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Leaching of Plasticized PVC: Effect of Irradiation

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Abstract

Highly irradiated (2–26 MGy) polyvinyl chloride was leached in an alkaline solution to investigate the impact of high doses on the leaching process and on the nature of the leaching products. The results show that leaching is controlled by diffusion phenomena as described by Fick's second law. The apparent diffusion coefficient (Da) of plasticized PVC leaching products can be calculated for each sample. Irradiation at high dose causes Da to diminish; this can be attributed to crosslinking and grafting reactions occurring during irradiation. The material microstructure thus becomes less permeable during radiolysis, which slows down the migration of species. Organic products of leaching are plasticizers contained in plasticized PVC or their degradation products. The main organic leaching products are phthalic ions formed by hydrolysis of phthalic esters in alkaline leaching solution.

Keywords: Leaching, Irradiation, PVC

1. Introduction

Polyvinyl chloride (PVC) has been widely used in numerous applications (medical, food packaging, chemical and nuclear industries) for many years because of its excellent properties and low cost. PVC being a brittle material, additives and plasticizers are added to enhance its flexibility and stability. Most of the plasticizers are phthalic anhydride esters. It is well known that these compounds are potentially toxic for human health [1]; the technological applications of PVC could be limited by environmental degradation such as oxidation, irradiation, hydrolysis and leaching.

Few papers have been published concerning the effects of leaching on PVC. These studies involved leaching of various plasticized PVC compounds containing various additives, mainly plasticizers. Plasticized PVC compounds are generally used in medical and food applications, in which they may be irradiated to low doses (i.e. 1–50 kGy) for sterilization or bactericide treatment. Some plasticized PVCs are also used in the nuclear industry and could be exposed to high irradiation doses (up to several MGy) during their service lifetime and after final disposal. Most PVC leaching studies have been carried out on unirradiated PVC. In a few cases the authors were interested in leaching of PVC irradiated to low doses (several kGy), but to our knowledge no study concerning the leaching of PVC irradiated to high doses (several MGy) has yet been published.

According to the literature on leaching of unirradiated plasticized PVC, the leaching products are composed mainly of plasticizers. Among the plasticizers used in plasticized PVC formulations, the leaching of di(2-ethylhexyl)phthalate (DEHP) has been studied most extensively; this plasticizer is often added to PVC to obtain sufficient flexibility for various applications. Several authors reported increasing DEHP release during the experimental period [2-4]. The extraction of DEHP was highly dependent on the temperature of the leaching solution, but also on the plasticized PVC formulation and on the initial quantity of DEHP [2-4]. Kim et al. showed that DEHP migration in organic solution from sheets of unirradiated plasticized PVC was described by Fickian diffusion behavior [5]. Mersiowky et al. showed that, for some PVC formulations, plasticizers like DEHP and butylbenzyl phthalate (BBP) were leached in variable quantities (loss of up to 30% of these compounds) [6-8]. Shin et al. studied the leaching of flexible PVC containing di-isononyl phthalate (DINP) in aqueous solutions of NaOH [9]. They attributed the extraction of phthalic acid and isononyl alcohol to hydrolysis of DINP by the alkaline solution.

Very few authors have investigated the leaching behavior of irradiated plasticized PVC. Demertzis et al. studied leaching of PVC packaging material irradiated to 44 kGy in organic solution [10] and showed that large amounts of radiolysis products were extracted, but they did not clearly identify the irradiation-related products.

The aim of this study was to understand how high irradiation doses (up to 26 MGy) interfere with leaching phenomena. In order to achieve a predictive model of leaching, it is important to understand the migration process of leaching products from irradiated plasticized PVC. As high irradiation doses result in chemical changes in the polymer, migration mechanisms were established and major products of leaching were identified. We investigated the leaching of

plasticized PVC (Plastisol[®]), but also of pure PVC (not containing any additives): leach tests were performed on both kinds of PVC to compare the leaching of organic products from highly irradiated pure and plasticized PVC. The experiments were carried out in aqueous alkaline solution to ensure they were representative of a potential waste repository.

2. Experimental

2.1 Samples

The “pure PVC” used in these experiments was in fact a 50:50 mixture of two types of PVC manufactured by Solvay: Solvin[®] 266SF (made by suspension polymerization) and Solvin[®] 372LD (made by emulsion polymerization). The pure PVC was procured in white powder form with a particle size below 100 µm. The plasticized PVC was a Plastisol[®] flexible plate one centimeter thick. Leach tests with plasticized PVC were carried out on massive cubic PVC samples and on crushed samples with the same particle size as the pure PVC. The plasticized PVC comprised only 27% pure PVC, the remainder being organic and inorganic additives. The principal additives were plasticizers: di-isononyl phthalate, di-*n*-butyl phthalate, and 2-ethylhexyl diphenyl phosphate.

2.2 Irradiation

One-gram bulk or powder samples were irradiated by a γ source (⁶⁰Co, 1.0×10^{17} Bq) at room temperature in air. The samples were irradiated homogeneously by rotating them during the treatment and the dose rate was about 10 kGy·h⁻¹. The extent of chemical changes produced by irradiation depends on the energy absorbed by the system. The absorbed dose was determined using the alanine EPR method [11] or Perspex dosimeters (routine measurements).

2.3 Experimental Leaching Procedure and Analysis

One-gram pure or plasticized PVC samples were placed in a 60 mL glass bottle and leached in massive (bulk plasticized PVC only) or powder form (crushed plasticized PVC or pure PVC). The samples were leached in a saturated (4 g·L⁻¹) Ca(OH)₂ solution. The leaching solution was maintained at 20°C or 50°C with a drying oven and renewed daily during the two first weeks of the experiment, and monthly thereafter.

2.3.1 Quantitative Analysis

In order to quantify all the organic products released, we monitored the leaching process by Total Organic Carbon (TOC) measurement [12], based on quantifying the organic carbon after strong oxidation of organic compounds into CO₂, and after complete elimination of the inorganic carbon. The carbon was oxidized using a sodium persulfate solution (Na₂S₂O₈); the sample was also subjected to the radiation of a UV lamp to favor oxidation. The instrument was calibrated with standard solutions of potassium hydrogen phthalate (C₈H₅KO₄). The TOC analysis results for the leaching solution are indicated in terms of the PVC mass.

2.3.2 Qualitative Analysis

The organic leaching products were separated and identified by HPLC-UV. The identification was then refined by ion chromatography. The device characteristics are indicated below:

- HPLC-UV:
 - Column: YMC-ODS, 250 × 4.6 mm, 5 μm
 - Detection: 254 nm
 - Flow rate: 1 mL·min⁻¹
 - Elution solvent: CH₃CN/H₂O
- Ion chromatography:
 - Column: IonPac® AS11
 - Detection: Conductivity meter
 - Flow rate: 1 mL·min⁻¹
 - Elution solvent: KOH

3. Results and Discussion

3.1 Irradiated Plasticized PVC Leaching Process

3.1.1 Quantitative Analysis of Plasticized PVC Leaching: Effect of Leaching Temperature

Plasticized PVC irradiated to 4 MGy was leached at 20°C and 50°C (**Figure 1**). The results show that the temperature increases the leach rate of organic products although the maximum

quantity of leaching products released (obtained by extrapolation of the curves) appears to be the same at 20°C and 50°C.

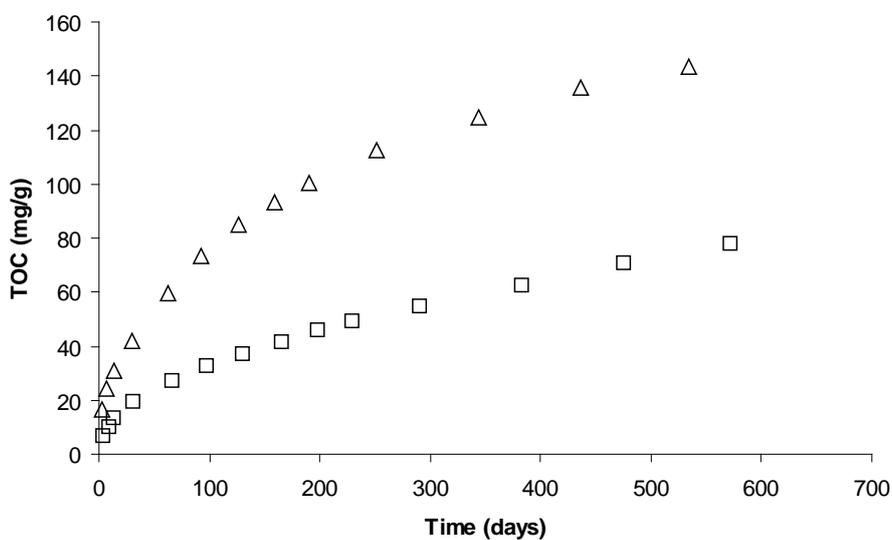


Figure 1. TOC measurements of unirradiated plasticized PVC leached at 20°C and 50°C (△ Leaching at 50°C, □ Leaching at 20°C)

Figure 2 shows that leaching of organic compounds in alkaline solution is proportional to the square root of time. This behavior is characteristic of material transfer controlled by diffusion phenomena described by Fick's second law.

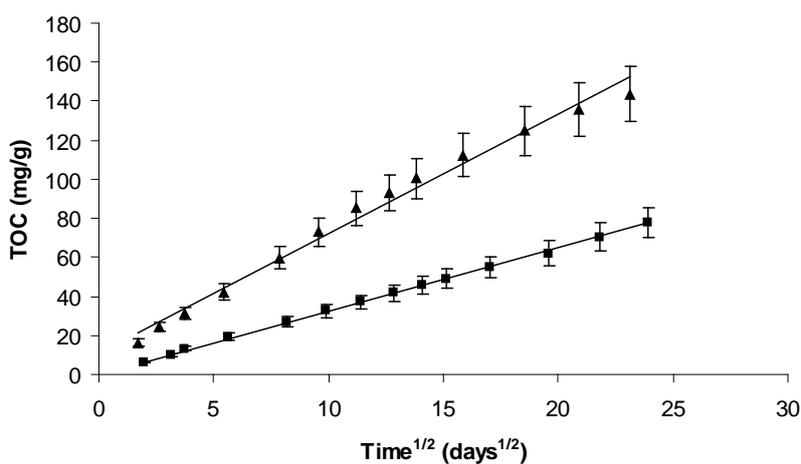


Figure 2. TOC measurements of unirradiated plasticized PVC leached at 20°C and 50°C, evolution in days^{1/2} (▲ Leaching at 50°C, ■ Leaching at 20°C)

Kim et al. noted this diffusion behavior in the case of DEHP migration in organic solution from sheets of unirradiated plasticized PVC [5]. In our study, we quantified all organic compounds leached by TOC measurements. We considered that our limit conditions are close to those of a semi-infinite medium:

- The medium is limited on one side by the exchange surface area between the material (PVC) and the leaching solution. The concentration of leached organic compounds in solution is constant and near zero (ensured by frequent renewal of the leaching solutions).
- The PVC material is considered semi-infinite toward the core of the PVC sample. The initial concentration of organic compounds remains constant and homogeneous in the core of the material during the experiment.

Applying these conditions to Fick's second law yields an expression accounting for the migration process of organic compounds from irradiated plasticized PVC (equation 1).

$$Q(t) = 2Q' \frac{S}{V} \sqrt{\frac{Da \cdot t}{\pi}} \quad (1)$$

where:

$Q(t)$: quantity of organic compounds leached at time t , evaluated by TOC measurement at time t (mg of TOC per g of material).

Q' : maximum limiting quantity of organic compounds leached, evaluated by TOC' measurement (mg of TOC per g of material). TOC' is comparable to TOC measure at constant level.

V : total sample volume (m^3).

S : exchange surface area, i.e. total sample external surface area (m^2).

Da : apparent diffusion coefficient ($m^2 \cdot s^{-1}$).

Leaching of organic compounds being a linear function of $t^{1/2}$ (**Figure 2**), we concluded that leaching is diffusion-controlled. The slope (s) of these curves allowed us to calculate Da , the other terms being determined experimentally as discussed below:

- The total sample volume V was measured by helium pycnometry. The exchange surface area S was measured on a massive PVC sample, assuming cubic samples. Several experiments showed that S/V was relatively constant at $685 m^{-1}$.
- TOC' is the maximum quantity of organic compounds released from each sample. This quantity was determined from the maximum TOC value reached for each sample, i.e. the

constant TOC obtained by extrapolating the $\text{TOC} = f(t)$ curves. $\text{TOC}' = 140 \pm 9 \text{ mg}\cdot\text{g}^{-1}$ in both cases (at 20°C and 50°C), the leaching process being slower for unirradiated plasticized PVC leached at 20°C.

- The slope s of the $\text{TOC} = f(t^{1/2})$ curve was evaluated by linear regression:

$s = (1.1 \pm 0.1) 10^{-2} \text{ mg}\cdot\text{g}^{-1}\cdot\text{s}^{1/2}$ for unirradiated plasticized PVC leached at 20°C.

$s = (2.7 \pm 0.3) 10^{-2} \text{ mg}\cdot\text{g}^{-1}\cdot\text{s}^{1/2}$ for unirradiated plasticized PVC leached at 50°C

From equation 1 we can calculate Da , the diffusion coefficient of the total amount of organic compounds leached from plasticized PVC:

$Da = (1.1 \pm 0.1) \times 10^{-14} \text{ m}^2\cdot\text{s}^{-1}$ for unirradiated plasticized PVC leached at 20°C.

$Da = (6.0 \pm 0.6) \times 10^{-14} \text{ m}^2\cdot\text{s}^{-1}$ for unirradiated plasticized PVC leached at 50°C.

This increase of Da as a function of temperature is quite similar to the evolution of Da noted by Kim et al. [5], who studied DEHP diffusion from a PVC/DEHP mixture in acetonitrile. They reported that the diffusion coefficient D corresponding to the migration of DEHP in acetonitrile increased from $2.72 \times 10^{-14} \text{ m}^2\cdot\text{s}^{-1}$ at 30°C to $10.1 \times 10^{-14} \text{ m}^2\cdot\text{s}^{-1}$ at 60°C. The small difference between our diffusion coefficient values and those of Kim et al. is certainly due to the nature of the leaching solution, as organic solvents facilitate the migration of organic compounds from PVC.

3.1.2 Quantitative Analysis of Plasticized PVC Leaching: Effect of Irradiation Dose

Leach tests were carried out at 50°C on plasticized PVC with unirradiated samples and samples irradiated between 2 and 26 MGy. The results of TOC measurements (**Figure 3**) showed that the higher the irradiation dose, the lower the maximum TOC' value obtained by extrapolation of $\text{TOC} = f(t)$ curves, i.e. the smaller the quantities of leaching products (**Table I**). The maximum amount of compounds released from unirradiated PVC was about twice the quantity released from PVC irradiated to 26 MGy. Irradiation thus diminishes decreases the amount of leaching products.

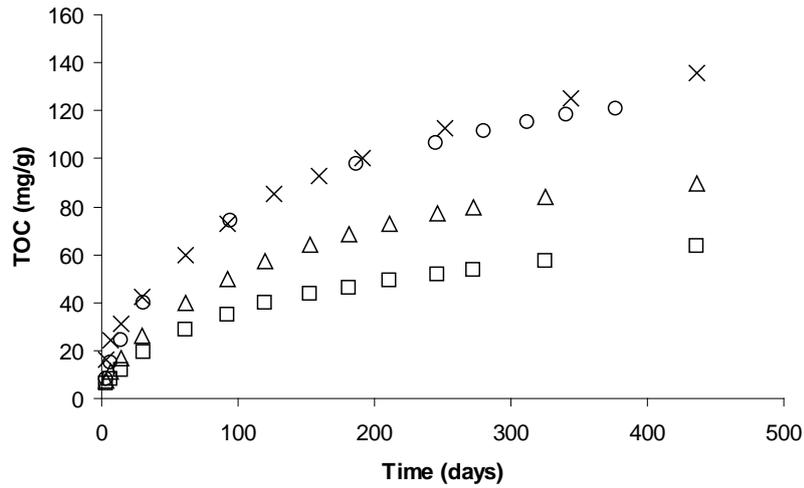


Figure 3. TOC measurements of unirradiated and irradiated plasticized PVC leached at 50°C
 (× Leaching of unirradiated PVC, ○ Leaching of PVC irradiated to 2 MGy,
 △ Leaching of PVC irradiated to 18 MGy, □ Leaching of PVC irradiated to 26 MGy)

Moreover, the leaching process slows down as the irradiation dose increases. This slowdown is clearly highlighted by comparing the slope of the $TOC = f(t^{1/2})$ curves, which decreases as the irradiation dose increases (**Table II**). The slope of the 26 MGy curve is about half the slope obtained with unirradiated PVC. We can conclude that after irradiation to 26 MGy the diffusion kinetics are reduced by about half compared with diffusion from an unirradiated sample.

As noted above, the slopes of the TOC versus $t^{1/2}$ curves allowed us to evaluate the apparent diffusion coefficient (Da). The results are indicated **Table I** together with the other calculated terms.

Table I. Determination of Q' , slopes of the $TOC = f(t^{1/2})$ curves and apparent diffusion coefficient (Da) with increasing irradiation doses

Dose (MGy)	$Q' = TOC'$ (mg·g ⁻¹)	Slope (s) (mg·g ⁻¹ ·s ^{1/2})	Da (m ² ·s ⁻¹)
0	140	2.7×10^{-2}	$(6.0 \pm 0.6) \times 10^{-14}$
2	130	2.4×10^{-2}	$(5.6 \pm 0.6) \times 10^{-14}$
18	100	1.7×10^{-2}	$(4.8 \pm 0.5) \times 10^{-14}$
26	75	1.2×10^{-2}	$(4.2 \pm 0.4) \times 10^{-14}$

The evolution of the apparent diffusion coefficient (Da) during irradiation shows that the higher the irradiation dose, the lower the value of the apparent diffusion coefficient. This may be

attributable to crosslinking and grafting reactions occurring under irradiation. Crosslinking could occur by reaction between two macroradicals in the PVC matrix [13-15]; grafting could occur by reaction of a radical formed by radiolysis of plasticizers on PVC macromolecules [16-18]. Such reactions can change the material microstructure, and could account for the reduction in the apparent coefficient of diffusion, the transfer of organic compounds being reduced because the polymer microstructure is less permeable to the migration of organic species.

3.2 Qualitative Analysis of Leaching Products

3.2.1 Pure PVC versus Plasticized PVC

In order to determine the origin of the leaching products, we studied leaching of pure PVC and crushed plasticized PVC. Oxidative radiolysis of PVC macromolecules produces scission reactions and the formation of oxidized products [19]; oxidative radiolysis of several MGy could induce these reactions in sufficient amounts to produce short hydrophilic compounds and thus potential leaching products. In all the experiments (at 20°C or 50°C with unirradiated samples or samples irradiated to several MGy), plasticized PVC released about 100 times more organic compounds than pure PVC. Even in the case of pure PVC irradiated to several MGy the quantity of Total Organic Carbon measured in the leaching solution reached a steady-state value of about 0.6–0.8 mg TOC per gram of pure PVC. In comparison, the results obtained for plasticized PVC ranged from 70 to 140 mg TOC per gram of plasticized PVC. We can therefore consider that when PVC is heavily degraded by oxidative radiolysis, scission reactions and the formation of oxidized products are not significant enough to produce short hydrophilic leaching compounds. We can also predict that the majority of leaching compounds in the case of plasticized PVC consist of leached additives or their degradation products.

3.2.2 Analysis of Organic Products Leached from Plasticized PVC

Our first experiment consisted in identifying plasticizing compounds in leaching solution by HPLC-UV. The chromatogram for a leaching solution of irradiated plasticized PVC is shown in **Figure 4**.

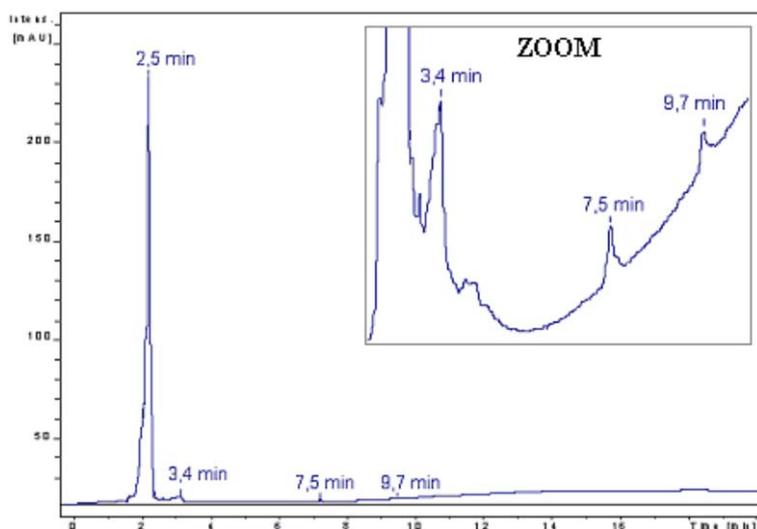


Figure 4. HPLC-UV chromatogram of the leaching solution of irradiated plasticized PVC (2 MGy)

To identify the leaching products, we compared HPLC-UV chromatograms of the pure plasticizers in plasticized PVC (di-isononyl phthalate, di-*n*-butyl phthalate, and 2-ethylhexyl diphenyl phosphate) with the chromatogram of the leaching solution shown in **Figure 4**. Phenol, a standard derivative product of 2-ethylhexyl diphenyl phosphate formed by radiolysis [20], was also studied.

The results show that di-*n*-butyl phthalate, 2-ethylhexyl diphenyl phosphate, and phenol belong to the leaching products (**Table II**). The corresponding peaks are very small and the quantity of these compounds in solution was determined. The measurement results show that these products are leached in small quantities. In comparison with TOC measurements of the leaching solution, the plasticizer concentrations correspond to only a few percent of the leached organic compounds (**Table II**). We therefore focused on the first wide massive peak at 2.5 minutes on the HPLC-UV chromatogram (**Figure 4**). This peak, which appears at short retention times, probably corresponds to very polar or ionic products. Ion chromatography performed to identify these products.

Leaching solutions of plasticized PVC were analyzed by ion chromatography to quantify the ionic leaching products. These analyses show that the main leaching products are phthalic ions. In all the leaching solutions of plasticized PVC studied, the quantities of phthalic ions measured by ion chromatography represent a large fraction of the TOC in the leaching solution (**Table II**). The phthalic ions, which are the main leaching products, are formed by basic hydrolysis, due to the alkaline leaching solution, of phthalic esters (di-*n*-butyl phthalate, di-isononyl phthalate) contained in plasticized PVC.

Table II. Identification and quantification of organic products released by leaching of plasticized PVC

Retention time (min)	Compounds	Concentration of compounds in leaching solution (expressed as a % of measured TOC)
9.7	2-ethylhexyl diphenyl phosphate	
7.5	di- <i>n</i> -butyl phthalate	< 5%
3.4	phenol	
2.5	phthalic ions	60-70%

4. Conclusion

Leaching in alkaline solution of organic compounds from plasticized PVC is controlled by diffusion phenomena described by Fick's second law, allowing the apparent diffusion coefficient (D_a) of organic compounds to be determined by experiments carried out on unirradiated or irradiated PVC. The impact of high doses on the leaching process consists of a decrease in D_a due to the modification of the PVC microstructure by radiation-induced crosslinking and grafting reactions. Leached organic products comprise a few plasticizers contained in plasticized PVC: di-*n*-butyl phthalate and 2-ethylhexyl diphenyl phosphate. Phenol, a degradation product of 2-ethylhexyl diphenyl phosphate, is also released. The main organic leaching products are phthalic ions formed by hydrolysis of phthalic esters contained in plasticized PVC.

The fact that the leaching products are mainly composed of phthalic ions resulting from hydrolysis of di-*n*-butyl phthalate and di-isononyl phthalate can explain the reduction in the maximum quantity of leached compounds, represented by TOC'. Radiolysis involves grafting by reaction of a radical formed by plasticizer radiolysis on PVC macromolecules [16-18]. This phenomenon implies that when PVC is irradiated a quantity of phthalic esters is consumed by grafting reactions. The quantity of leachable organic products thus decreases during irradiation since an increasing quantity of phthalic esters is involved in grafting reactions and cannot be leached.

The effect of temperature can be explained by the fact that leaching of organic compounds from plasticized PVC is controlled by diffusion phenomena, and is thus sensitive to a temperature rise. The modification of the behavior with the temperature is also ascribable to

the hydrolysis reactions producing phthalic ions from the corresponding phthalic esters, this type of reaction being favored by higher temperatures.

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