

Leaching of Plasticized PVC: Effect of Irradiation

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Received 9 November 2007; accepted 24 September 2008

DOI 10.1002/app.29612

Published online 5 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Highly irradiated (2–26 MGy) polyvinyl chloride (PVC) 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 (D_a) of plasticized PVC leaching products can be calculated for each sample. Irradiation at high dose causes D_a to diminish; this can be attributed to cross-linking 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 the hydrolysis of phthalic esters in alkaline leaching solution. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1372–1377, 2009

Key words: leaching; irradiation; PVC

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 health¹; the technological applications of PVC could be limited by environmental degradation such as oxidation, irradiation, hydrolysis, and leaching.

Few articles 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 more specifically as seals 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 leach-

ing 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 mainly composed 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.⁵ showed that DEHP migration in organic solution from sheets of unirradiated plasticized PVC was described by Fickian diffusion behavior. Mersiowky et al.^{6–8} 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). Shin et al.⁹ studied the leaching of flexible PVC containing di-isononyl phthalate (DINP) in aqueous solutions of NaOH. 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.¹⁰ studied leaching of PVC packaging material

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irradiated to 44 kGy in organic solution 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. 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. Samples were preferentially used as bulk materials to have them in the same shape as in the industrial application but crushed samples were used to accelerate some kinetics.

EXPERIMENTAL

Samples

The "pure PVC" used in these experiments was in fact a 50 : 50 mixture of two types of PVC manufactured by Solvay S.A. (France): 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 of 1 cm 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 phosphite.

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 method¹¹ or Perspex dosimeters (routine measurements).

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 or 50°C with a drying oven and renewed daily during the first 2 weeks of the experiment, and monthly thereafter.

Quantitative analysis

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.

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 as follows:

- HPLC-UV:
Column: YMC-ODS, 250 \times 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

RESULTS AND DISCUSSION

Irradiated plasticized PVC leaching process

Quantitative analysis of plasticized PVC leaching:
Effect of leaching temperature

Plasticized PVC irradiated to 4 MGy was leached at 20 and 50°C (Fig. 1). The results show that the temperature increases the leach rate of organic products. With a proper extrapolation of the curves, the calculation of the maximum quantity of leaching products

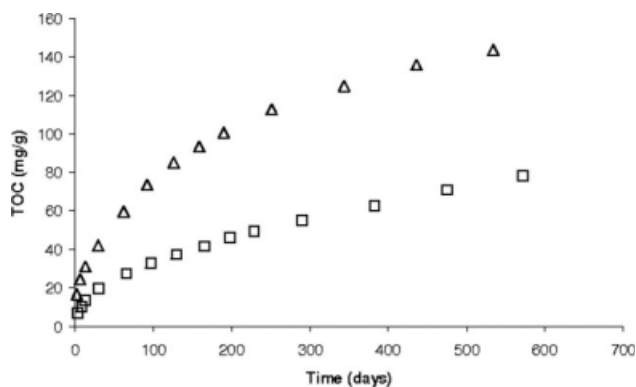


Figure 1 TOC measurements of unirradiated plasticized PVC leached at 20 and 50°C. (Δ , leaching at 50°C; \square , leaching at 20°C).

released at an infinite time appears to be the same at 20 and 50°C (though it is not obviously visible in Fig. 1 as the scale the graph is highly zoomed).

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.

Kim et al.⁵ noted this diffusion behavior in the case of DEHP migration in organic solution from sheets of unirradiated plasticized PVC. 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 and unirradiated plasticized PVC [eq. (1)].

$$Q(t) = 2Q^l \frac{S}{V} \sqrt{\frac{D_a \cdot t}{\pi}} \quad (1)$$

where $Q(t)$ is the quantity of organic compounds leached at time t , evaluated by TOC measurement at time t (mg of TOC per g of material); Q^l is the maximum limiting quantity of organic compounds

leached, evaluated by TOC^l measurement (mg of TOC per g of material). TOC^l is comparable with TOC measure at constant level; V is the total sample volume (m^3); S is the exchange surface area, i.e., total sample external surface area (m^2); D_a is the apparent diffusion coefficient ($\text{m}^2 \text{s}^{-1}$).

Leaching of organic compounds being a linear function of $t^{1/2}$ (Fig. 2), we concluded that leaching is diffusion-controlled. The slope (s) of these curves allowed us to calculate D_a , 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^l 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. $\text{TOC}^l = 140 \pm 9 \text{ mg g}^{-1}$ in both cases (at 20 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:

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

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

From eq. (1) we can calculate D_a , the diffusion coefficient of the total amount of organic compounds leached from plasticized PVC:

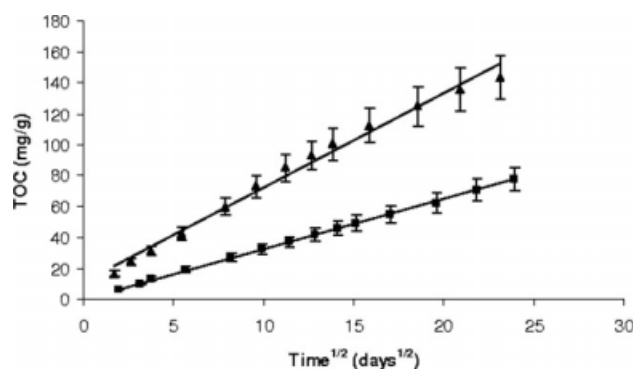


Figure 2 TOC measurements of unirradiated plasticized PVC leached at 20 and 50°C, evolution in $\text{days}^{1/2}$ (\blacktriangle , leaching at 50°C; \blacksquare , leaching at 20°C).

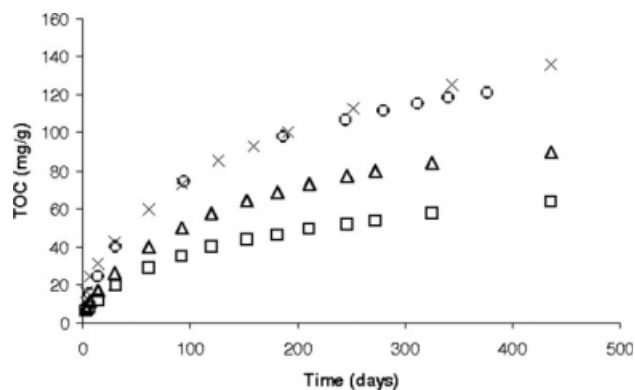


Figure 3 TOC measurements of unirradiated and irradiated plasticized PVC leached at 50°C. (×, leaching of unirradiated PVC; ○, leaching of PVC irradiated to 2 MGy; △, leaching of PVC irradiated to 18 MGy; □, leaching of PVC irradiated to 26 MGy).

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

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

This increase of D_a as a function of temperature is quite similar to the evolution of D_a noted by Kim et al.,⁵ who studied DEHP diffusion from a PVC/DEHP mixture in acetonitrile. They reported that the diffusion coefficient D_a corresponding to the migration of DEHP in acetonitrile increased from $2.72 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ at 30°C to $10.1 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ 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.

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 (Fig. 3) showed that the higher the irradiation dose, the lower is the maximum TOC^l 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 decreases the amount of leaching products.

Moreover, the leaching process slows down as the irradiation dose increases. This slowdown is clearly highlighted by comparing the slope of the $\text{TOC} = f(t^{1/2})$ curves, which decreases as the irradiation dose increases (Table I). 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 when compared with diffusion from an unirradiated sample.

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

The evolution of the apparent diffusion coefficient (D_a) 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 the 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 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.

Qualitative analysis of leaching products

Pure PVC versus plasticized PVC

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 products¹⁹; 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 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 TOC 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

TABLE I
Determination of Q^l , Slopes of the $\text{TOC} = f(t^{1/2})$ Curves, and Apparent Diffusion Coefficient (D_a) with Increasing Irradiation Doses

Dose (MGy)	$Q^l = \text{TOC}^l$ (mg g ⁻¹)	Slope (s) (mg g ⁻¹ s ^{1/2})	D_a (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}	$(4.2 \pm 0.4) \times 10^{-14}$

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.

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. This sample irradiated at 8 MGy can be considered as a good compromise to identify leaching products. Indeed, the shorter the irradiation is, the higher is the leached species concentration (Fig. 3 shows that TOC yields are still large), but the impact of irradiation on chemical compounds should also be important.

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 min on

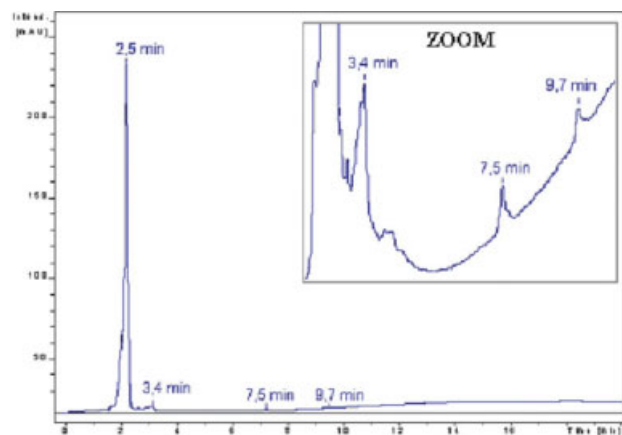


Figure 4 HPLC-UV chromatogram of the leaching solution of irradiated plasticized PVC (8 MGy). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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	<5%
7.5	Di- <i>n</i> -butyl phthalate	
3.4	Phenol	
2.5	Phthalic ions	60–70%

the HPLC-UV chromatogram (Fig. 4). This peak, which appears at short retention times, probably corresponds to very polar or ionic products. Ion chromatography performed to identify these products. It has to be also noticed that we did not measure any peaks corresponding to the di-isononyl phthalate though this plasticizer is in the initial composition. It may also be due to the too low concentrations in the leaching solutions for identification by UV analysis.

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 hydrolysis, due to the leaching solution, of phthalic esters (di-*n*-butyl phthalate, di-isononyl phthalate) contained in plasticized PVC. It is therefore difficult to have precise quantification of the initial phthalate compounds leached in the solutions.

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 results in the decrease in D_a because of the modification of the PVC composition and internal structure 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 the 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 TOC¹. 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.

The authors thank J. Vicente (CEA/DEVM, Cadarache) for irradiations and S. Castell (CEA/DEN, Cadarache) for ion chromatography experiments. They also thank M. Troulay and K. Ressayre for their experimental support during this work.

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