyrene nanocomposite film. The food simulants were used to assess the effects of storage time, diffusion coefficient and concentration distribution on the migration behaviour.

- nanosilver migration and its diffusion coefficient increased by increasing of storage time
- The concentration of nanosilver in simulants was detectable, but amount of migrated nanosilver from polystyrene nanocomposite into 3% acetic acid solution was higher compared to10% ethanol and 95% ethanol during 10 day storage.
- The diffusion coefficient was directly related to the concentration of silver.
- Among the simulants, the highest diffusion coefficient and the biggest migration rate observed at 3% acetic acid. Diffusion coefficients in the various simulant were as followed: 3% acetic acid > 10% ethanol > 95% ethanol.
- Diffusion coefficient was for nanocomposite contacted with simulants 3% acetic acid > 10% ethanol > 95% ethanol.
- Silver nanoparticles were distributed more uniformed in the 3% acetic acid.
- The predicted models showed various behaviors for liquid and solid phase. Models were obtained either power or exponential functions.

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CC

Nomenclature

3% AA	3% Acetic acid
10% EOH	10% Ethanol
95% EOH	95% Ethanol
C	Concentration of silvermol m^{-3}
C_0	Initial Concentration of nanosilver in nanocompositemol m-^{3}
D	Diffusion coefficient of nanosilver m^2s^{-1}
L	Thickness of nanocomposite cm
W	Width cm
PS	Polystyrene
N	Flow fluxmol m^2/s
R^2	The coefficient of determination
σ	Standard deviation
δ	Relative error

Subscripts

S	simulant
Nc	nanocomposite
ex	experimental
sim	simulated