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Styrene monomer migration from polystyrene based food packaging nanocomposite: Effect of clay and ZnO nanoparticles

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ABSTRACT

Inhibition from migration of plastic ingredients such as styrene monomer (SM) is very important in food packaging industry. Styrene monomer is one of the substances which can potentially migrate from polystyrene based packaging. In the present study, organoclay and zinc oxide nanoparticles (ZnO-NPs) were used for decreasing of the SM migration into food simulants (10 and 50% ethanol (v/v)). A used GC–FID method for measuring of the migrated SM showed good precision and accuracy. Maximum reduction of SM migration into 10% and 50% ethanol (24 h storage at 40 °C) were observed in the polystyrene/nanoclay and polystyrene/ZnO samples, respectively. The SM migration data in 50% ethanol at 5 °C followed from Fickian diffusion law and the lowest diffusion coefficient (2.89×10^{-14} cm^2/s) was observed in the polystyrene/ZnO/nanoclay samples.

1. Introduction

General purpose Polystyrene (GPPS) is one of the most consumable polymer in production of the plastic packaging used in food industry (Gennari et al., 2012). This is due to its good applied properties such as high stiffness, strength, low cost, lightweight and transparency which has been caused to widespread usage in production of disposable containers (Ho et al., 2018).

The styrene monomer (SM) remaining in PS products during the polymerization process, has the potential to migrate into the foodstuff in contact with the packaging material (El-Ziney, 2016a; Gennari et al., 2012).

Styrene was listed as "reasonably anticipated to be a human carcinogen" by the National Toxicology Panel (NTP) (National Toxicology Program, 2011). Therefore, in recent years, there has been enhanced concern about the migration of SM from polystyrene based packaging materials into food stuffs (Hahladakis et al., 2018). The central nervous system (CNS) and the respiratory system are the most sensitive sites in human body to SM (El-Ziney, 2016b; Niaz et al., 2017). Styrene also has a toxic effect on the liver and its toxicity may damage to the cardiovascular system (El-Ziney, 2016b; Niaz et al., 2017). SM is listed in EU Regulation 10/2011 without specific migration limit (SML) (The European Commission, 2011). On the other hand, the FDA regulations give the maximum limits of residual SM in the polymer. The US FDA regulates that the residual SM level in food grade PS intended for non-fatty foods and fatty foods must not be more than 1% (10,000 mg/kg) and 0.5% (5000 mg/kg), respectively (US Food and Drug Administration, 2015).

Migration modelling can be regarded as a valid and reliable tool for prediction of the concentration of migrant under specified contact conditions (Begley et al., 2005; Choi et al., 2005). In the migration model experiments, FSs are used to simplify the analytical systems (Souza and Fernando, 2016; Tawfik and BaAbdullah, 2014; The European Commission, 2011). It is necessary to use both conventional FSs and standardized migration test conditions which are supposed to simulate the migration behavior of migrants from food contact materials (FCMs) into foods that occurs during real-life use (Groh and Muncke, 2017; The European Commission, 1982). The migration of SM from thermoset polyester (Jickells et al., 1993) and polystyrene into various foods and FSs has been well studied (Davies, 2007; El-Ziney, 2016a; Genualdi et al., 2014; Jin et al., 2017; Khaksar and Ghazi-Khansari, 2009; Lickly et al., 1995; Ramesh and Duda, 2001; Reid et al., 1980; Till et al., 1987; Verzera et al., 2010) and diffusion coefficient (D_p) of SM calculated (Lickly et al., 1997, 1995; Murphy et al., 1992; Paraskevopoulou et al., 2012; Snyder and Breder, 1985, 1983; Till et al., 1982; Varner and Breder, 1981). These studies have indicated

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that fat content of food, temperature, FSs type, contact time and sampling methods can affect the magnitude of SM migration.

Currently, possibly the most study on nanotechnology in food technology is related to production of high quality and advanced food packaging such as biodegradable, nano-composite, nano-active and intelligent packaging (Echegoyen and Nerín, 2013). On the other hand, the nanoparticles (NPs) seem to have ability to decrease the migration of monomers and additives from plastic matrix.

The oxo-biodegradable polymers are produced by incorporation of pro-oxidants and photo-catalysts such as zinc oxide nanoparticles (ZnO-NPs) in polymer matrix are one of the new study field of nanotechnology in food packaging sector (Ammala et al., 2011; Bandyopadhyay and Basak, 2007; Nakatani et al., 2015; Nakatani and Miyazaki, 2013). The overall oxo-biodegradation of polymers can be potentially increased by simultaneous use of montmorillonite nanoclay (NC) and a pro-oxidant (Reddy et al., 2009). The clay montmorillonite (MMT) has been extensively studied as nanofiller in food packaging materials mainly to improve thermal, mechanical and gas barrier properties (Duncan, 2011; Gokhale and Lee, 2014; Kuorwel et al., 2015; Maisanaba et al., 2018; Störmer et al., 2017). The organomodification of MMT and production of organoclay (OC), increases its affinity with the less polar polymer such as PS (Maisanaba et al., 2016).

Different methods have been used to determine styrene and other volatile compounds in food and food simulants (Nerin et al., 1998, 1995, 1993). Recent studies in the field of migration of SM from PS to FCMs, focused on more simple, low-cost, rapid, precise and sensitive measurement methods (Moradi et al., 2017), the effect of some processes like recycling on the amount of SM migration (Lin et al., 2017), and the effect of various parameters on the quantity of styrene intake from foods packed in PS package (El-Ziney, 2016a). Studies on the PS/OC and PS/ZnO-NPs nanocomposites have indicated that adding of these NPs to polystyrene matrices can improve their mechanical, barrier and thermal properties (Hooda et al., 2017; Jassim et al., 2016; Kaya et al., 2016; Liu and Xu, 2016; Yang et al., 2014). To the best of our knowledge, no study was found to change the structure of the polystyrene FCMs by nanofiller in order to reduce the amount of SM migration.

The aims of the present study were: (1) to evaluate the potential inhibitory effect of spherical ZnO and platelet-type OC nanoparticles against migration of SM from PS based nanocomposites to FSs (2) to investigate the effect of nanoparticles on the diffusion coefficient of SM in the polymer.

2. Material and methods

2.1. Reagents and standards

The materials used in this study were GPPS (grade 1540), SM (> 99 wt%) both supplied by Tabriz Petrochemicals Industries Co., Tabriz, Iran, and OC, Cloisite® 15A, supplied by Southern Clay Products Co., USA. ZnO-NPs powder (ZnO, > 99% pure, average particle size: 20 nm, and nearly spherical crystal morphology), was purchased from US research nanomaterials Inc., Texas, USA. Standard stock solutions of the SM (1000 mg/L) were prepared in ethanol (SSS_e), hexane (SSS_h) and dichloromethane-methanol solutions (1:2 in volume) (SSS_d). All other chemicals and solvents were purchased from Merck Co., Germany in analytical grade.

2.2. Nanocomposites preparation method

Virgin PS and PS nanocomposite sheets were produced as described in previous work (Abolghasemi Fakhri et al., 2018). Sheets were converted into bowl dishes by thermoforming, for migration test. The samples were placed in intimate contact with each other in an oxygen-barrier plastic wrap immediately after molding, then stored in a freezer at approximately −10 °C (Lehr et al., 1993; Murphy et al., 1992). The freezer storage was for approximately 6 months before use (Lehr et al., 1993). Our previous study showed that the best dispersion quality in ternary nanocomposites, was obtained in the PS/1% ZnO/3.51% C15A system. Thus in this study 1 and 3.51 (wt%) were selected as the amount of the ZnO and C15A nanoparticles, respectively (Abolghasemi Fakhri et al., 2018). The composition and density of nanocomposites are listed in Table 1.

Table 1
The composition and density of polystyrene nanocomposites.

Sample name	PS (wt%)	ZnO-NPs (wt %)	Cloisite® 15A (wt %)	Density (kg/m^3)
Ps	100	0	0	1034.89
PS/ZnO	99	1	0	1059.34
PS/C15A	96.49	0	3.51	1102.12
PS/ZnO/C15A	95.49	1	3.51	1110.26

2.3. Morphological studies by atomic force microscopy (AFM)

The surface topography and roughness parameters of samples were investigated using an atomic force microscopy (Nanosurf Mobile S, Switzerland). The AFM was operated in tapping mode under atmospheric conditions, using a rectangular silicon cantilever (ContAL-G). The arithmetic mean deviation of the roughness profile (profile roughness) or average roughness (R_a) is the arithmetic mean of the height deviations from the profile mean value (Z) and was calculated as:

$$R_a = \frac{\sum_{i=1}^{N} Z_i - \bar{Z}}{N} \quad (1)$$

And

$$\bar{Z} = \sum_{j=1}^{N} \frac{Z_i}{N} \quad (2)$$

Where: Z is arithmetic means of heights (nm), Z_i is the values of all height (nm) and N is number of data points in the profile. The standard deviation of the assessed profile roughness or the root mean square (RMS) of roughness (R_q) is the root of mean square of height deviations from the mean of heights. R_q was calculated as:

$$R_q = \frac{\sum_{i=1}^{N} (Z_i - \bar{Z})^2}{N} \quad (3)$$

2.4. SM measurement

2.4.1. Migration tests conditions

Migration tests were conducted using single sided measurements by filling each PS dish with FS. This method simulates real conditions and avoids from overestimate of SM migration (Genualdi et al., 2014; Lickly et al., 1995; Lin et al., 2017; Linssen et al., 1991; Linssen et al., 1992). Two FSs were used including 10% (v/v) ethanol/water solution (simulant A) and 50% (v/v) ethanol/water solution (simulant D_1) (representing aqueous foods and oil in water emulsions, respectively) according to the (EU) No 10/2011 Regulation (The European Commission, 2016). Three dishes of each sample filled with FSs and covered carefully with aluminum foil, and sealed using adhesive aluminum foil tape, and then time and temperature were set according to the conditions of Commission Regulation (EU) No 10/2011 (The European Commission, 2016).

One of our goals in this study was to measure the amount of SM migration into simulant A and D_1, as aqueous foods and oil in water emulsions, respectively, at ambient temperature (22 °C). Since aqueous foods and oil in water emulsions are not usually kept at ambient temperature for a long time (due to spoilage), and in order to place the

samples in contact with the food simulants in a manner representing the worst of the foreseeable conditions of use at ambient temperature, and on the other hand, considering that for contact time between 6 h and 24 h (6 h < T ≤ 24 h), the test time of 24 h should be used (The European Commission, 2016), the study aimed at determining of migration of SM in the storage period of 24 h at this temperature. According to Commission Regulation (EU) No 10/2011 for contact temperature between 20 and 40 °C (20 °C < T ≤ 40 °C), the test temperature of 40 °C should be used (The European Commission, 2016). Therefore these migration tests were performed at 40 °C for 24 h. The other purpose of this study was to determine the amount of transferred SM into simulant A as aqueous foods at high temperature (around boiling water temperature, ie, 100 °C) during short time storage (5 min < T ≤ 0.5 h) and at low temperatures (refrigerator temperature, ≤ 5 °C) during long time storage (10 days < T ≤ 30 days). According to Commission Regulation (EU) No 10/2011, for contact temperature between 70 and 100 °C (70 °C < T ≤ 100 °C), the test temperature of 100 °C should be used (The European Commission, 2016). Also, according to this regulation, for contact time between 5 min and 0.5 h, the test time of 0.5 h, and for contact time between 10 days and 30 days, the test time of 10 days should be used. Thus the experimental conditions for these two tests were selected as 100 °C for 0.5 h and 5 °C for 10 days. It should be noted that in the present study the transfer of styrene into 10% ethanol solution during long storage time (10 days) at low temperature (5 °C) was studied under stirring conditions during the exposure period. Since migration should mimic the real situation, in this case, the test was considered as "extraction", where stirring is used for shortening the time required for extraction.

The real surface contact was 113 cm^2 and the volume of simulant was 175 ml and the surface to volume ratio was 6.457 cm^2/10 mL simulant. According to the (EU) No 10/2011 Regulation for materials and articles below 500 mL, the contact surface is assumed to be 6 dm^2 per kg food (The European Commission, 2011). The time and temperature conditions are shown in Table 2. After the pre-determined contact periods, 20 ml of the FS was collected from the dish for analysis of SM. Blanks simulants were used as reference and analyzed in the same way.

2.4.2. Extraction of SM from simulants and PS sheet

For measurement of migrated SM, the migrant was extracted from simulants with hexane before GC injection based on previous studies (Choi et al., 2005; Paraskevopoulou et al., 2012). Styrene is very soluble in nonpolar solvents such as hexane (dielectric constant = 1.9) compared to polar solvents such as dichloromethane (dielectric constant = 9.1) (Linssen et al., 1992; Nieh et al., 2003; Rees, 1974; Smallwood, 1996). The detailed procedure is described as follows: A total of 5 mL of n-hexane was added to 20 mL of the FS in a centrifuge tube. The centrifuge tube was closed and the mixture was shaken for 20 min and then was placed for more than 1 h at room temperature in order to phase separation. The upper layer of the hexane fraction was collected and transferred to 5 mL glass vial. 1 μL of the aliquot of the hexane extract was injected into the GC-FID.

A dissolution-precipitation method was used to extract residual SMs from PS samples based on literature methodology (Gennari et al., 2012; Lin et al., 2017). 0.25 g of each PS samples was completely dissolved in 10 mL dichloromethane under slightly shaking and then 20 mL methanol was added to precipitate the polymer. The solution was placed for 1 day and then centrifuged at 4000 rpm for 10 min (6 times) to re-precipitate the polymer. The supernatant clear layer was collected and transferred to gas tight glass vial. This procedure was repeated once again. The clear supernatant was filtered with Millex (PTFE 0.22 μm) and transferred to another gas tight glass vial to analyze by GC-FID. Dichloromethane-methanol solution (blank) was used as reference and analyzed in the same way. All tests were conducted in triplicate and the average of results was reported.

Table 2
The time and temperature conditions used in this study.

Temperature	Time	Food simulant
5 °C	10 days	Simulant A
40 °C	24 h	Simulant A
100 °C	30 min	Simulant A
40 °C	24 h	Simulant D_1

2.4.3. SM determination in simulants and PS sheet

The quantitative analysis of the styrene in migration test samples and residual monomer test samples was carried out by the external standard procedure and was based on peak area of the chromatograms of styrene obtained from the samples and calibration standards.

To establish the calibration curve for migration test performed with ethanol 10% as food simulant, the working standard solutions of the SM were prepared by diluting SSS_e with ethanol 10% solution to a final monomer concentration of 0.02, 0.04, 0.08, 0.16, 0.40, 1.00 and 2.49 μg/mL. The SM was extracted from working standard solutions with hexane before GC injection using exactly the same procedure as migration test samples.

For the quantification of styrene in the migration test performed with ethanol 50% as food simulant, the SSS_e was diluted with ethanol 50% solution. The concentrations of styrene in prepared working standard solutions to establish the calibration curve were 0.02, 0.04, 0.08, 0.16, 0.40, 1.00 and 2.49 μg/mL. The SM was extracted from working standard solutions with hexane before GC injection using exactly the same procedure as migration test samples.

To determine the amount of residual SM in the polymer, the SSS_d was diluted with dichloromethane-methanol solution (1:2 in volume). Six concentrations of 0.50, 0.65, 1.25, 2.49, 4.98 and 9.96 μg/mL were prepared to establish the calibration curve.

All standard solutions were prepared at room temperature and measured at room temperature immediately after preparation. Calibration curves were constructed by linear regression of the peak area against concentration of the calibration standard. Calibration curves were constructed with three replicates.

2.4.4. Gas chromatography conditions

The analysis was performed using a gas chromatograph (PerkinElmer Clarus 500, USA) with a HP-5MS fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 mm film thickness) and FID detector. The detection and injection temperatures were 200 °C. The following temperature program was used: 40 °C for 4 min, then 20 °C/min to 120 °C and held for 3 min, followed by 40 °C/min to 280 °C which was held for 5 min. Samples were injected in splitless mode. Helium and nitrogen were used as carrier gas for migration test and residual SMs extraction test, respectively, both at a constant flow rate of 1.8 mL/min.

2.4.5. Validation

Calibration and linearity, limit of quantification (LOQ), limit of detection (LOD), accuracy and precision were assessed for validation of the methods. The linearity of the responses was investigated by standard solutions with seven and six different concentrations, for migration and residual monomer test, respectively. LOD and LOQ were calculated considering both the sensitivity and the noise in the chromatographic analyses and were defined as the SM concentration which provided a signal equal to 3 and 10 times the noise. The accuracy of the methods was assessed through recovery using three different spiked levels (approximately equivalent to 1, 1.5 and 2 times of the concentration of the SM in each sample) and %recovery was calculated as the percentage between the theoretical concentration and calculated concentration. Precision was evaluated with relative standard deviation (RSD). The RSD was obtained for five replicate determination of 0.08 μg/mL SM and 1.25 μg/mL SM, for migration and residual monomer test, respectively. %RSD was calculated as:

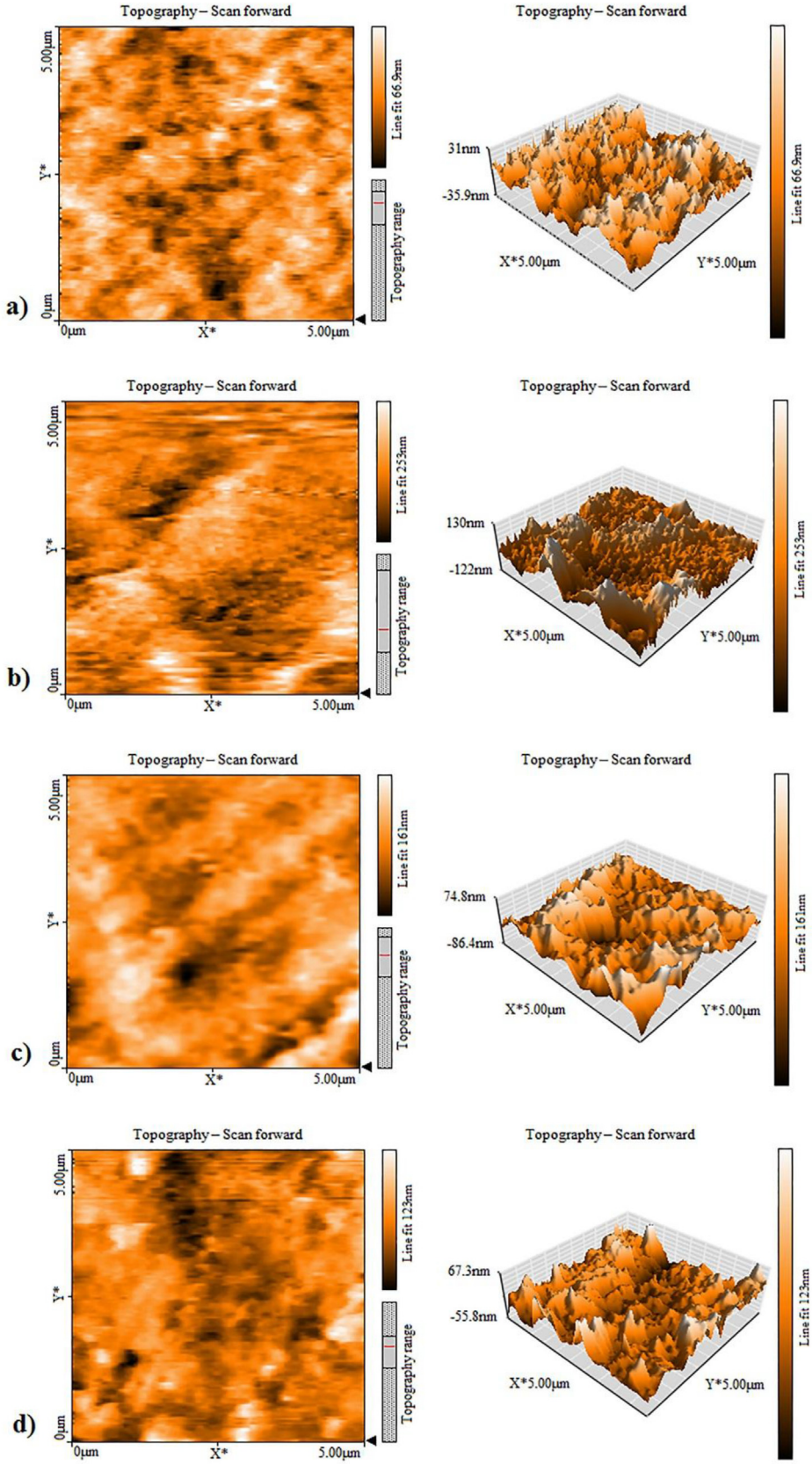

Fig. 1. AFM 2-D image and its corresponding 3-D image of the pristine polystyrene (a), polystyrene/ZnO (b), polystyrene/C15A (c), and polystyrene/ZnO/C15A (d) sheet in a scan area of 5 × 5 µm. *(in color)*. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 3
Roughness parameters of PS and PS nanocomposite sheets.

Sample	R_a (nm)	R_q (nm)
Ps	6.17	7.17
PS/ZnO	21.76	28.61
PS/C15A	17.86	22.43
PS/ZnO/C15A	14.75	19.74

$$RSD = (\text{standard deviation of all values} / \text{mean value}) \times 100 \quad (4)$$

2.5. Migration kinetic of SM

The diffusion of the SM from PS sheets described by mathematical modelling based on Fick's second law. For the one-dimensional diffusion through an infinite plate, Fick's second law of diffusion is commonly expressed as (Lickly et al., 1995; Murphy et al., 1992; Piringer and Baner, 2000):

$$\partial C/\partial t = D\ (\partial^2 C/\partial x^2) \quad (5)$$

Where D (m^2/s) is the diffusion coefficient of the migrant in the plate, C (kg/kg) is the migrant concentration in the plate at position x and time t, x (m) is the thickness of the plate and t (s) is the time.

In the early phase of migration process (for the case of $M_{F,t}/M_{P,0} < 0.6$, where $M_{p,o}$ is the initial amount of migrant in the polymer (mg) and $M_{F,t}$ (mg) is the mass migrates from the P to F at time t (s)), the migration model based on Fick's second law can be used as follows (Chung et al., 2002; Paraskevopoulou et al., 2012):

$$\frac{M_{F,t}}{M_{P,0}} = \frac{2}{L}\left(\frac{D_P t}{\pi}\right)^{0.5} \quad (6)$$

Or

$$M_{F,t} = 2C_{P,0}A\rho_P\left(\frac{D_P t}{\pi}\right)^{0.5} \quad (7)$$

Where subscripts P and F denote the polymer and the FS respectively, $M_{F,t}$ (mg) is the mass migrates from the P to F at time t (s), L (cm) is the thickness of the polymer, A (cm^2) is the contact area with the polymer, C_0 (mg/g) is the initial concentration of the migrant, p (g/cm^3) is the density, D is diffusion coefficient (cm^2/s).

In this case, the D_p can be determined by calculating the slope from the linear relationship between $M_{f,t}/AC_{p,0}$ and $t^{0.5}$. The slope is to be:

$$2\rho_P\left(\frac{D_P}{\pi}\right)^{0.5} \quad (8)$$

The Equation (6) is based on several assumptions, such as the solvent phase is infinite, the partition coefficient is negligible, there are no concentration gradients in the external phase because it is well mixed (Chung et al., 2002; Genualdi et al., 2014; Paraskevopoulou et al., 2012), which are not fully satisfied in test conditions. Nevertheless, this model is often used by researchers (Choi et al., 2005; Lehr et al., 1993; Linssen et al., 1992) to estimate diffusion coefficient of styrene in polystyrene packaging materials. The D_p calculated by applying this equation to the experimental data is understood as apparent diffusion coefficient applicable for the regulatory migration test of food contact materials, which the experimental set-up of this study simulates (Choi et al., 2005).

Four PS samples were subjected to migration testing at 5 °C and five predetermined time intervals (17, 24, 37, 61 and 85 h) and evaluated for their diffusion coefficients (D_ps) in 50% ethanol as FS and the D_ps were calculated using Equation (7). The 50% ethanol (v/v) was used as a FS representing oil in water emulsions (e.g. some milk products), which should be kept at the refrigerator temperature (~4 °C). According to Commission Regulation (EU) No 10/2011 for contact temperature ≤ 5 °C, the test temperature of 5 °C should be used (The European Commission, 2016). The reported value of D_p for each sample is average of three replicates.

2.6. Statistical analysis

Statistics on a completely randomized design were performed with the analysis of variance (ANOVA) procedure in SPSS (Version 22, SPSS Inc., Chicago, IL, USA) software. Duncan's multiple range test was used to detect the presence of significant differences between the analyzed samples. The model was statistically significant with a p-value ≤ 0.05. Statistical analysis for detection of presence of differences between the spiked and found values were performed using Student's t-test with t-critical = 4.3 for n = 3 and P = 0.05.

3. Results and discussion

3.1. Morphological studies by atomic force microscopy (AFM)

Sample surface roughness can affect the amount of SM migration. A rough-textured surface would be expected to have more contact surface area and enhanced SM migration. The two and three-dimensional surface topography and the roughness parameters (R_a and R_q) of the PS based sheets are shows in Fig. 1 and Table 3, respectively. Adding of NPs to PS sheets increased the roughness of their surfaces and the pristine PS and PS/ZnO nanocomposite sheets showed the highest and lowest surface smoothness, respectively (Fig. 1). The R_a and R_q for PS sheets were increased with adding of NPs to the matrix (Table 3). Also the ternary (PS/ZnO/C15A) nanocomposite sheet, has lower roughness compared to binary (PS/ZnO and PS/C15A) nanocomposite sheet (Fig. 1). The R_q and R_a values of the PS/ZnO nanocomposite were decreased when C15A was added to PS/ZnO sheet. Reduction in the surface roughness of ternary nanocomposite can be attributed to the more uniformly dispersion of ZnO-NPs with smaller agglomerates and more exfoliation of the stacks of layered silicate in nanocomposite due to the presence of ZnO and clay simultaneously (Abolghasemi Fakhri et al., 2018).

3.2. Methods validation

The linear ranges, correlation coefficients (R^2), LODs, LOQs, and methods precision for the styrene analyzed on GC are listed in Table 4. High values of R^2 indicated the good linearity of calibration curves. The RSD values suggested the reliability of the present methods for MS detection and indicated good precision of the methods. The recoveries of the spiked SM on the migration test samples (n = 3) and on the residual SMs extraction test samples (n = 3) ranged from 97.27 to 102.16%, and from 98.32 to 104.11%, respectively, indicating good accuracy from the chromatographic system (Table 4). Statistical

Table 4
The linear equations, linear ranges, correlation coefficients (R^2), LODs, LOQs, and methods precision for the SM analyzed on GC-FID.

Sample	Linear equation	Linear range (μg/mL)	Correlation coefficient (R^2)	LOD (μg/mL)	LOQ (μg/mL)	RSD (%)
SM in 10% ethanol	$y = 7825.89x - 109.72$	0.02 to 2.49	0.99986	0.008	0.018	4.7
SM in 50% ethanol	$y = 8076.90x - 137.65$	0.02 to 2.49	0.99961	0.008	0.018	5.8
SM in dichloromethane-methanol solution	$y = 585.11x - 71.82$	0.5–9.96	0.99978	0.063	0.188	7.6

analysis of these results using Student's t-test showed that there are no significant differences between the added and found values (t-Statistic values were less than 4.2). This demonstrated the developed method potentially applicable for the detection of MS in samples. Also the chromatograms of the blanks did not indicate any interference in the retention time (7.1 and 6.8 min for migration and residual SMs extraction test samples, respectively) band of the SM, indicating the solvents quality and the procedure efficiency. These results indicated the suitability of the proposed methods used for migration and extraction experiments.

3.3. Initial residual content of SM in PS samples

Initial concentration of SM was the same for all PS specimens and it was determined as 337.460 ± 56.36 mg/kg. The amount of residual styrene was less than the limit established by the US FDA (2015) (US Food and Drug Administration, 2015).

3.4. Migration of SM into simulants

3.4.1. Effect of FS on the migration of SM

The results obtained from migration tests are reported in Table 5. The maximum amount of styrene migrated from PS samples was observed in simulant D_1 after 24 h storage at 40 °C (0.0175 mg/dm^2).

The effect of the FSs on the migration after 24 h storage at 40 °C is shown in Fig. 2. The quantity of migrated styrene was significantly dependent on the simulant type. The transfer of the monomer to simulant A was considerably lower in comparison with simulant D_1 which could be attributed to higher solubility of SM in ethanol 50% than ethanol 10% solution (Choi et al., 2005). These results agreed with previous studies results which concluded that, the styrene migration in the ethanol solution with higher concentration is more than one with lower concentration (O'Neill et al., 1994; Tawfik and Huyghebaert, 1998; Till et al., 1982).

3.4.2. Temperature effect on the migration of SM

Fig. 3 shows the amounts of migrated SM from sheets into simulant D_1 after 24 h at two different temperatures (5 and 40 °C). All values were significantly ($p \leq 0.05$) increased with increasing of temperature. This is due to increased mobility of the migrant and weakening of monomer/polymer interaction. This results were in agreement with the results of other similar investigations which indicated that SM migration increased at higher temperatures (Choi et al., 2005; Lehr et al., 1993; Lickly et al., 1995; Lin et al., 2017; Linssen et al., 1992; Murphy et al., 1992; Oldring et al., 2014; Paraskevopoulou et al., 2012; Poças et al., 2012; Tawfik and Huyghebaert, 1998; Till et al., 1982). Since in this study SM migration into simulant A was not measured in the same contact time at two different temperatures, effect of temperature on the migration of SM was not discussed in this simulant.

Table 5
Values of SM migration from PS samples into simulant A and D_1 at different time and temperature conditions.

Sample	Simulant	Migration conditions	Amount of styrene migrated (μg/cm^2)*
PS	Simulant A	5 °C, 10 days**	0.139 ± 0.006^a
PS/ZnO	Simulant A	5 °C, 10 days**	0.107 ± 0.006^b
PS/C15A	Simulant A	5 °C, 10 days**	0.074 ± 0.004^c
PS/ZnO/C15A	Simulant A	5 °C, 10 days**	0.055 ± 0.005^d
PS	Simulant A	40 °C, 24 h	0.053 ± 0.003^a
PS/ZnO	Simulant A	40 °C, 24 h	0.047 ± 0.002^b
PS/C15A	Simulant A	40 °C, 24 h	n.d.
PS/ZnO/C15A	Simulant A	40 °C, 24 h	0.033 ± 0.001^c
PS	Simulant A	100 °C, 0.5 h	n.d.
PS/ZnO	Simulant A	100 °C, 0.5 h	n.d.
PS/C15A	Simulant A	100 °C, 0.5 h	n.d.
PS/ZnO/C15A	Simulant A	100 °C, 0.5 h	n.d.
PS	Simulant D_1	40 °C, 24 h	0.175 ± 0.008^a
PS/ZnO	Simulant D_1	40 °C, 24 h	0.084 ± 0.005^d
PS/C15A	Simulant D_1	40 °C, 24 h	0.137 ± 0.007^b
PS/ZnO/C15A	Simulant D_1	40 °C, 24 h	0.102 ± 0.010^c

*Mean of three determinations ± standard deviation (n.d.: not detectable).
**Extraction conditions Means with different letters within a column indicate significant differences ($p \leq 0.05$).

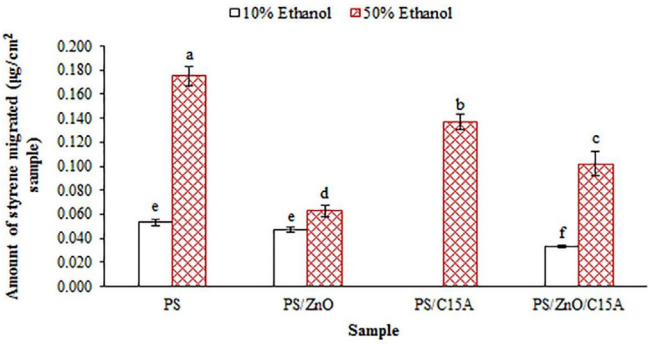

Fig. 2. Effect of FS on the migration of SM from PS samples at 40 °C. *(in color)*. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

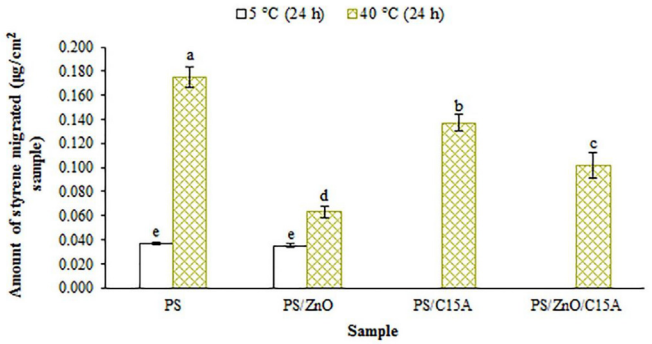

Fig. 3. Temperature effect on the migration of SM from PS samples into simulant D_1. *(in color)*. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

In our study, the SM migration from samples to simulant A after 0.5 h at 100 °C were < 0.018 μg/mL (PS depolymerizes (decomposes) at temperatures of 300 °C and higher (Ademović et al., 2017)). These results were resemble to findings obtained by Gennari et al. (2012) that reported no detection of SM migration from PS into 20% ethanol at 100 °C for 30 min (Gennari et al., 2012). It was attributed to the low initial concentration of SM in specimens, the low solubility of SM in aqueous system, and lower migrated amounts than the LOQ of the used method.

3.4.3. Effect of the nanoparticles on SM migration

Adding of C15A and ZnO-NPs into PS matrix induced a significantly decrease of SM migration in all conditions and time intervals ($p \leq 0.05$) (Table 5).

The lowest SM migration into the simulant A and D_1 at 40 °C (24 h) were related to PS/ZnO and PS/C15A sheets, respectively. In the latter case, the migration level was < 0.018 μg/mL. The presence of ZnO and clay simultaneously in PS/ZnO/C15A sample caused a 60.43% reduction in the transfer of SM from sheet in to simulant A at 5 °C (10 day), compared to pristine PS sheet.

The nanoparticles by influencing various factors such as: sample surface roughness, effective path length for diffusion, simulant/matrix interaction, and monomer/NPs interaction can affect the amount of SM

migration. A rough-textured surface would be expected to have more contact surface area. However, the PS sheet showed the highest migration level among all samples despite having the highest surface smoothness. Therefore, it can be concluded that other factors such as effective path length had a greater effect on SM migration.

The presence of ordered dispersed organic clay (OC) layers or ZnO-NPs with large aspect ratios, create tortuous path in the polymer matrix surrounding the particles and increase the effective path length for styrene diffusion (Llanos and Tadini, 2018; Peretz Damari et al., 2018; Vicente and Gil, 2017). This depends on the types and amounts of nanoparticles used and distribution level of NPs in the polymer (Kasirga et al., 2012). Our previous study indicated that the incorporation of C15A improved the dispersion of ZnO nanoparticles in the General purpose Polystyrene matrix and the presence of zinc oxide nanoparticles in PS/Cloisite 15A matrix caused to more exfoliated structure and smaller OC agglomerates (Abolghasemi Fakhri et al., 2018). Also the pristine PS had a lower density in comparison with all nanocomposites (Table 1), which means there were more pores in its matrix.

Migration is a two-step process: diffusion of the migrant through the polymer bulk phase to the polymer surface and subsequent dissolution of the migrant present at the surface in simulant (Linssen et al., 1991). Very low porosity of the nanocomposites structure may results in decreasing of simulant sorption into the polymer. The presence of polar ZnO-NPs at the PS surface may possibly increase the polarity of the PS surface which result in increased interaction of ethanol 10% with nanocomposite surface at 40 °C. On the other hand, with considering the low-polar nature of the C15A, interaction of the ethanol 50% with nanocomposite surface probably increases in the following order PS/ZnO < PS/ZnO/C15A < PS/C15A. These may lead to an increase in migration level of SM from PS/ZnO into ethanol 10% and from PS/C15A into ethanol 50% at 40 °C. It should be noted that the matrix/simulant interaction increases as the temperature rises and it decreases at low temperature (5 °C).

Another reason for less migration of styrene from nanocomposites could be attributed to limited mobility of styrene in the matrix due to the styrene/NPs interactions. However, for better understanding of mechanisms of nanoparticle effects on migration, a more detailed investigation should be done in further studies.

3.5. Migration kinetic of SM

Recently predictive mathematical modelling has been suggested as an effective and low-cost predicting tools and potential alternative to traditional simulation experiments (Arvanitoyannis and Kotsanopoulos, 2014). Results of single-point-in time migration give only limited information for evaluation of the migration behavior (O'Neill et al., 1994). Taking this into account, in this study a kinetic migration experiment was performed using ethanol 50%. D_p can be estimated by early time migration results before any significant partitioning occurred. It is stated that migration of SM is partition-limited in aqueous simulants, while few partition-limiting effects occur in food oil and that little or no partitioning effects are evident both in the fatty food simulant or in aqueous food simulant over short times of exposure (less than 1 day) (Genualdi et al., 2014; Lickly et al., 1995; Till et al., 1982). Thus, in this study only the early phase of migration process, in which the relationship between $M_{F,t}/C_{p,o}$ and $t^{0.5}$ is linear per eq. (7), was used to calculate D_ps. In our study, the linear region extends to $t^{0.5}$ ($s^{0.5}$) = 553, or 85 h. For this reason, the $M_{F,t}/A$ values were determined at the 85-h exposure time. The plots of $M_{f,t}/AC_{p,0}$ versus $t^{0.5}$ for SM migrating from samples are presented in Fig. 4. These plots indicate a linear relation which corroborate the validity of Equation (7) in Fick's second law. The obtained D_ps are shown in Table 6.

Only 3 points are available in Fig. 4 for PS/C15A and PS/ZnO/C15A. SM migration from these samples into 50% ethanol at 5 °C was not detectable for the first two times. It was attributed to the lower migrated amounts than the LOQ of the used method.

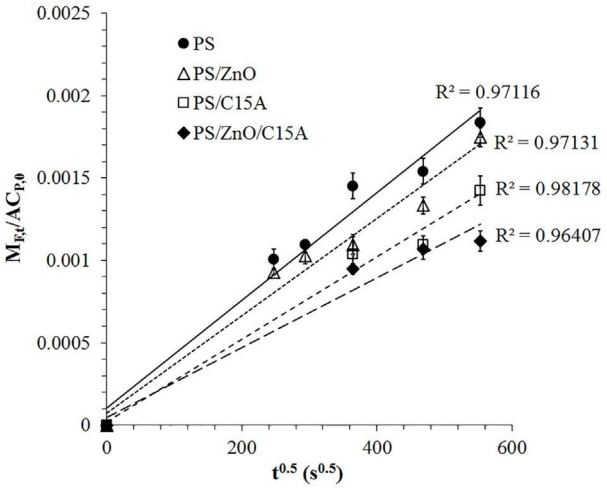

Fig. 4. Plots according to Equation (7) for evaluate the D_p of SM from samples to simulant D_1 at 5 °C. *(black and white)*.

Table 6
Diffusion coefficients for styrene migration from four PS sheets into simulant D_1 at 5 °C.

Sample	Diffusion coefficient (cm^2/s)
Ps	7.84×10^{-14}
PS/ZnO	6.13×10^{-14}
PS/C15A	4.07×10^{-14}
PS/ZnO/C15A	2.89×10^{-14}

Results indicated that diffusion of styrene in the samples decreased with increasing amounts of NPs. Nanoparticles reduced the migration rate and subsequently D_p of styrene molecules in the polymer, likely by creating a high density and low porosity structure of nanocomposites and high effective path length for SM diffusion.

Researchers reported D_p of 1.5×10^{-11} cm^2/s for SM migrating from crystalline PS to 100% ethanol at 40 °C (Snyder and Breder, 1985), and D_p values of 9.08×10^{-11} (at 25 °C) and 9.28×10^{-11} cm^2/s (at 4 °C) for SM migrating from non-expanded PS into 75% ethanol and isooctane, respectively (Paraskevopoulou et al., 2012). Genualdi et al. (2014) found D_p value of 3.11×10^{-10} cm^2/s for SM in GPPS at 40 °C (95% ethanol) (Genualdi et al., 2014). The D_p values of 3.69×10^{-14} (at 40 °C) and 9.96×10^{-15} cm^2/s (at 21 °C) for SM migrating from GPPS to cooking oil and 8% ethanol, respectively, and equivalent D_p values into both simulant at 49 °C ($D_p = 1.9 \times 10^{-13}$ cm^2/s) were obtained by Murphy et al. (1992) (Murphy et al., 1992). Till et al. (1982) obtained D_p values of 1.3×10^{-14} and 1×10^{-13} cm^2/s for styrene migration into water and corn oil, respectively, at 21.11 °C and values of 5×10^{-16} and 7×10^{-15} cm^2/s at 4.44 °C (Till et al., 1982).

The limited D_p data obtained with 50% ethanol did not allow a similar comparison for this FS. However, the D_ps of SM in our study were lower than most of the experimental data that mentioned above and resulted D_p for styrene in PS/C15A and PS/ZnO/C15A nanocomposites is somewhat close to the values obtained by Murphy et al. (1992) for cooking oil at 40 °C and for water at 21 °C reported by Till et al. (1982), respectively.

It should be noted that by utilizing the D_p data obtained from freshly molded samples, the amount of monomer that is predicted to migrate into foods would be the maximum amount that could migrate and, in most cases, would be more than would actually migrate, since during storage time between the production of a food packaging material and its actual use, vapor-phase migration will occur (Ayres et al., 1983; Lehr et al., 1993).

A variety of nanomaterials have been investigated as functional

additives in food packaging to enhance their antimicrobial, mechanical, thermal and other properties (Bumbudsanpharoke and Ko, 2015; Hasheminya et al., 2019, 2018). An important aspect to be considered is the potential for migration of NPs from nanocomposite packaging materials into food products. Some research on migration of nanoclay has been carried out by researchers (Das et al., 2011; Echegoyen et al., 2016; Hong et al., 2008). To ensure the safety of food packaging, safety evaluations and risk assessment are necessary (Chaudhry et al., 2008; Oldring et al., 2014). The safety assessment consists of a sequence of tests, including migration tests, designed to determine whether a substance poses a risk to human health (Cushen et al., 2013). Therefore, the migration testing is very important during the introduction process of a new food packaging material (Cushen et al., 2014). According to the current EU regulation on food contact materials "New technologies that engineer substances in particle size those exhibit chemical and physical properties that significantly differ from those at a larger scale, for example, nanoparticles. These different properties may lead to different toxicological properties and therefore these substances should be assessed on a case-by-case basis by the Authority as regards their risk until more information is known about such new technology" (The European Commission, 2011). In this regard, the montmorillonite clay modified by dimethyldialkyl (C16-C18)ammonium chloride only is authorized to be used up to 12% (w/w) in polyolefins in contact with dry foods to which simulant E (poly (2,6-diphenyl-p-phenylene oxide), particle size 60–80 mesh, pore size 200 nm) at room temperature or below and the sum of the specific migration of 1-chlorohexadecane and 1-chlorooctadecane shall not exceed 0.05 mg/kg food. Furthermore Regulation 10/2011 say "the particles can contain platelets in the nanoform that are only in one dimension thinner than 100 nm. Such platelets shall be oriented parallel to the polymer surface and shall be fully embedded in the polymer" (The European Commission, 2017).

In the present study, our goal was to investigate the effect of NPs with two different shape)spherical and platelet-type particles) and the effect of their simultaneous presence on the migration of SM as a polymeric matrix substance. In our study, simulants A and D1 were selected to measure the migration of styrene monomer from samples in the frame of EU Regulations. It should be noted that nanoparticles are not accepted in the FCMs for direct contact unless they were specifically evaluated and authorized. Current knowledge on the migration of NPs and their effects is limited and therefore further works is needed to fully assess any risks associated with human health and the environment (Kuorwel et al., 2015; Metak et al., 2015; Souza and Fernando, 2016). However, the results of this study could be the basis for future studies that aim to reduce the migration of SM into food packaged in PS based packaging materials. Undoubtedly, future research will be needed so that these additives can be safely used in food packaging systems and perhaps other authorized substances with the same properties could replace the nanoparticles used in this study, and, this study can thus provide an introduction to further studies in this field.

4. Conclusions

In this study, migration of SM from pristine polystyrene and its nanocomposites into 10 and 50% ethanol as food simulants was investigated. The results indicated that the migration of styrene from samples into simulants depends on FS and migration time and temperature condition. NPs could significantly ($p \leq 0.05$) hinder the release of SM, resulting in low SM migration amount of nanocomposites compared to the PS sheet without NPs. Moreover, a mathematical model based on the Fick's second law was validated to predict the extent of migration from the sheets into 50% ethanol under defined contact conditions. Migration was found to follow Fickian diffusion principles. The diffusion coefficient of styrene was estimated and was found to be decreased with NPs content. Further studies can be useful for finding new information on SM migration from PS nanocomposites into other FSs and into real foodstuffs, instead of FS.

Competing interests

The authors declare that there are no competing interests.

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