

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/259542381>

Silicon Migration from High-barrier Coated Multilayer Polymeric Films to Selected Food Simulants after Microwave...

Article in *Packaging Technology and Science* · August 2014

DOI: 10.1002/pts.2055

CITATIONS

5

READS

72

6 authors, including:



Shyam S Sablani

Washington State University

203 PUBLICATIONS 3,518 CITATIONS

[SEE PROFILE](#)



Juming Tang

Washington State University

357 PUBLICATIONS 9,239 CITATIONS

[SEE PROFILE](#)



Jeffrey L Ullman

University of Utah

39 PUBLICATIONS 383 CITATIONS

[SEE PROFILE](#)



Kanishka Bhunia

Washington State University

12 PUBLICATIONS 54 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Phytosanitary measures against quarantine pests [View project](#)



Applying different Electrolyzed water solutions (Acidic and Neutral) for inactivating different pathogenic bacteria in minimally processed foods, RTE products, and fresh produce [View project](#)

Silicon Migration from High-barrier Coated Multilayer Polymeric Films to Selected Food Simulants after Microwave Processing Treatments

By Sumeet Dhawan,¹ Shyam S. Sablani,^{1*} Juming Tang,¹
Gustavo V. Barbosa-Cànovas,¹ Jeffrey L. Ullman^{1,2} and Kanishka Bhunia¹

¹Department of Biological Systems Engineering, Washington State University, 213 L.J. Smith Hall, Pullman, WA 99164, USA

²Agricultural and Biological Engineering, University of Florida, PO Box 110570, Gainesville, FL 32611, USA

The use of microwave (MW) technology for in-package food sterilization and pasteurization has the potential for widespread use in the food industry. Because the use of MW technology requires that food be processed inside its packaging, the interaction between food and its packaging during processing must be studied to ensure package integrity as well as consumer safety. In this study, two commercially available multilayer films developed for retort sterilization were evaluated for their suitability to MW processing. Film A was composed of oriented nylon/coated polyethylene terephthalate/cast polypropylene (CPP); film B consisted of oriented nylon/coated nylon/CPP with overall oxygen transmission rates $<0.2 \text{ cc/m}^2 \cdot \text{day}$. Silicon (Si) was a major component in the coated polyethylene terephthalate layer and food-contact CPP layer. This study evaluated the influence of MW processing on Si migration from films into selected food-simulating liquids (FSLs; water and 3% acetic acid) using inductively coupled plasma-mass spectroscopy, as compared with conventional thermal processing. This study also assessed migration of Si into FSL in terms of process temperature (70–123 °C) and time (18–34 min). A Fourier transform infrared spectrometer was used to evaluate the stability of the silicon–oxygen (Si–O) bonds in the metal-oxide coated and food-contact layer of the packaging film. Overall, there were no significant differences ($p > 0.05$) between the level of Si migration from films to FSL and the stability of Si–O–Si bonds during MW processing as compared with the conventional thermal processing. However, we found that the final processing temperature and time had a significant ($p < 0.05$) impact on Si migration into the FSL. Copyright © 2013 John Wiley & Sons, Ltd.

Received 14 February 2013; Revised 21 May 2013; Accepted 28 October 2013

KEY WORDS: metal-oxide coating; migration; microwave processing; ICP-MS; FTIR

INTRODUCTION

The use of microwave (MW) technology for sterilization and pasteurization of in-packaged, low-acid ($\text{pH} > 4.6$) foods is an advanced thermal method with a much shorter processing time than conventional thermal processes such as retort treatment. MW technology improves the quality of processed foods and may help meet increasing consumer demand for high quality, shelf-stable products.¹ Several MW systems for sterilization of in-packaged foods have been commercialized in Europe and Japan.² In the United States, the Advanced Thermal Processing Research Team at Washington State University developed a 915-MHz, single-mode MW sterilization system for processing in-packaged foods.³ This research team received US Food and Drug Administration acceptance for a petition to preserve a

*Correspondence to: S. S. Sablani, Department of Biological Systems Engineering, Washington State University, 213 L.J. Smith Hall, Pullman, WA 99164, USA.
E-mail: ssablani@wsu.edu

homogenous, low-acid food using the MW sterilization system in October, 2009. The acceptance of this petition was followed in December, 2010 by the acceptance of a second petition to preserve non-homogeneous foods using the MW sterilization system technology.⁴ Currently, the MW technology is being researched for pasteurization of multi-component foods with enhanced physical and quality attributes.⁵

Microwave processing is a promising preservation technology that is predicted to gain widespread use in the commercial food industry.⁶ The first commercial MW-assisted thermal sterilization unit has been rolled out and is currently being operated on a trial basis by the US food company, AmeriQual, at one of their facilities.⁷ However, during in-package MW pasteurization and sterilization, packaging material is exposed to temperature and radiation that may alter the mechanical and mass transfer (barrier and migration) properties of the packaging structure.⁸ Therefore, research on the interaction between packaging material and MW processing during sterilization and pasteurization is essential to ensure consumer safety. Selecting appropriate packaging materials will not only help extend the shelf-life of foods but also ensure minimum chemical and additive migration in the processed foods.^{9,10}

The last decade has seen a sharp increase in new multilayer, polymeric-based packaging materials with a desirable gas barrier and mechanical properties for thermal sterilization applications. To further improve gas barrier properties, the industry has developed silicon (Si) and aluminium (Al) metal-oxide coated, high-barrier multilayer polymeric films to withstand thermal sterilization treatment. Such films are now commercially available. In addition, polyolefin layers, which function as a food-contact and sealant layer in multilayer, polymeric films, contain various classes of additives, such as antioxidants, antistatic, anti-block and slip agents to improve their functionality and fabrication process.¹¹ Anti-block agents help minimize adhesion between the different polymeric layers, and thus improve the processability of multilayer films. Different types of anti-block additives include synthetic silica, zeolites, natural silica and talc, which contain the metal Si in various forms.¹² Quantifying silicon and aluminium particles' migration from packaging materials into food-simulating liquids (FSLs) after thermal processing is one means of determining the migration of coating particles and additives into real food systems.

Migrating additives and metals can compromise the sensory quality of foods and increase the toxic substances in packaged products. Therefore, it is imperative to food safety that researchers examine the influence of thermal food processes on the migration tendencies of metals and additives.^{13,14} The migration tendencies of metals such as silicon and aluminium can be established by applying a popular analytical technique for elemental analysis, known as inductively coupled plasma-mass spectrometry (ICP-MS). This technique has a high sensitivity, in the range of parts per billion (ppb) levels.

Snyder and Breder¹⁵ developed a migration cell for evaluation of two-sided migration of plastic food packaging components such as polymeric additives, as well as chemical contaminants such as antioxidants, ultraviolet absorbers and monomers into various FSLs. In their study, plastic food packaging materials such as polystyrene were stacked in discs on a copper wire and placed in migration cells filled with an FSL. Small volumes of aliquots were withdrawn from the cell at regular intervals, which enabled quantitative analysis of the migrant components. However, this type of migration cell cannot be used to study the migration of coating and additives from flexible polymeric pouches during thermal processing, because of the inability to simulate thermal process conditions and study in situ process-package interaction. Therefore, in our study, we developed a test cell that can be placed in an oil bath for studying chemical or metal migration from polymeric pouches to FSL under a wide range of thermal processing conditions.

Migration from polymeric pouches during MW processing under controlled temperature-time process conditions can also be established using a single-mode lab scale MW digestion system to represent closely the industrial scale MW processing system. Several studies have been conducted to compare the migration of additives from polymer packaging with food during domestic MW heating and conventional heating. Studies by Alin and Hakkarainen¹³ and Jeon *et al.*¹⁶ showed no significant MW-induced, non-thermal effects of increasing migration of additives into different FSL. However, a third study showed significantly higher overall migration from poly(vinyl chloride) during domestic MW heating compared with conventional heating.¹⁷ Much of the migration research related to MW heating has concentrated on domestic MW heating as compared with industrial MW heating. Little research has been conducted to develop a methodology for studying the migration of additives from

packaging material into food during industrial MW pasteurization and sterilization. Therefore, this study aims to ensure the safety of MW-based industrial processes.

Microwave processing has significantly less effect on the gas barrier property of multilayer polymeric packaging films and lidstocks than the conventional retort process for the same level of sterilization.^{8,18} This implies that the reduced overall MW processing time compared with conventional retorting plays a role in reducing the deterioration of the gas barrier layer in the packaging film after thermal treatment. However, to the best of our knowledge, no experimental research has explored the impact of MW pasteurization and sterilization processing conditions on the migration of coating particles from high-barrier coated multilayer polymeric packages to food as compared with conventional retort processes. Studies of this nature would provide valuable information on the possibility of adopting commercially available conventional retort packaging materials to industrial MW processes and help ensure food safety.

Thus, the objectives of this work are (a) to develop a methodology for examining migration of Si and Al from multilayer polymeric pouches to FSL after MW and conventional thermal processing; (b) to determine the influence of MW pasteurization and sterilization treatments on the migration of Si from metal-oxide coated multilayer polymeric films to FSL compared with conventional heating; and (c) to explore the stability of coating particles and additives in metal-oxide coated, multilayer food packaging materials as an influence of MW process conditions compared with conventional heating.

MATERIALS AND METHODS

Migration test cell

An aluminium test cell was designed and fabricated for use in migration studies from flexible multilayer polymeric pouches to FSL during conventional retort thermal processing. Retort parameters were simulated by placing the cell in an oil bath, set at the operating temperature of conventional heating process, to achieve the target sterilization level.

Design criteria

A detailed schematic diagram for the design of the cell is shown in Figure 1. The design was guided by the following criteria:

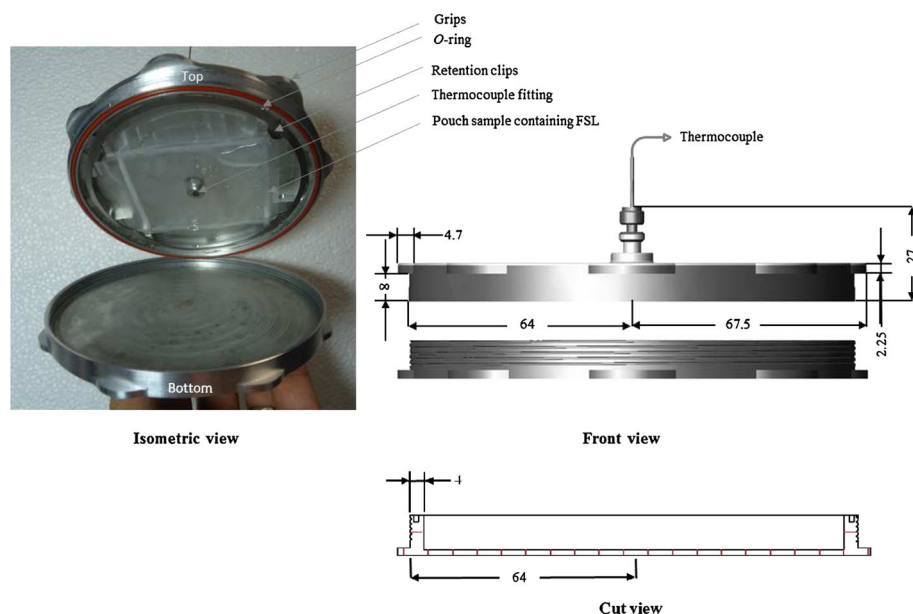


Figure 1. Picture and schematic diagram of migration test cell. Dimensions shown are in millimeter.

- Simulate a come-up time (CUT; the time required for the FSL in the pouch to reach the target process temperature) similar to that required by flexible pouches under commercial process conditions for conventional thermal processing.^{19,20}
- Incorporate a thermocouple to measure the temperature of the FSL accurately at the half depth of the pouch to ensure good contact with the food medium.
- Hold flexible multilayer polymeric pouches of dimensions 3×2.25 in. containing 13.5 ml of FSLs. Overall, the simulant volume-to-surface area of the pouch was not less than 2 g/in^2 , to prevent the possibility of low solubility of migrant particles in the FSL. This prevents the underestimation of migration, a limitation set by US Food and Drug Administration²¹ for a chemical migration study.
- Allow simulation of pasteurization and sterilization temperature-time process conditions.

The top part of the test cell is composed of a retention clip for clamping the multilayer, polymeric pouch in the cell. The top portion of the cell also includes a screw cap closure, through which a 0.032 in. type T thermocouple (Omega Inc., Stamford, CT, USA) is inserted for monitoring the temperature of the FSL in the pouch. Once the CUT is calculated for the FSL, experiments are carried out in similar cells without the thermocouple attachment. The bottom and top portions of the cell are opened and closed along machine lines. An O-ring in the top portion of the cell helps ensure a hermetic seal of the migration cell (Figure 1).

Metal-oxide coated multilayer polymeric films

This study evaluated two high gas barrier, multilayer films fabricated by the EVAL Co. of America (Houston, TX, USA). Film A was laminated and composed of an outer layer of $15 \mu\text{m}$ of oriented nylon (ON), a middle layer of $12 \mu\text{m}$ of polyethylene terephthalate (PET) containing metal-oxide coating on either side of PET and an inner layer of $70 \mu\text{m}$ of cast polypropylene (CPP) that directly contacts the food surface. Film A is also known as ON//coated PET//CPP. Film B was also laminated and consists of a middle layer of $15 \mu\text{m}$ of nylon coated with metal-oxide on either side of the nylon layer, sandwiched between an outer layer of $15 \mu\text{m}$ of ON and an inner layer of $50 \mu\text{m}$ of CPP. Film B is denoted as ON//coated nylon//CPP. The coating applied to improve the gas barrier properties of the functional barrier polymer layer (polymer layer that is responsible for gas barrier properties) usually consists of inorganic, metal-oxide coating particles.

Characterization of the metal-oxide coated multilayer polymeric film

Silicon concentration in both of the multilayer polymeric films A and B containing FSL was analysed before and after processing by MW digestion coupled with ICP-MS. A Discover SP-D CEM MW system (CEM Corporation, Matthews, NC, USA) was used for multilayer polymeric film digestion. Before and after thermal processing, dry film samples (0.05 g) of 1 in^2 surface area were weighed into a 35 ml quartz test cell, and 5 ml of nitric acid (HNO_3) (69–70% reagent grade, Mallinckrodt Baker Inc., Phillipsburg, NJ, USA) was added. The following programme was used for digestion: the temperature was raised to 220°C in 5 min and held for 6 min. After cooling to ambient temperature in 3 min, the digested solution was diluted with Milli-Q water (Millipore Corporation, Billerica, MA, USA) to 25 ml and analysed by ICP-MS.

Food simulants

Water was used to simulate aqueous foods and was prepared by passing distilled water through Milli-Q water purification system (Millipore Corporation, Billerica, MA, USA). Aqueous acetic acid (3%) (w/v) (reagent grade, J.T. Baker, Mansfield, MA, USA) having a density of 1.05 g/cm^3 was used to simulate low-acid foods, on the basis of the US Food and Drug Administration recommendation.²¹ Thirty grammes of acetic acid was weighed accurately and made up to 1000 ml with Milli-Q water in a volumetric flask to give 3% (w/v) aqueous acetic acid. Similar food simulants are also approved by the European Commission for migration analysis of plastic packaging constituents, which come in contact with foodstuffs.²²

Thermal treatment

Conventional heating. Flexible pouches with dimensions of 3 in. \times 2.25 in. were prepared from each of the films discussed earlier. These pouches were then filled with 13.5 ml FSL, for an overall volume-to-specimen surface area of 2 ml/in². Pouches were sealed with a minimum headspace using an impulse sealer (MP-12; J. J. Elmer Corporation, St. Louis, MO, USA) with a 4 s dwell time. To study migration during conventional thermal sterilization conditions, the pouches containing FSL were placed in migration test cells and heated to sterilization temperature (121 °C) in an oil bath (HAAKE W15, Thermo Electron Corporation, Waltham, MA, USA) using fisher bath oil (Fisher Scientific, Hanover Park, IL, USA) as a heating medium. The two FSLs had CUT of 5 min to reach the sterilization temperature that was measured using a 0.032 in. type T thermocouple (Omega Inc., Stamford, CT, USA). The thermocouple was incorporated in the cell to accurately measure the temperature of the FSL at a position at the half depth of the pouch. The migration cells were heated for 40 min at 121 °C (CH1) to simulate industrial sterilization schedules for conventional thermal retorting for single meal-sized pouches containing low-acid foods. The process condition represents the level of sterilization at the cold location of single meal pouches close to $F_0 = 6$ min, which is generally used for commercial retail markets.¹⁸ Once heating was complete, the migration test cell was removed from the oil bath and immediately cooled in a tray containing ice/water mixture. The pouches were removed from the cell, and the FSL was collected for migration studies.

Microwave heating. Flexible pouches with dimensions of 2.5 in. \times 2 in. were prepared from each of the films discussed earlier and filled with 10 ml FSL to have an overall volume-to-specimen surface area of 2 ml/in². A Discover SP-D CEM MW system (CEM Corporation, Matthews, NC, USA) was used to simulate the four processing periods of MW-assisted thermal sterilization, namely pre-heating, MW heating, holding at target temperature and cooling.²³ The Discover SP-D CEM MW system has a 35 ml quartz test cell with a maximum working volume of 25 ml, which was utilized to process the flexible pouches containing FSL in a water medium (Figure 2). Temperatures of the test cell were continuously monitored during processing using an infrared sensor, which was calibrated using a fibre optic temperature probe to increase accuracy. The time-temperature combination for CEM-based MW process was selected to match closely with the commercial sterilization and pasteurization schedules for single meal-sized pouches containing low-acid foods. This created a fair comparison of the packaging-food interaction during MW heating with the conventional heating process.^{23,24} Details of the various treatments are outlined in Table 1. After heating, air at ambient temperature was allowed to pass through the system to cool the MW cell containing the test pouch to ambient temperature. Figure 3 shows representative temperature-time profile during conventional (CH1) and MW (MW1)

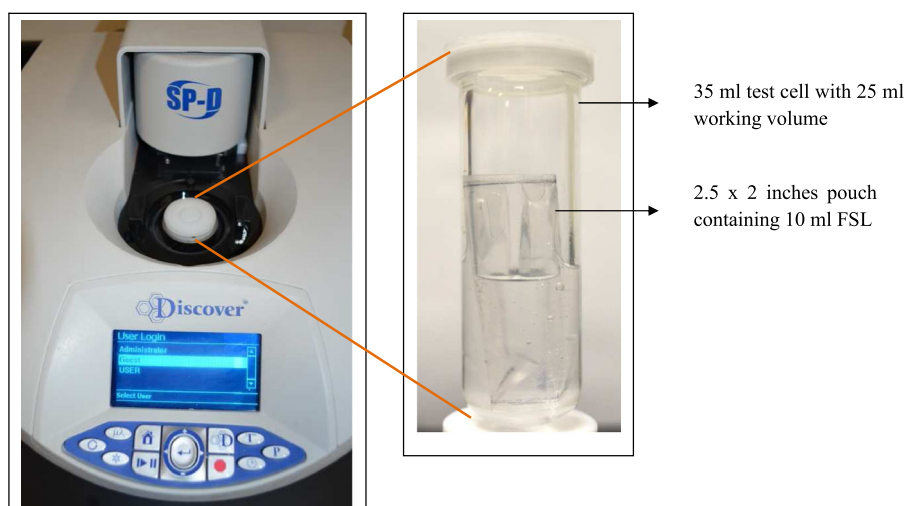


Figure 2. Picture of the test cell in the CEM microwave system containing the flexible pouch with FSL. Pouch samples are completely submerged in water in the test cell during processing.

Table 1. Microwave processing conditions used in the current study.

Treatment	Stage						
	Preheating from 25 °C			Processing at target temperature			Total time (min)
	End temperature (°C)	Ramp time (min)	Hold time (min)	Temperature (°C)	Ramp time (min)	Hold time (min)	
MW1	70	9	1	123	4	4	18
MW2	50	9	1	90	4	4	18
MW3	50	9	1	70	4	4	18
MW4	70	9	1	123	12	12	34
MW5	50	9	1	90	12	12	34
MW6	50	9	1	70	12	12	34

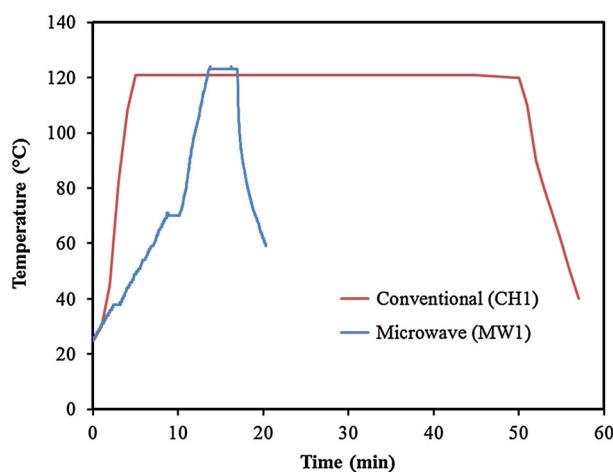


Figure 3. Representative temperature-time profile during conventional (CH1) and microwave (MW1) heating.

heating for the same level of sterilization at the cold location of single meal pouches close to $F_0=6$ min. FSL collected from the pouch was utilized to quantify the level of migration.

Inductively coupled plasma-mass spectrometry

The elemental analysis of the FSL in the thermally processed, flexible polymeric pouches was performed using an ICP-MS method. ICP-MS (Agilent 7500cx system, Agilent Technologies, Santa Clara, CA, USA) equipped with a double bypass quartz spray chamber and a concentric quartz nebulizer was used to analyse the migration of metals in FSL, with argon used as the carrier gas. ICP-MS operating conditions were plasma operated at a power of 1600 W; flow conditions of the argon gas were 15 L/min plasma gas, 1 L/min auxiliary gas, 0.9 L/min nebulization gas and 0.25 L/min make-up gas. A full quantitative method was utilized in the ICP-MS system for measuring the Al and Si concentrations in the FSL.²⁶

Quantitative analysis was conducted, on the basis of a calibration curve developed with the Si and Al AccuTrace reference standards (AccuStandard, New Haven, CT, USA). For analysing the metal concentration in water as FSL, eight standard solutions with concentrations of 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 5.0 and 10.0 µg/ml were obtained by diluting the stock standard solution (1000 µg/ml) with 2% HNO₃. The responses were linear over the concentration ranges, with a correlation coefficient greater than 0.995 for both Si and Al. On the other hand, while analysing metal concentration in 3% acetic acid as FSL, the standard solutions were obtained by diluting the stock solution in 3% acetic acid to

avoid any potential effect of matrix (extract that can increase or decrease the analyte signal). Correlation coefficients of 1.000 and 0.997 were obtained for the Si and Al calibration standard solutions prepared in 3% acetic acid, respectively. All FSL sample studies for migration were quantified against these calibration curves. After processing, 2% HNO₃ was added to the aqueous FSL (water) to attain the same acidic concentration for accurate comparison with the calibration curve. Furthermore, collision reaction cell technology in the Agilent ICP-MS was used to reduce the potential polyatomic interferences that ²⁸Si suffers from 2% HNO₃. The use of glassware was avoided during preparation of samples to minimize the influence of dissolution of Si from the glassware. Food simulant blanks were prepared by keeping the FSL in contact with the unprocessed polymer pouch for a similar duration of time as that of the thermal process. All measurements were carried out in triplicate, in which each measurement included analysis of the FSL from an individually processed pouch and subtracted from the blank values. Limit of detection and limit of quantification for the instrument were set at three and ten times the standard deviation of the signal for blank measurement, respectively. In this study, the limit of detection and limit of quantification were 10 and 30 ppb, respectively. Recovery and repeatability of the method was verified by placing blanks and two samples of known concentration levels after every ten measurements. This helped establish the quality assurance and accuracy of the method.

Fourier transform infrared-attenuated total reflectance spectroscopy

Fourier transform infrared (FTIR) spectroscopy was applied to investigate the influence of thermal processing on the surface characteristics of the multilayer polymeric films with 3% acetic acid as the FSL. FTIR spectra of the polymeric films were recorded using a germanium 45° attenuated total reflectance (ATR) crystal on a Shimadzu IR Prestige 21 FTIR spectrometer (Shimadzu Corporation, Kyoto, Japan) equipped with KBr beam splitter and a deuterated L-alanine doped triglycene sulfate detector. The spectra were collected over the wave number range of 4000–800 cm⁻¹ by accumulating 64 scans at a resolution of 4 cm⁻¹ to study the stability of the silicon–oxygen (Si–O) bonds in the food-contact layer (polypropylene) and the metal-oxide coated layers of the two multilayer films (PET for film A; nylon for film B). However, because the analysis was performed in reflection mode, only the surface in contact with the crystal was characterized, because the wave protrudes less than 0.7 microns. To enable the characterization of the coated PET and nylon layers, separate films were fabricated with the coated polymeric layers on the surface (coated PET//ON//CPP; coated nylon//CPP). These two films with coated layers on the surface were processed at selected conditions (see profiles in Figure 3, CH1 and MW1) and analysed for the stability of the metal-oxide coating. All spectra pre-treatments were performed using Omnic v8 (Thermo Fisher Scientific, Madison, WI, USA). Processing included baseline correction, ATR correction, smoothing and normalization on the specific band of the polymer matrix. All experiments were performed in triplicate, and results are displayed as the mean value of measurements.

Data analysis

The metal migration data for the two films before and after thermal processing were examined using a completely randomized design. Data were analysed using the general linear model, and significant differences ($p < \alpha$) in metal concentration at various temperature and time treatments were determined with Fisher's least significant difference test ($\alpha = 0.05$). Data analysis was conducted with statistical software SAS version 9.2 (SAS Inst. Inc., Cary, NC, USA).

RESULTS AND DISCUSSION

Film characterization

The proposed method of MW digestion coupled with ICP-MS was applied to analyse the two films for their silicon and aluminium concentrations before and after thermal processing. Pouches containing FSL were made from the two films and subjected to the MW (MW1) and conventional (CH1) thermal processing applications. After processing, the FSL was removed, and the film was dried and MW

digested before analysing the films for Si concentration using ICP-MS. The concentration of Si in film A decreased from 64.5 ± 2.1 to $63 \pm 3.0 \mu\text{g/in}^2$ film after the MW treatment, whereas in the retort treatment, the concentration of Si in film A decreased to $61 \pm 2.6 \mu\text{g/in}^2$ film. The Si concentration for film B decreased from 61 ± 3.1 to $47 \pm 0.6 \mu\text{g/in}^2$ film after the MW treatment and $52 \pm 6.8 \mu\text{g/in}^2$ film after the retort one. The decrease in the average Si concentration after the two thermal treatments indicates a dissociation of Si from the metal-oxide coated multilayer polymeric packaging films. The diffusion coefficient of coated PET present in film A could be lesser than that of coated nylon in film B leading to the lesser Si migration from film A compared with film B. However, there was no significant difference ($p > 0.05$) in the final Si concentration between the conventional and MW thermal process for both films A and B. The concentrations of Al in both films were found to be below 10 ppb, the detection limit of the analytical instrument employed in this study. MW heating did not induce any additional Si migration compared with conventional heating.

Migration study

The amount of Si and Al migrating into the FSL from the polymeric pouches during thermal processing was quantified to assess the effect of conventional heating versus MW processing on migration of break-down products of additive and metal-oxide coating particles. However, the concentrations of Al were found to be below 10 ppb, the detection limit (three times the standard deviation of the signal for blank measurement) of the ICP-MS employed in the study, and hence, only concentration of Si in the FSL was reported in this section to describe the migration of additives and metal-oxide coating constituents into food. Additionally, the influence of final MW process temperature and MW processing times on the Si migration in water were also evaluated.

Effect of type of thermal process

The effect of MW treatment (MW1) on the migration of Si from films A and B into the two FSL was assessed and compared with conventional heating (CH1). The processing conditions for MW1 and CH1 closely match the temperature-time combinations required for similar level of sterilization of single meal-sized pouches or trays containing low-acid foods.^{23,25} Table 2 reports the values for Si migration from both of the films into water and into 3% acetic acid after the two processes. Blank values of 0.04 and 0.02 mg/Kg for water and 3% acetic acid as FSL, respectively, were subtracted to attain the final Si migration concentration. In both FSLs, there was no significant difference ($p > 0.05$) in the amount of Si migration from the two films when processed with MWs compared with conventional heating for the same level of sterilization. Thus, MW processing had no significant non-thermal influence on Si migration.

Regarding FSL, the Si migration was higher in water compared with 3% acetic acid for films A and B processed with both MW and conventional thermal processes. The higher Si migration in water could be attributed to the increase in solubility of Si in water at higher temperatures. Table 2 shows no significant difference ($p > 0.05$) in Si migration between films A and B in both of the FSLs after thermal processing, with and without MW application. Therefore, there was substantial alteration between PET and nylon as a functional barrier layer (the polymer layer responsible for gas barrier properties) in terms of Si migration.

Table 2. Concentration (mg/kg FSL) of silicon migrated from films A (ON//coated PET//CPP) and B (ON//coated nylon//CPP) to FSL during MW1 and CH1 treatments.

Film	FSL	Process	
		Conventional heating	Microwave
A	Water	0.92 ± 0.18^a	1.05 ± 0.17^a
	3% Acetic acid	0.55 ± 0.03^a	0.60 ± 0.05^a
B	Water	1.25 ± 0.12^a	1.07 ± 0.04^a
	3% Acetic acid	0.60 ± 0.03^a	0.51 ± 0.03^a

Values are means \pm standard deviation

^aMeans with same letter is not significantly different ($p > 0.05$).

Regarding food regulation, there are no established limits on the migration of metal-oxide coating particles and metals from additives such as anti-block agents. Previous studies on migration of clay minerals present in packaging material to food in terms of Al and Si concentrations suggest that the migration limit of such metals is close to 9 mg/kg of food, on the basis of an opinion by European Food Safety Authority.²⁶ However, the highest value of Si migration obtained in this study was significantly less than the suggested limit.

Effect of microwave process temperature

The effect of final MW process temperature on the migration of Si from the two films into water is illustrated in Figure 4. The process temperatures were chosen to represent sterilization (MW1) and pasteurization (MW2 and MW3) conditions. An increase in MW process temperature from 70 to 123 °C led to a significant increase ($p < 0.05$) in Si migration into water for the two films. At 70 °C, the amount of Si migration from films A to B into water was 0.10 and 0.12 mg/Kg, respectively. There was a 3.5-fold and 10-fold increase in levels of Si migration from film A, when the temperature was increased from 70 °C to 90 °C and 123 °C, respectively. On the other hand, Si migration for film B increased by nearly four times and nine times to a concentration level of 0.46 and 1.07 mg/Kg as the temperature was increased from 70 °C to 90 °C and 123 °C, respectively. These observations suggest that the level of Si migration is strongly dependent on the final treatment temperatures. Temperatures close to sterilization process conditions could cause metal-oxide coating particles and additives in the coated layer and food-contact layer, respectively, to undergo physicochemical modifications, possibly leading to their migration into the FSL.

Effect of microwave process time

Results for migration of Si into water during MW processing under two time periods for films A and B are shown in Figures 5 and 6, respectively. MW1, MW2 and MW3 underwent a total processing time of 18 min, while MW4, MW5 and MW6 underwent a total processing time of 34 min at the three process temperatures (Table 1) to elucidate the influence of increased holding time at the final processing temperature. For film A, there was a significant increase ($p < 0.05$) in Si migration when the total processing time was increased from 18 to 34 min at 70 and 90 °C. However, the increase in processing time did not lead to a significant increase ($p > 0.05$) in migration at 123 °C for film A (Figure 5). On the other hand, for film B, there was a significant increase ($p < 0.05$) in Si migration at all three processing temperatures, when total processing time increased from 18 to 34 min (Figure 6). It is notable that the

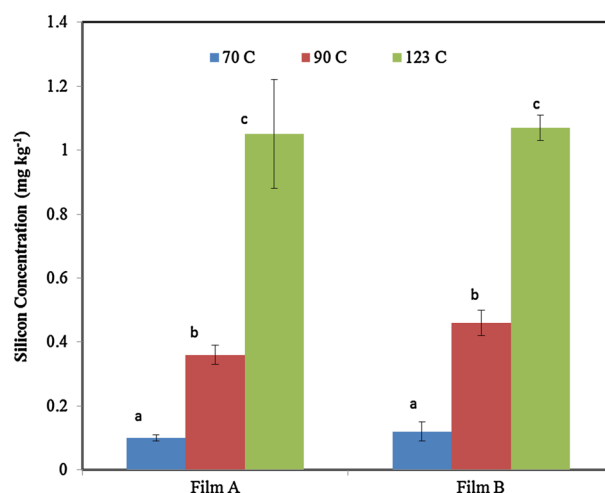


Figure 4. Silicon migration (mg/kg FSL) from the two films to aqueous FSL as an influence of MW process temperature for a total processing time of 18 min (MW1 treatment). Mean values with different letters are significantly different ($p < 0.05$).

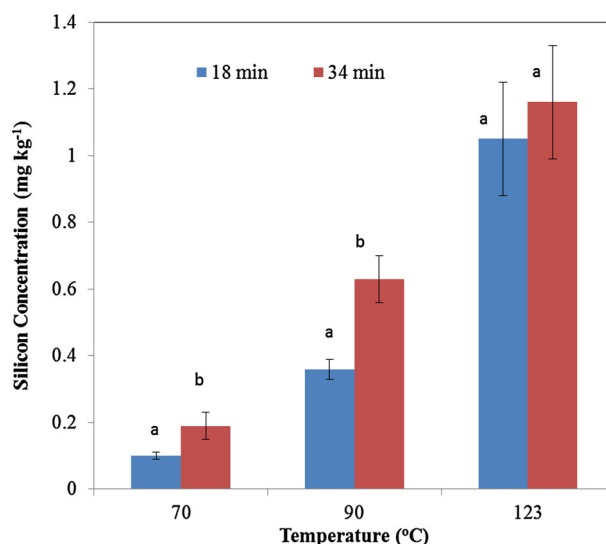


Figure 5. Silicon migration (mg/kg FSL) from the film A to aqueous FSL as an influence of MW process time. Mean values of three replicates with different letters are significantly different ($p < 0.05$).

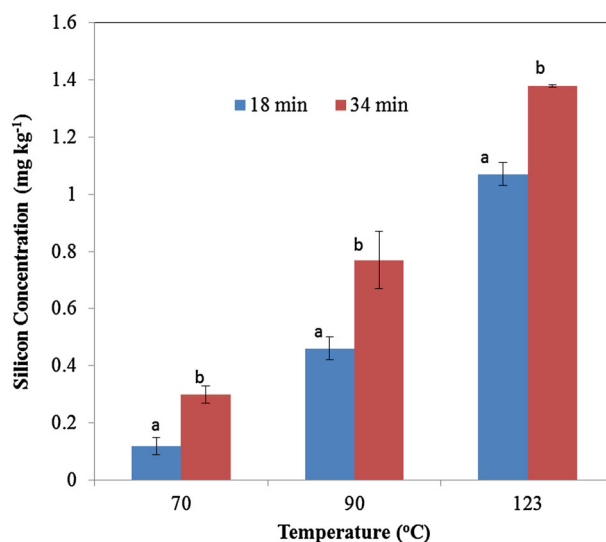


Figure 6. Silicon migration (mg/kg FSL) from the film B to aqueous FSL as an influence of MW process time. Mean values of three replicates with different letters are significantly different ($p < 0.05$).

percentage increased in migration at 123 °C was 10% and 29%, when processing time was increased for films A and B, respectively. On the other hand, increasing processing time at pasteurization temperatures (70 and 90 °C) led to 68% more Si migration for both films. Hence, the influence of total processing time on the migration of Si to water for film A was found to be less at sterilization temperatures compared with that at pasteurization temperatures. Contrary, for film B, the total processing time had a significant influence on migration of Si at both pasteurization and sterilization temperatures.

Fourier transform infrared-attenuated total reflectance spectroscopy

To explore the influence of MW (MW1) and conventional (CH1) thermal processing on the chemical structure of the silicon–oxide bonds present in the metal–oxide coated barrier layer and the food-contact

layer of films A, corresponding FTIR spectra in the $800\text{--}1300\text{ cm}^{-1}$ range are compared in Figure 7a and b, respectively. The characteristic bonds of interest to the study of silica bond stability in the metal-oxide coated layer and the additives in the food-contact layer include the Si–O–Si stretching ($1050\text{--}1300\text{ cm}^{-1}$) and Si–O stretching ($800\text{--}1050\text{ cm}^{-1}$).²⁷ Figure 7a illustrates the small decrease in the absorption of the peaks at 972 , 997 and 1167 cm^{-1} in the metal-oxide coated layer of film A after both MW and conventional heat treatment. This decrease in absorption suggests that thermal treatment altered both the Si–O–Si and Si–O stretching bonds in the metal-oxide coated polymer layer, which could lead to loss of stability in the coating particles. On the other hand, the spectra from the food-contact side of film A reveal a slight broadening of the peaks at 1200 and 1265 cm^{-1} after thermal treatment, implying instability in the Si–O–Si stretching bond present in the additives in the food-contact polymer layer (Figure 7b). In a previous study, broadening of absorption bands corresponding to Si–O stretching was used to explain the distortion of tetrahedral sheets present in the montmorillonite structures.²⁸ Therefore, the minor chemical modifications discussed earlier in the metal-oxide coated barrier layer and the food-contact layer may explain the small concentrations of Si migration from the food packaging film into the FSL after thermal processing.

In the case of film B, the FTIR-ATR results for the coated polymeric layer revealed insignificant changes at 1167 cm^{-1} (Figure 8a) after thermal treatment. Also, the spectra for the food-contact layer of film B illustrates a slight broadening of the peak at 1200 and 1265 cm^{-1} after thermal treatment,

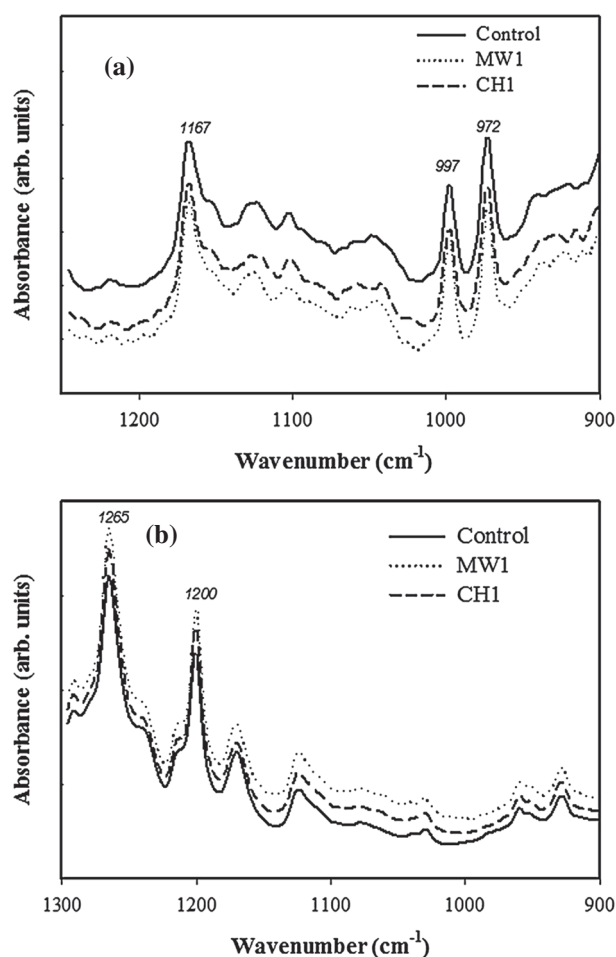


Figure 7. FTIR-ATR spectra of film A. (a) Coated metal-oxide layer before (control) and after MW1 and CH1 treatments. (b) Food-contact layer before (control) and after MW1 and CH1 treatments. Spectrum represents average of three replicates.

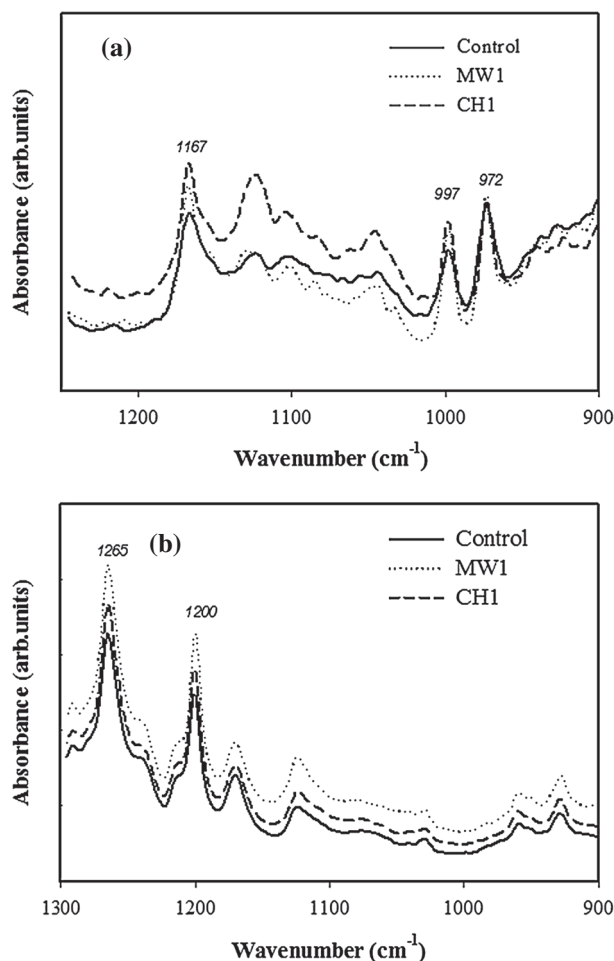


Figure 8. FTIR-ATR spectra of film B. (a) Coated metal-oxide layer before (control) and after MW1 and CH1 treatments. (b) Food-contact layer before (control) and after MW1 and CH1 treatments. Spectrum represents average of three replicates.

very similar to the peaks observed for the food-contact side of film A (Figure 8b). These observations suggest that both MW and conventional heating at sterilization temperatures (MW1 and CH1) had little influence on the silicon–oxygen chemical structures in the coating and additive particles. Hence, there was no marked difference between the influences that MW sterilization and the conventional retort sterilization had over Si migration.

CONCLUSIONS

The results of this study indicate that Si may migrate from two commercially available, high gas barrier, multilayer coated films into FSLs, which represent aqueous and low-acid foods. No significant difference was found in Si migration after MW heating compared with conventional retort process conditions. The final MW process temperature had a strong influence in the level of Si migration for the two films. On the other hand, the total MW processing time had a higher impact on Si migration at pasteurization temperatures (70 and 90 °C) compared with sterilization temperatures (123 °C). FTIR assisted in the study of the chemical stability of the Si–O–Si bonds present in the metal-coated and food-contact layer. No significant difference was found between the stability of the bonds when processed with MW versus conventional retort sterilization. However, overall migration of Si was found to be <1.5 mg/Kg FSL in all cases, suggesting that selected films can be used for MW

processing applications. This study shows that there was no significant non-thermal influence of MW heating on the migration of metal-oxide coating and additive constituents in terms of silicon, as compared with conventional thermal heating.

ACKNOWLEDGEMENTS

This work was funded in part by the Food Security USDA Special Research grant numbers 2008-34477-09142 and 2009-34477-20304, and by the USDA NIFA Research grant number 2011-68003-20096. The authors acknowledge technical assistance of Matthew Smith, Jonathan P Lomber, Xiaojiao Lu, [Zhouhong Wang](#), Feng Liu and Zhongwei Tang of Washington State University. The authors would like to thank Robert Armstrong and Masakazu Nakaya of EVAL Company of America for providing the packaging materials for testing.

REFERENCES

1. Guan D, Plotka VCF, Clark S, Tang J. Sensory evaluation of microwave treated macaroni and cheese. *Journal of Food Processing and Preservation* 2002; **26**: 307–322.
2. Ramaswamy H, Tang J. Microwave and radio frequency heating. *Food Science and Technology International* 2008; **14**(5): 423–427.
3. Tang J, Liu F, Patfiak K, Eves EE. Apparatus and method for heating objects with microwaves 2006; *US Patent 7119313 B2*.
4. Food Production Daily. Researcher hails ‘major milestone’ for microwave sterilization technology 2011; <http://www.foodproductiondaily.com/Processing/Researcher-hails-major-milestone-for-microwave-sterilization-technology> [accessed 29 March 2012].
5. Microwave Pasteurization 2011; <http://microwavepasteurization.wsu.edu/> [accessed 29 March 2012].
6. Brody AL. The coming wave of microwave sterilization and pasteurization. *Food Technology* 2012; **66**(3): 78–80.
7. Food Production Daily. Microwave sterilization system rolled out in US 2012; <http://www.foodproductiondaily.com/Processing/Microwave-sterilization-system-rolled-out-in-US> [accessed 31 October 2012].
8. Dhawan S, Sablani SS, Barbosa-Canovas GV, Tang J. Morphological and oxygen barrier changes of two multilayer polymeric films subjected to microwave sterilization. Paper presented at: *Institute of Food Technologists (IFT) Annual Meeting* 2010; IFT Paper No. **232–12**.
9. Ozen BF, Floros JD. Effects of emerging food processing techniques on the packaging materials. *Trends in Food Science and Technology* 2001; **12**: 60–67.
10. Guillard V, Mauricio-Iglesias M, Gontard N. Effect of novel food processing methods on packaging: structure, composition, and migration properties. *Critical Reviews in Food Science and Nutrition* 2010; **50**: 969–988.
11. Lau OW, Wong SK. Contamination in food from packaging material. *Journal of Chromatography A* 2000; **882**: 225–270.
12. Wells Plastic. Antiblocks 2012; <http://www.wellsplastics.com/httdocs/antiblocks.html> [accessed 30 November 2012].
13. Alin J, Hakkarainen M. Type of polypropylene material significantly influences the migration of antioxidants from polymer packaging to food simulants during microwave heating. *Journal of Applied Polymer Science* 2010; **112**: 107–113.
14. Mauricio-Iglesias M, Jansana S, Peyron S, Gontard N, Guillard V. Effect of high-pressure/temperature (HP/T) treatments of in-package food on additive migration from conventional and bio-sourced materials. *Food Additives and Contaminants* 2010; **27**(1): 118–127.
15. Snyder RC, Breder CV. New FDA migration cell used to study migration of styrene from polystyrene into various solvents. *Journal Association of Official Analytical Chemists* 1985; **68**(4): 770–775.
16. Jeon JY, Kim HY. Microwave irradiation effect on diffusion of organic molecules in polymer. *European Polymer Journal* 2000; **36**: 895–899.
17. Galotto MJ, Guarda A. Comparison between thermal and microwave treatment and the overall migration of plastic materials intended to be in contact with foods. *Packaging Technology and Science* 1999; **12**(6): 277–281.
18. Mokwena KK, Tang J, Dunne CP, Yang TCS, Chow E. Oxygen transmission of multilayer EVOH films after microwave sterilization. *Journal of Food Engineering* 2009; **92**: 291–296.
19. Chung HL, Birla SL, Tang J. Performance evaluation of aluminum test cell designed for determining the heat resistance of bacterial spores in foods. *LWT- Food Science and Technology* 2008; **41**: 1351–1359.
20. Kong F, Tang J, Rasco B, Crapo C. Kinetics of salmon quality changes during thermal processing. *Journal of Food Engineering* 2007; **83**: 510–520.
21. US Food and Drug Administration. Guidance for industry: preparation of premarket submissions for food contact substances: chemistry recommendations 2007; <http://www.fda.gov/Food/GuidanceComplianceRegulatoryInformation/GuidanceDocuments/FoodIngredientsandPackaging/ucm081818.htm> [accessed 29 March 2012].
22. EEC, European Commission Directive. 85/572/EEC of 19 December 1985 laying down the list of simulants to be used for testing migration of constituents of plastic materials and articles intended to come into contact with foodstuffs. *Official Journal of European Communities* 1985; **372**: 14–21.

23. Tang Z, Mikhaylenko G, Liu F, Mah JH, Tang J, Pandit R, Younce F. Microwave sterilization of sliced beef in gravy in 7 oz trays. *Journal of Food Engineering* 2008; **89**: 375–383.
24. Guan D, Gray P, Kang DH, Tang J, Shafer B, Ito K, Younce F, Ynag TCS. Microbiological validation of microwave-circulated water combination heating technology by inoculated pack studies. *Journal Food Science* 2003; **68**: 1428–1432.
25. Mokwena KK, Tang J, Laborie MP. Water absorption and oxygen barrier characteristics of ethylene vinyl alcohol films. *Journal of Food Engineering* 2011; **105**: 436–443.
26. Mauricio-Iglesias M, Peyron S, Guillard V, Gontard, N. Wheat gluten nanocomposite films as food-contact materials: migration tests and impact of a novel food stabilization technology (high pressure). *Journal of Applied Polymer Science* 2010; **116**: 2526–2535.
27. Lynch ME, Folz DC, Clark DE. Effect of microwaves on the migration of lithium and silicon from lithium disilicate ($\text{Li}_2\text{O}-2\text{SiO}_2$) glass. *Food Additives and Contaminants* 2008; **25**(4): 519–526.
28. Mauricio-Iglesias M, Gontard N, Gastaldi E. Impact of high pressure treatment on the structure of montmorillonite. *Applied Clay Science* 2011; **51**: 174–176.