2007 International Nuclear Atlantic Conference - INAC 2007
Santos, SP, Brazil, September 30 to October 5, 2007
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-02-1

ε-CAPROLACTAM MIGRATION FROM IRRADIATED PA-6 FOOD PACKAGING: KINETIC SIMULATION AND MEASUREMENT

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ABSTRACT

Migration of low molecular mass compounds (LMMC), such as monomers and additives, from plastic packaging into food simulants is a very important issue, concerning public health and chemical contamination of foods. Sterilization of food packaging materials with ionizing radiation is considered an alternative to other sterilization methods, but when polymers are irradiated, LMMC may be formed, as radiolisys products. According to the Brazilian legislation, specific migration tests, such as those of LMMC from packaging into simulants, should be carried out at certain temperature and time, depending on the real conditions of contact. In this work, multilayer flexible films with polyamide 6 (PA-6), used for meat foodstuffs, were studied. The ε-caprolactam (PA-6 monomer) specific migration into acetic acid 3% simulant at 40°C during 10 days and at 100°C during 30 minutes was performed. The initial monomer level in the irradiated and non irradiated PA-6 films was quantified by high resolution gas chromatography (HRGC). Radiation doses were 3 and 7kGy. ε-caprolactam specific migration was carried out only with non irradiated films. The results showed that radiation causes a significant change in the monomer level, up or down, depending on the multilayer film type. The kinetic of the ε-caprolactam migration at both temperatures, 40 and 100°C was clearly explained by the numerical simulation, combining an Arrhenius equation with the Fick´s second law, although this kinetic was not experimentally studied. This simulation allowed to predict diffusion parameters estimates, like diffusion coefficients and activation energies of ε-caprolactam in the films or simulant.

1. INTRODUCTION

The migration of compounds from packaging into food is an important aspect concerning safety of foods and packaging materials. Plastic additives, frequently used to improve polymer properties, and residual monomers or oligomers, as well as plastic reaction by-products and degradation compounds, are not chemically bounded to the polymer molecules

and can, therefore, move freely within the polymer matrix [1]. Sterilization of food packaging materials with ionizing radiation is considered an alternative to other methods, e.g. chemical or heat treatment. Depending on the nature of the polymer and the specific irradiation conditions (absorbed doses, dose rate, temperature) changes in the packaging material may occur with production of free radicals, hydroperoxides, carboxyclic acids, carbonyl compounds, discoloration, chain scission, crosslinking, changes in the mechanical properties etc., as reported in the literature[2-5].

In the present work, part of a major one, we simulated the effects of gamma irradiation on the migration kinetics of ε-caprolactam (polyamide 6 monomer) from multilayer flexible films, used for meat foodstuffs packaging. The simulation was based on the initial concentration of ε-caprolactam, experimentally measured in the polymer packaging, which changed according to the radiation doses. The other parameters are kept the same as those obtained for non irradiated simulation in the kinetic specific migration. The initial monomer concentration in the irradiated and non irradiated PA-6 films was quantified by high resolution gas chromatography (HRGC). Radiation doses were 3 and 7kGy. It was not possible to measure ε-caprolactam migration in irradiated films on current conditions, in order to compare the results with the simulation ones. The kinetic of the ε-caprolactam was clearly explained by the numerical simulation, combining an Arrhenius equation with the Fick´s second law, although this kinetic was not experimentally studied.

2. METHODOLOGY

2.1. Materials and Solutions

It was used two different kinds (L1 and L2) of films containing polyamide 6 (PA-6), commercially available in Brazil as meat foodstuffs packaging. The monomer ε-caprolactam (purity >98%, Sigma Aldrich) was used as analytical standard and caprilolactam (purity 99%, Sigma Aldrich) as internal standard. Methanol, ethanol, dichloromethane and acetone, HPLC grade, were purchased from Tedia Company (Fairfield, USA).

A 1250μg/ml standard stock solution of ε-caprolactam and a 70μg/ml internal standard solution of caprilolactam prepared in methanol were kept at 0ºC for no more than 3 months. Working methanol solutions were then prepared as needed. Calibration was performed with diluted working solutions in methanol.

2.2. Extraction and Quantification Procedure to Determine Residual Monomer in the Polymer

A solvent extraction using methanol was performed. Samples (0.5000g) of multilayer films containing PA-6 were manually cut into 1cm^2 pieces and extracted with 30.0ml of methanol under ultrasonic bath during 60 min. A 5ml aliquot was collected from the methanol extract and filtered in PTFE filter. A 4ml aliquot was taken from the filtered methanol extract and put into a volumetric flask. The internal standard solution was added and the volume was adjusted with methanol. Then this solution was injected in the GC-FID, as showed in the validated method, described in [6, 7].

2.3. Migration Test Procedure

It was used a specific migration essay, well described in [8]. In a general way, non irradiated packaging films were cut in pieces of 6 cm^2 (2 X 3 cm^2) of area and each one was put inside a glass proof tube containing 20mL of acetic acid 3% solution, and then was hermetically closed. The tubes were kept at 40 ±1°C for 10 days or at 100 ±1°C for 30 minutes. After contact time, the amount of monomer in the stimulant solution was determined by HRGC.

2.4. Numerical Simulation

For this study, it was applied a numerical simulation based on mathematical model of the diffusive process of migration. Details of this method are in [10-12]. It is important to mention that initial concentration is an experimentally measuring input parameter of the simulation. Diffusive coefficients of ε-caprolactam in packaging film or in the simulant are not available in the literature. They had to be obtained by the simulation. Temperature effects are included by an Arrenhius term on the diffusive coefficient [13].

3. RESULTS AND DISCUSSION

Table 1 shows the initial concentrations of ε-caprolactam in the polymer of two samples of irradiated and non irradiated plastic packaging.

Table 1. ε-caprolactam amount in irradiated and non irradiated plastic packaging.

ε-caprolactam levels (mg . kg^{-1} of film packaging)		
Doses	Packagings	
	L1	L2
0 kGy	2440.22[a]	2413.87[a]
3 kGy	2682.85[b]	2394.13[b]
7kGy	3362.50[a]	2656.62[a]

Values within a column followed by different letters are significantly different at the Tukey ($p<0.05$) test.

These results represents the quantity of ε-caprolactam present per mass unit of plastic film.

The dose of 3 kGy resulted in an increase of 10.0 % for L1 and a decrease of 0.8 % for L2, when compared with the non irradiated correspondent films. The dose of 7 kGy showed an increase of 37.8 % and 10.0% in the initial ε-caprolactam concentration, for both films.

Table 2 shows the ε-caprolactam migration results.

Table 2. ε-caprolactam migrated levels from packaging films into 3% acetic acid simulant.

Packagings	e-caprolactam levels (mg . kg^{-1} of simulant)	
	40°C – 10 days	100°C – 30 minutes
L1	9.49	7.20
L2	9.65	8.38

This migration results shows the ε-caprolactam levels that migrated per mass unit of the simulant solution. The values obtained were lower than the maximum limit values established in the Brazilian legislation [9,14], which is 15mg ε-caprolactam.kg^{-1} of simulant.

Figures 1 and 2 show the migration kinetics simulation of ε-caprolactam from the L1 and L2 packaging films into 3% acetic acid food simulant after irradiation with 3kGy and 7kGy, and for non irradiated ones. Current conditions of temperature were used.

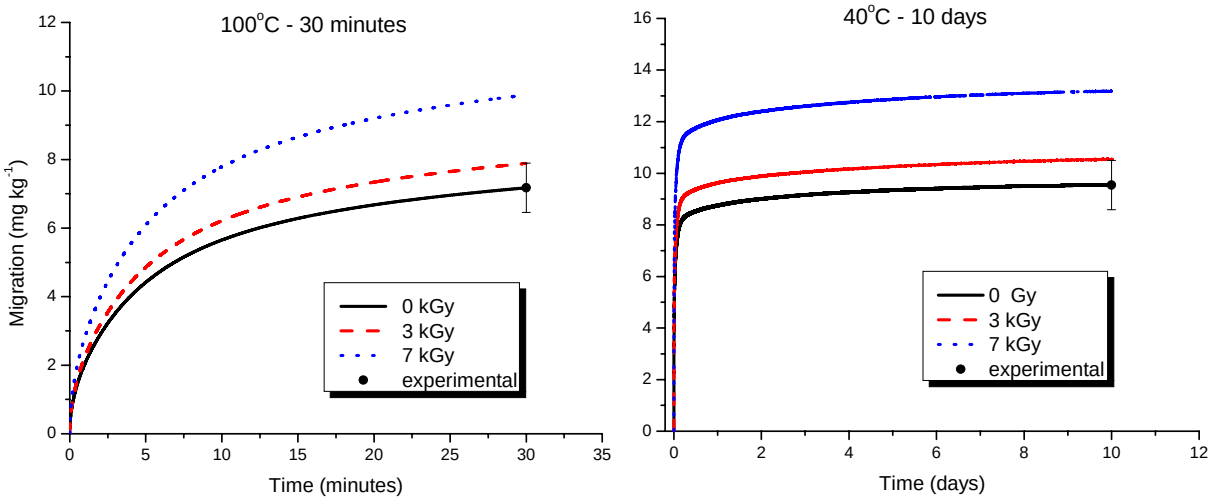

Figure 1. **Simulation of the ε-caprolactam kinetic migration from L1 plastic packaging film into 3% acetic acid food stimulant at 100°C (left) and 40°C (right). Irradiated conditions imparted 3kGy and 7kGy to the film. Non irradiated kinetic is also shown.**

As shown in the right side of Figures 1 and 2 (40°C-10 days), where there are a long time of contact, almost every amount of monomer showed enough time to left the film and drop into the simulant solution. This already happens after 1.5 days.

Simulations of L2 packaging films show a small change in migration kinetics from 0 to 3kGy. This packaging film should have more radiation resistant components in its composition at this radiation level.

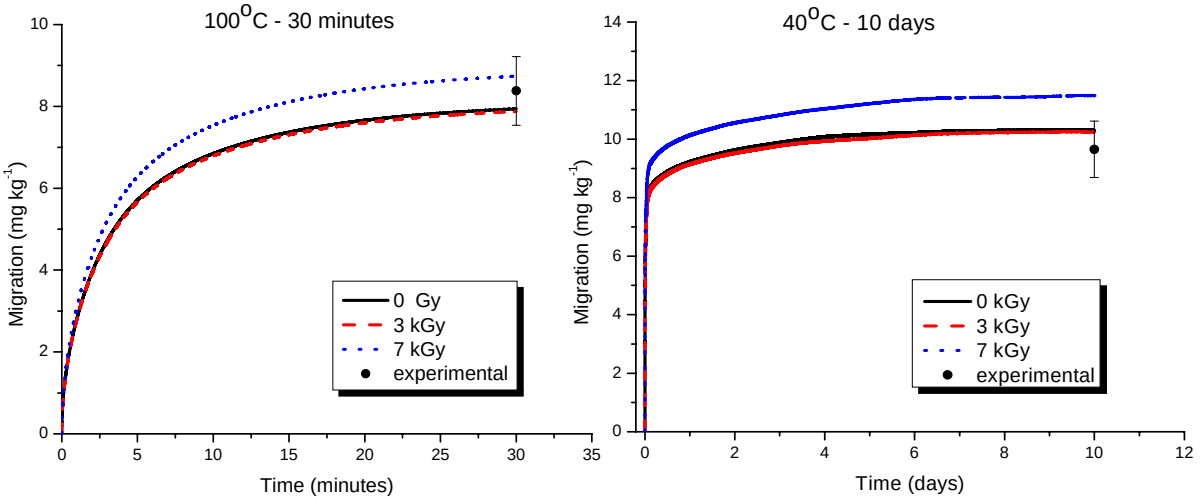

Figure 2. Simulation of the ε-caprolactam kinetic migration from L2 plastic packaging film into 3% acetic acid food stimulant at 100°C (left) and 40°C (right). Irradiated conditions imparted 3kGy and 7kGy to the film. Non irradiated kinetic is also shown.

3. CONCLUSIONS

ε-caprolactam levels in the irradiated or non irradiated packaging films and for non irradiated films into the simulant after normative intervals and under normative temperatures only permitted to obtain these interesting simulations shown on the migration kinetics graphics of Figures 1 and 2.

With this numerical procedure it is possible to calculate the level of monomer that migrates at any time and any temperature under which the packaging film is submitted to.

It was supposed that initial ε-caprolactam concentration profile is constant inside the packaging film, although any distribution is possible, as input parameter for simulation.

It is of great importance to be able to, at least, simulate possible chemical contamination, when experiments are not performed. This is more crucial when polymer radiolysis could generate dangerous substances, which can not be detected.

ACKNOWLEDGMENTS

The authors thank the CTR irradiator staff Carlos, Elizabeth and Helio. Monteiro, Araújo and Félix thank also PADC-FCF/UNESP, CAPES and FAPESP.

REFERENCES

1. A. L. Brody, & K. S. Marsh, *The Wiley Encyclopedia of packaging technology* (2nd ed.), John Wiley & Sons, New York & United States (1997).
2. R. Buchalla, C. Schottler, and K. W. Bogl, "Effects of ionizing radiation on plastic food packaging materials: A review. Part 1. Chemical and physical changes." *Journal of Food Protection*, **56**, pp. 991-997 (1993a).
3. R. Buchalla, C. Schottler, and K. W. Bogl, "Effects of ionizing radiation on plastic food packaging materials: A review. Part 2. Global migration, sensory changes and the fate of additives." *Journal of Food Protection*, **56**, pp. 991-997 (1993b).
4. S. Chytiri, A. E. Gouklas, K. A. Riganakos, A. Badeka, and M. G. Kontominas, "Volatile and non-volatile radiolysis products in irradiated miltilayer coextruxed food packaging films contained a buried layer of recycled low density polyethylene." *Food Additives and Contaminants*, **22(12)**, pp. 1264-1273 (2005).
5. A. E. Gouklas, K. A. Riganakos, and M. G. Kontominas, "Effect of ionizing radiation on physicochemical and mechanical properties of commercial multilayer coextruded flexible plastics packaging materials." *Radiation Physics and Chemistry*, **68**, pp. 865-872 (2003).
6. H.P. Araujo, M. Monteiro "Desenvolviemnto e validação de metodologia analítica para determinação de caprolactama em embalagens de poliamida destinadas ao acondicionamento de alimentos", XXCBCTA. Curitiba, 2006
7. H. P. Araújo, M. Padula, J. E. Manzoli, and M. Monteiro." *Irradiated and non-irradiated multilayer polyamide 6 films: development and validation of a HRGC method to determine caprolactam.*" *Polymer Sci A*, 2007 (submitted).
8. J. S. Félix, M. Padula, J. E. Manzoli, and M. Monteiro, "Migração de caprolactma de embalagens de poliamida para simulante ácido acético 3%. Parâmetros de Validação do Método Analítico." *Ciência e Tecnologia de Alimentos*, 2006 (*in press*).
9. ANVISA, National Health Surveillance Agency, Resolution nº. 105, Brazil, 1999.
10. J. E. Manzoli, M. Monteiro, P. Rela, and J. S. Félix, "Initial concentration profile influence on migration measurements from plastic packaging: A simulation study," *Proceeding of XVIII IMEKO World Congress*, Rio de Janeiro, 2006, CDROM.
11. J. E. Manzoli and M. Monteiro, "Mathematical Model for the migration of Tinuvin-P from bottles into N-Heptane," *Proceeding of Macro 2006 - World Polymer Congress*, Rio de Janeiro, 2006, CDROM.
12. J. E. Manzoli, F. M. L. Rosa, J. S. Félix, and M. Monteiro, "Migration measurements from plastic packaging: a simulation study on influence of initial concentration profile," *Metrology and Measurements Systems*, vol. XIV, pp.117-124 (2007).
13. L. L. Kathan, *Migration from Food Contact Materials*, Blackie Academic & Professional, London & England (1996).
14. ANVISA, National Health Surveillance Agency, Decree nº .55.871, Brazil, 1965.