Phtalate Migration Study from PVC Grafted by Gamma Radiation

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ABSTRACT

PVC is a useful polymer used for many applications, as packaging of food, blood and in contact with body fluids. The most widely-used plasticizer, to make it flexible, is the phthalate DEHP, and its toxicity is a problem. A special radiation grafting of PVC allows an important reduction of thrombogenic properties, and it could cause changes in the DEHP migration too. In this work it is presented the methodology using gas chromatography and numerical simulation for the measurement of DEHP migration from PVC grafted with monomer DMAEMA. The grafting could be an interesting way to reduce DEHP migration.

Key words: *grafting, PVC, migration, phtalate, simulation*

INTRODUCTION

Migration or diffusion of substances from plastic packaging or ducts into food, medicine or body fluids is a very important issue concerning public health and chemical contamination [1,2]. Flexible Polyvinyl Chloride, PVC, is an useful polymeric material used in packaging of food, intravenous tubing and bags, catheters, nasogastric tubes, dialysis bags and tubing, blood bags, transfusion tubing, air tubes. In order to make the PVC flexible, it is added some substances to its polymer matrix, called plasticizers [3]. The most widely-used plasticizer is a phthalate called di-2-ethyl hexyl phthalate (DEHP). The acute toxicity of DEHP is 30g/kg in rats (oral) and 24g/kg in rabbits (dermal). The European Commission has banned the use of DEHP and some other phthalates in PVC toys.

The American Academy of Pediatrics has advocated not to use medical devices that can leach DEHP into patients and, instead, to resort to DEHP-free alternatives. In this work it is used the FID gas chromatography, GC-FID, for the measurement of DEHP amount migrated [4,5] from PVC grafted by radiation with the monomer Dimethylaminoethyl Methacrylate, DMAEMA [6], into simulant of acid (acetic acid) and fat (n-Heptane) medium. We believe that radiation grafting [7] could be an interesting way to reduce DEHP migration, and its quantification could use the procedure described here. A computer simulation algorithm for this migration [8-11] and the calibration curve of the CG-FID apparatus are presented and it is shown the first preliminary results. Some informative aspects of the grafting process were described. This grafted polymer will be further grafted again with Heparin for purposes that are not the scope of this work.

METHODOLOGY

Plasticizer quantification

The DEHP quantification was done using ASTM D2124-99 (Revised in 2004) [12]. The percent amount of plasticizer inside the samples was determined. The ASTM D2124-99 recommends 6h as extraction time. To verify the extracted material dependence with time, five essays are desired to be done in triplicate, from 6 to 36h. Ethilic Ether is too volatile, so a reflux condenser was used, using ethanol as cooling fluid. After plasticizer extraction, films were analysed by FTIR to verify the complete extraction.

Gamma Irradiation / Grafting

It was used ^{60}Co gamma irradiator Gammacell model 220, always at 5 kGy [6]. Dose rates of 2.5; 1.25; 0.75 and 0.25 kGy/h were used. Film samples of 20x20mm were immersed in vessels with DMAEMA (dimethilaminoethil metacrilate) solution 30% v/v of water (7ml). Nitrogen gas bubbles during 5 minutes before the sealing, to purge Oxygen. The sealed vessels waited 24 hours before radiation session, to promote film swelling.

After irradiation, PVC-g-DMAEMA films were washed in current water to remove homopolymer and solution residues. Following, films were identified and maintained at 37^{o}C in a stirred bath for 12 hours. Following, films were maintained at rest by 12 h. After, the samples were washed with neutral soap and current water, following a rinsing process with distilled water and a new rinsing process with methanol. Methanol excess was removed with a absorbent paper and a session of 4h and 37^{o}C on a vacuum stove.

Specific Migration

It was made *total immersion* essays, where contact time of the polymer with simulant was only 30 minutes at 100^{o}C. For comparison with the numerical simulation, the kinetic of migration is needed.

It was used acetic acid, 30% v/v, and n-Heptane as simulants (fat and acid media). Injections into the CG-FID system were 1μl of n-Heptane solution. So, the n-Heptane simulant was sampled directly (1μl), but the amount of DEHP inside the acetic acid simulant was extracted by a technique as follows: 2ml of acetic acid is added to 1ml of pure n-Heptane and this 2-phase liquid is agitated during one hour. So, the 1μl is collected from the n-Heptane phase, which "absorbed" every DEHP from the acetic acid phase.

Specific Migration Simulation

It was used finite differences and diffusion equation is solved by a numerical simulation procedure [11]. The numerical solution uses a non-uniform mesh of points for the discretization of *x* domain [10]. The density of points is higher close to interfaces. Each point is labeled as illustrated in Figure 1.

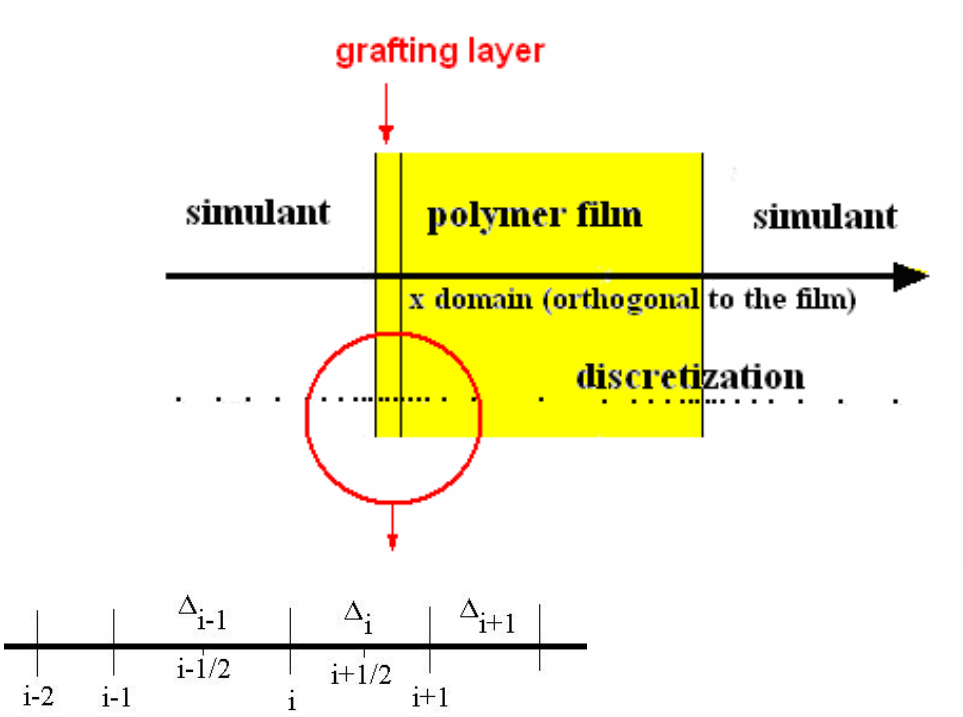

Figure 1: Sketch of the polymer film/simulant system for numerical treatment. The continuous x domain is shifted to a finite number of points (discretization). Below: indication of the interval and point labels.

The *x* domain was discretized in *n* points by using a three-point finite difference scheme, which generates the following form for the diffusion equation:

$$\frac{d}{dx}D(x)\frac{d}{dx}C(x)\overset{N}{\cong}\frac{d}{dx}D(x)\left[\frac{C_{i+1/2}-C_{i-1/2}}{\Delta_i+\Delta_{i-1}}2\right]=$$

$$=\left(D_{i+1/2}\frac{C_{i+1}-C_i}{\Delta_i}-D_{i-1/2}\frac{C_i-C_{i-1}}{\Delta_{i-1}}\right)\frac{2}{\Delta_i+\Delta_{i-1}}=$$

$$=\left(\frac{2D_{i+1/2}}{\Delta_i(\Delta_i+\Delta_{i-1})}\right)C_{i+1}+$$

$$-\left(\frac{2D_{i+1/2}}{\Delta_i(\Delta_i+\Delta_{i-1})}+\frac{2D_{i-1/2}}{\Delta_{i-1}(\Delta_i+\Delta_{i-1})}\right)C_i+$$

$$+\left(\frac{2D_{i-1/2}}{\Delta_{i-1}(\Delta_i+\Delta_{i-1})}\right)C_{i-1}=\frac{C_{j+1}-C_j}{\Delta t}$$

Equation (1)

$_i$ (or X_i) is the non-constant distance between successive points *i*. *D* is diffusion coefficient. *j* is the index for time step evolution.

Partition coefficient is supposed to act as a factor multiplying the initial concentration profile, present inside the polymer packaging. In order to calculate or made an indirect

measurement of diffusion coefficient of the migrant inside the polymer, D_p, some amounts had to be determined previously, and used as input variables in the simulation. These input amounts are: initial concentration profile, partition coefficient, diffusion coefficient of the migrant inside simulant, thickness of the polymer film.

RESULTS and DISCUSSION

The system CG-FID was calibrated through the preparation of known DEHP into n-Heptane solutions, of 1.85; 3.67; 7.35 and 11.02 p.p.m. (or μg/ml), as shown in Figure 2.

The preliminary results of GS-FID are shown in Table 1. As said, it was not done yet the kinetic of migration measurements. Only one point after 30 minutes of contact was measured, for every sample.

A general view of these results shows the expected enhancement of migration on the non-polar simulant n-Heptane, compared to the polar acetic acid. The sample 02F had some undesirable contamination and should be excluded. Doing so, we have 10% of result dispersion for n-Heptane, and 16% of dispersion for acetic acid, from the mean value. This are interesting results for the initial migration estimative but they are not good enough to initialize a validation procedure.

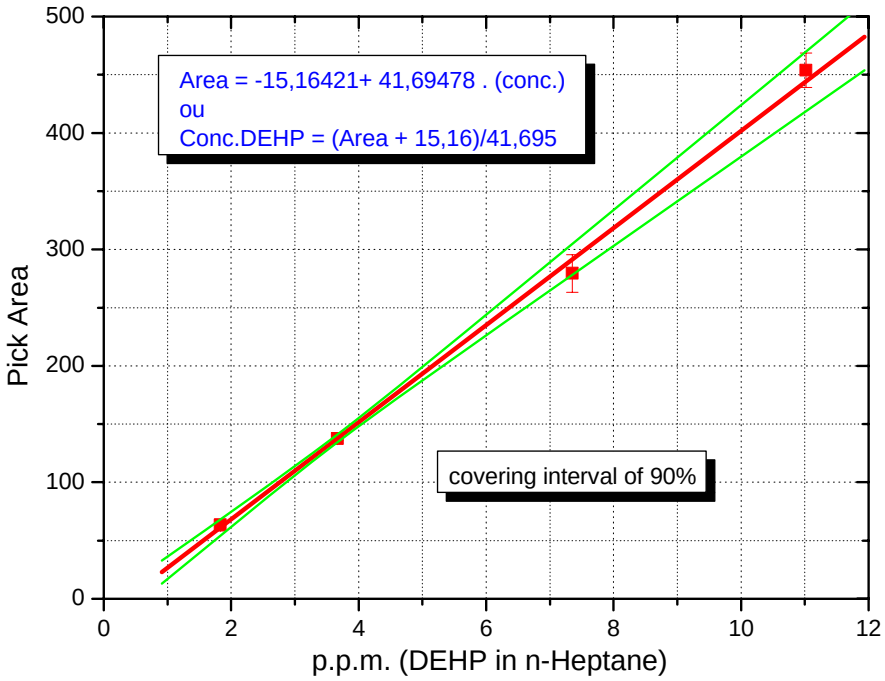

Figure 2. Preliminary Calibration Curve of the CG-FID system.

Table 1: Preliminary migration results of DEHP from PVC and PVC-gr-DMAEMA to n-Heptane and to Acetic Acid obtained by gas chromatography-FID. Differences on samples are only due to operator or date of preparation.

sample:	migration to n-Heptane (mg/l)	sample:	migration to Acetic Acid (mg/l)
4F	913,87	01F	1,84
7F	753,03	02F	41,63
8F	888,62	10F	1,46
9F	771,21	15F	1,83
13F	1039,63	2K	1,59
1K	893,69	2V	1,72
1V	928,88	14V	1,73
11V	942,35	18V	2,47
15V	801,33	20V	1,84
17V	791,04	24V	1,59

Using the numerical procedure, results of a hipotetic example of kinetic of migration simulation of a phtalate from a flexible PVC packaging into solid cheese were obtained. This situation is possible to be measured by total immersion and gas chromatography procedure, just described here and simulated with the mathematical model.

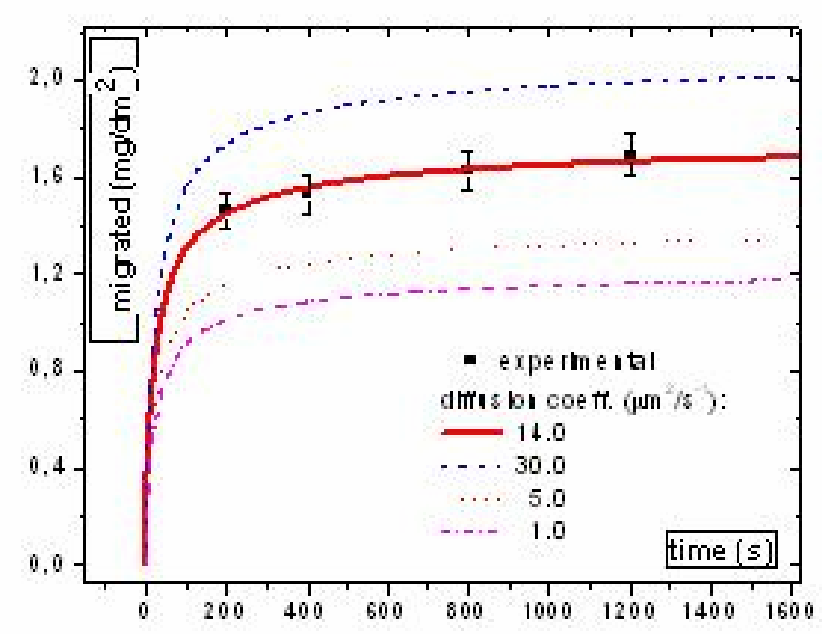

Figure 3. Kinetic of migration of DEHP from flexible PVC packaging into solid cheese. Points are supposed experimental results, from total immersion contact and gas chromatography essay. Lines are simulated results using this algorithm.

Points indicated supposed experimental results, based on tables and producers of packaging information. Curves are the simulated ones. Only the solid curve fits the experimental results. So, this procedure could be used to measure the diffusion coefficient of this phtalate inside the PVC. It was found the value 14 $\mu m^2/s$. Some variations from this value cause the other migration kinetics shown.

CONCLUSIONS

It was shown an experimental procedure to quantify the amount of plasticizer migrated from polymer packaging film into simulant of food, blood or body fluids. It was also shown a numerical simulation procedure that permits a better comprehension of the diffusion microscopic process and that allows the estimation of quantities, like diffusion coefficients of the materials and the kinetic of migration. The results shown initial application of these procedures on radiation grafted PVC, a very interesting new material to be used mainly for medical applications.

ACKNOWLEDGMENTS

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