

# Migration of Additives in Simulated Landfills and Soil Burial Degradation of Plasticized PVC

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**ABSTRACT:** Commercial sunflower oil was epoxidized, and epoxidized sunflower oil (ESO) was used as a thermal stabilizer for polyvinyl chloride (PVC). Semirigid and plasticized formulations stabilized with ESO were realized. Three plasticizers were used: dioctyle phthalate (DOP), diisodocycle phthalate (DIDP), and diisononyle adipate (DINA). Leaching tests simulating real landfill conditions were performed. The two model leachates selected for laboratory leaching tests were solution of acetic acid and distilled water, respectively, corresponding to simulants for domestic waste leachates and rainfall on wastes deposited in bulk. The leaching tests were carried out at 25 and 50°C during 15 days. The variation of the mass of the samples

was followed as a function of time. On the other hand, the ageing of the PVC samples was investigated in a landfill soil for 6 months. The modifications of the structure of the polymer were followed by Fourier transform infrared spectroscopy (FTIR). Furthermore, the variation of density and mechanical properties (tensile and shore D hardness) were considered. The results showed that both nature and content of plasticizer influence the migration of the PVC additives used. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 525–531, 2009

**Key words:** epoxidized sunflower oil; plasticizers; biodegradation; landfill; PVC

## INTRODUCTION

Polyvinyl chloride (PVC) is one of the main plastics produced in large quantities. Its use is widespread and diverse, ranging from every day products to highly specialized applications.<sup>1</sup> PVC is still the main polymer of additive consumption as most of the plasticizers and heat stabilizers representing together one-third of the additives production are used there.<sup>2</sup> Plasticizers, primarily phthalates, are added to the originally rigid PVC to make flexible products. Stabilizers are indispensable to provide the necessary stability of the PVC against heat, light, and weathering. Applicable stabilizers are heavy metal and organotin compounds as well as organic costabilizers, depending on the desired product properties.<sup>3</sup>

After their service life, the greater part of postconsumer PVC products is assigned to demolition waste or municipal solid waste (MSW). Currently, the most common option is to dispose end-of-life PVC products in sanitary landfills. Landfills and their long-term behavior, however, constitute a source of uncertainty and risk.<sup>1</sup> The loss of additives may occur when PVC products are placed as wastes in

landfill sites, and in this case, it could be a hazard to the environment.<sup>4</sup> The loss of additives from polymer material is a complex process, involving three physical processes: (1) diffusion of additives up to the interface, (2) transport through the interface, and (3) loss of additives from the surface into the surrounding medium.

The loss of additives from the surface of polymer material into the surrounding medium can take place through three specific processes:<sup>5</sup>

- Evaporation: at which the additive goes into the surrounding gas medium (most often the air).
- Extraction: during which the additive goes into the surrounding liquid medium.
- Migration: at which the additive, in direct contact with the surface of the other material, migrates into that material.

Because of the concern on the release of phthalate esters into the environment, extensive investigations have been focused on the extraction and determination of released phthalates.<sup>6</sup> Although no direct evidence has been found on the toxic effects of phthalates to human beings, it has been proved that high dosage and long-term exposure of diisooctyle phthalate (DOP or DEHP), diisononyle phthalate (DINP), and dibutyle phthalate (DBP) to rodents resulted in liver cancer and adverse effects on the reproductive development for young male rats. In

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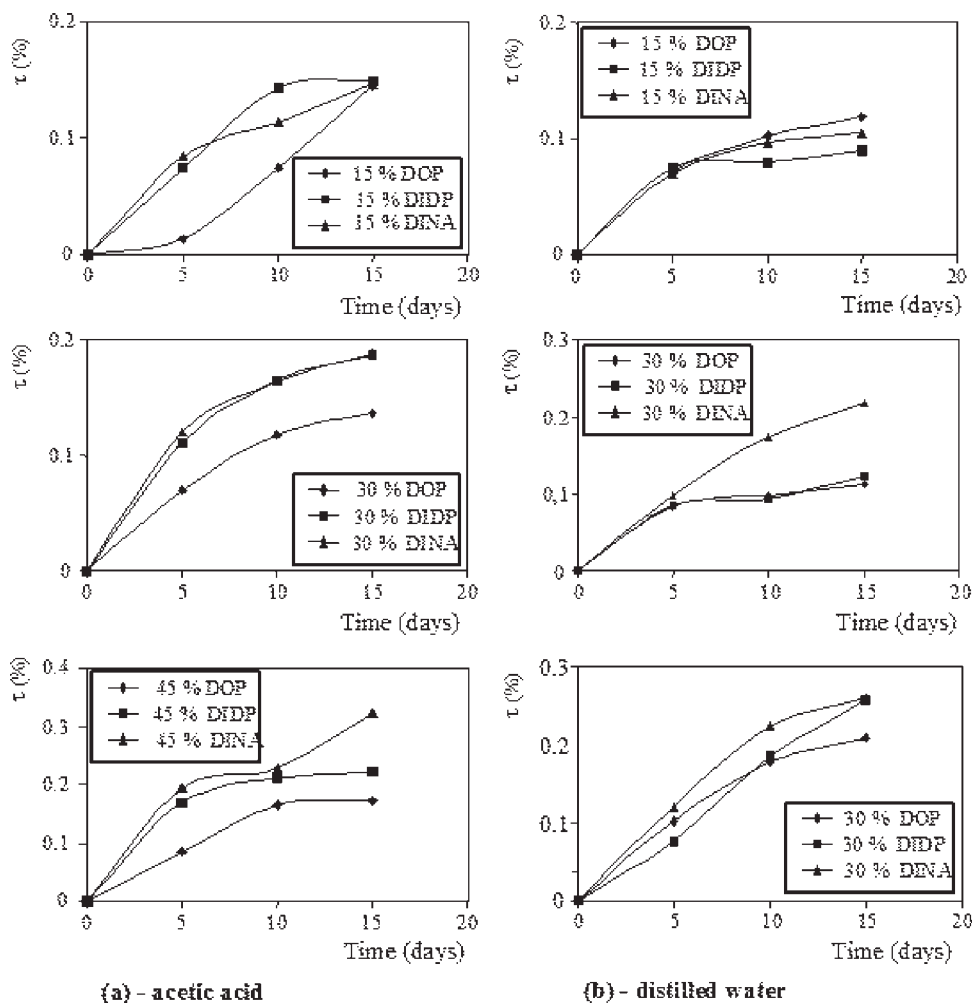


Figure 1 Effect of the nature of the plasticizer on the rate of mass variation at 25°C.

addition, phthalates were suspected to increase asthma and bronchial obstruction in children.<sup>7</sup> On the other hand, phthalates with long chains have a low biodeterioration under normal conditions of water treatment worn and are only partially degraded in the current installations of treatment of the lixivats and water in which they accumulate on solids in suspension.<sup>1</sup> Today, all the phthalates used in great quantities in the PVC products are omnipresent in the environment.

Concerning heat stabilizers, lead-based compounds are widely used in many PVC applications.<sup>3</sup> They are classified like toxic for the reproduction, harmful, dangerous for the environment (ecotoxic), and presenting a danger of cumulated effects.<sup>7</sup>

In previous works,<sup>8,9</sup> commercial sunflower oil was epoxidized, and the effects of epoxidized sunflower oil (ESO) on the thermal degradation and stabilization of PVC in the presence of metal carboxylates (Ba/Cd and Ca/Zn stearates) were investigated. Vegetable oils are renewable raw materials. Their conversion to useful intermediates for polymeric materials is signifi-

cant because of their low cost, ready availability, and possible biodegradability.

The use of environmentally benign additives is another way to improve the health and environmental issues. For that purpose, alternative plasticizer [diisononyl adipate (DINA)] and heat stabilizer (ESO) are used. The object of this work is to gain knowledge of the release of additives from semirigid and plasticized PVC stabilized with ESO and to compare the behavior of the formulations based on the proposed alternative additives to that of traditional formulations based on phthalate plasticizers [DOP and diisodicyclo phthalate (DIDP)].

## EXPERIMENTAL

### Materials

A suspension PVC (Shintech SE 1200 grade 1) produced by INC-USA was used. Commercial plasticizers (DOP, DIDP, and DINA) from "Société Générale des Plastifiants" (Tunisia), Zn stearate from Aldrich,

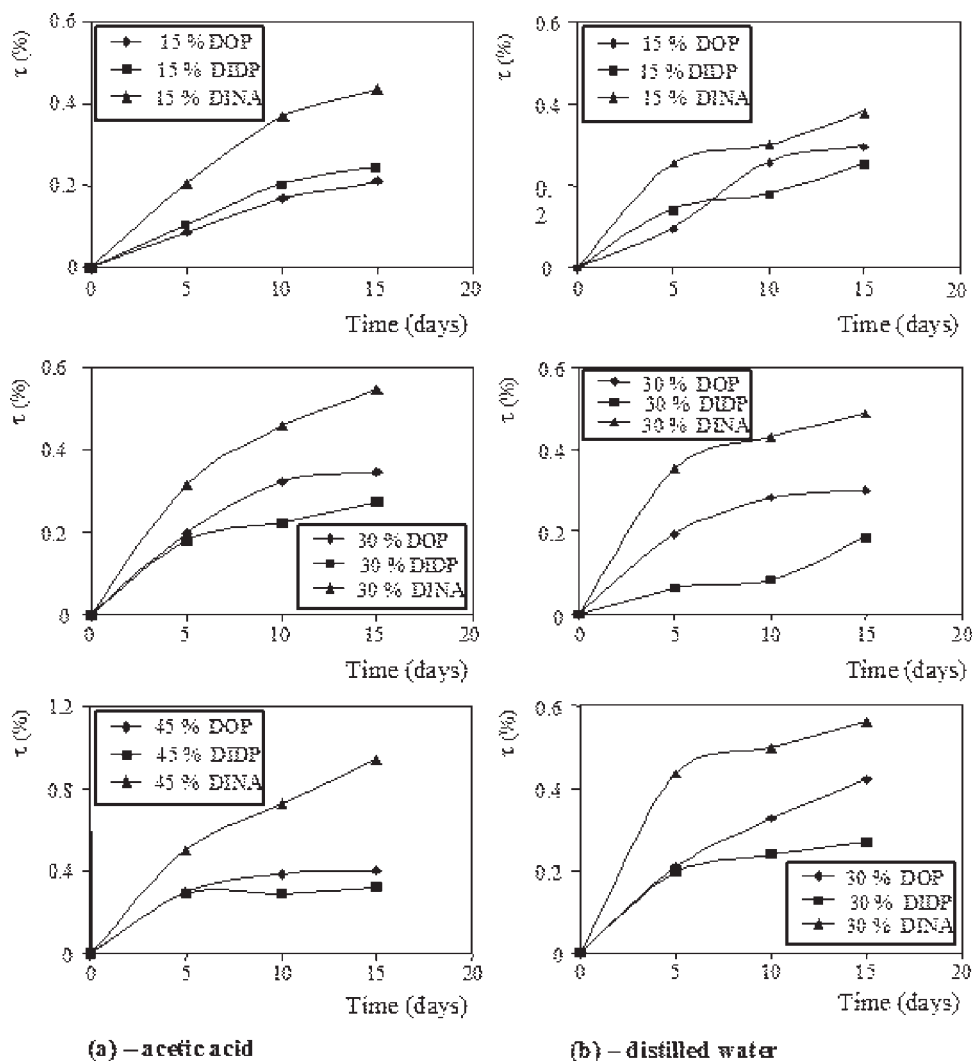


Figure 2 Effect of the nature of the plasticizer on the rate mass variation at 50°C.

Ca stearate from Prolabo, and stearic acid (stearine JOS) from SO. G. I.S.P.A (Italy) were used as received. ESO was especially prepared as described previously.<sup>8</sup> The level of oxirane oxygen was 6.4%.

### Preparation of PVC films

Formulations containing 1 wt % of Zn stearate, 1 wt % of Ca stearate, 5 wt % of ESO, 1 wt % of stearic acid, 15 wt % (semirigid PVC), 30 or 45 wt % (plasticized PVC) of plasticizer were prepared. Three plasticizers were considered: DOP, DIDP, and DINA. PVC and additives were mixed in a two-roll mill at 140°C and melt compressed at 170°C under a pressure of 300 kN/m<sup>2</sup> to obtain the desired thickness (2 ± 0.1 mm).

### Leaching tests

Leaching tests simulating real landfill conditions were performed using samples of PVC films cut into small strips about 25-mm long and 10-mm wide and

placed in 20 mL vessels. To each vessel, 15 mL of either distilled water or a simulated leachate was added, and the vessels were sealed and placed in an oven at different temperatures (25 and 50°C) for 15 days. A suitable simulant for domestic waste is a solution of 5000 ppm of acetic acid, buffered to pH 5 with sodium hydroxide.<sup>4</sup> Each sample was taken off, wiped, and weighed every day. The rate of variation of the mass was determined as a function of time following the relation:

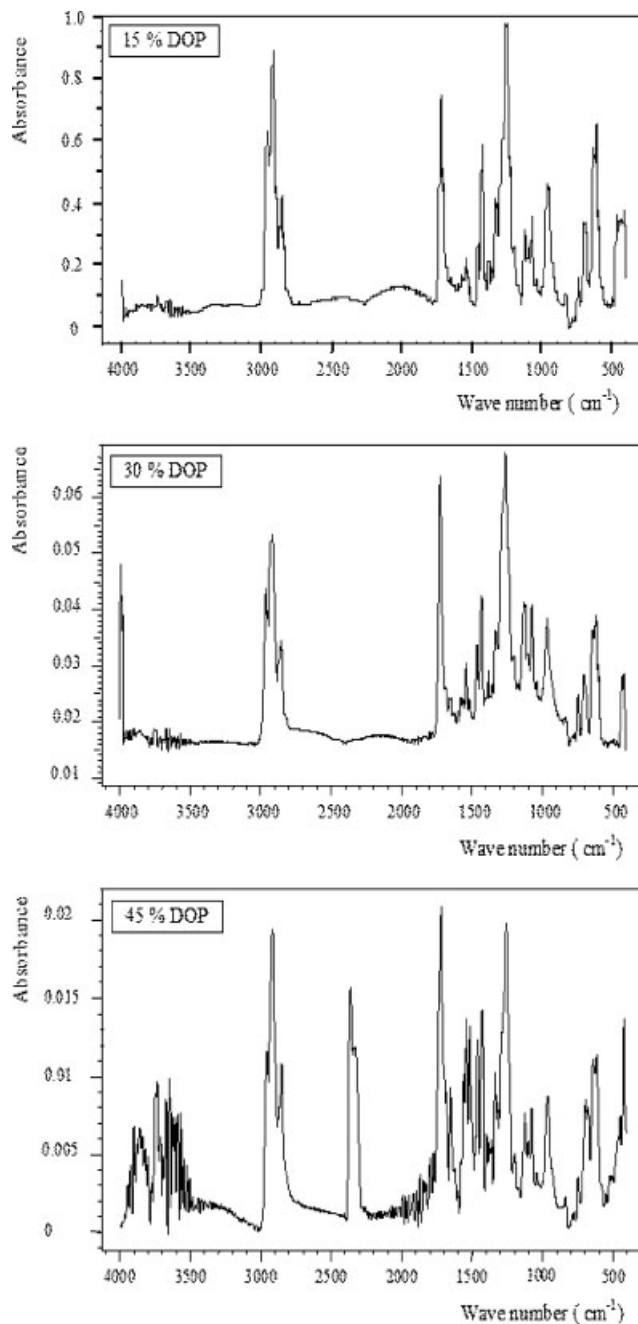
$$\tau = (m_t - m_0/m_0) \times 100 \quad (1)$$

where  $m_0$ , is initial mass before immersion and  $m_t$ , is mass of the sample at the time  $t$ .

$m$  and  $m_0$  were measured to an accuracy of 10<sup>-4</sup> g.

### Soil burial degradation test

Square samples of 10 cm were buried in the ground at a depth of 1 m; the site was located near a



**Figure 3** FTIR spectra of the samples plasticized with DOP after 6 months of soil burial.

landfill. After 6 months, the samples were taken off and characterized (Fourier transform infrared spectroscopy (FTIR), density, tensile, and shore D hardness).

#### FTIR analysis

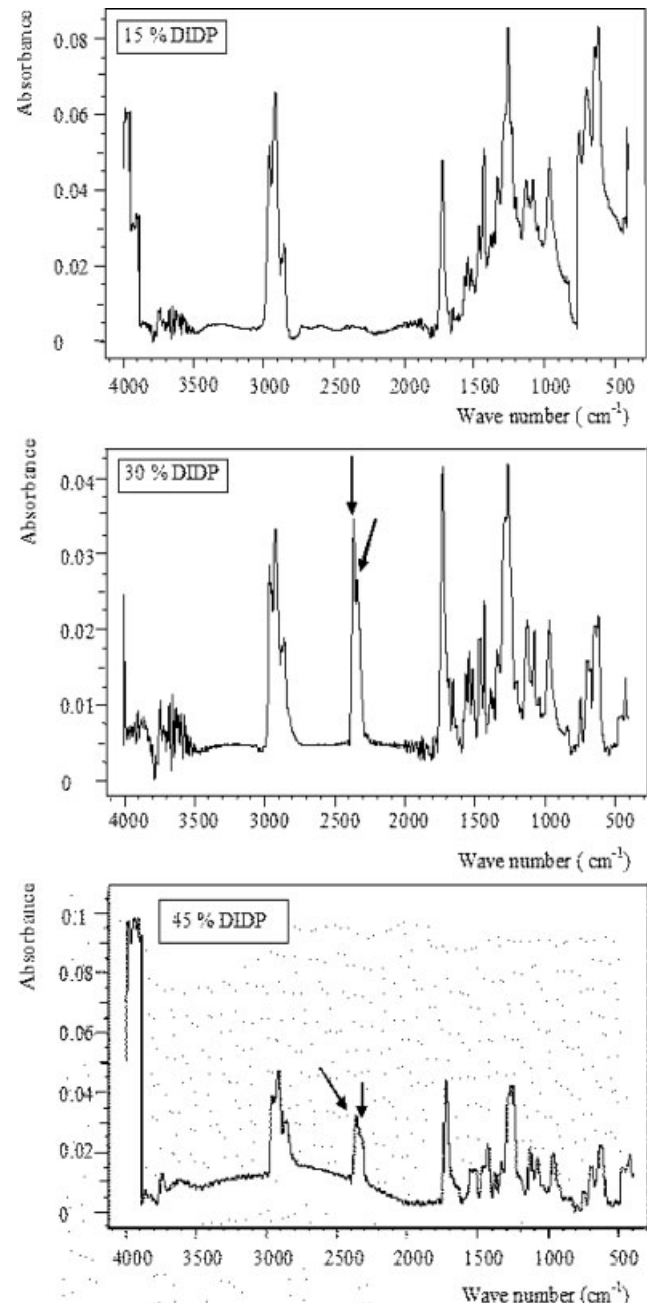
The PVC samples were dissolved in tetrahydrofuran. After evaporation of the solvent and drying at 40°C during 24 h, a polymeric film was recovered and analyzed with a JASCO-FTIR-430 spectrophotometer.

#### Density measurements

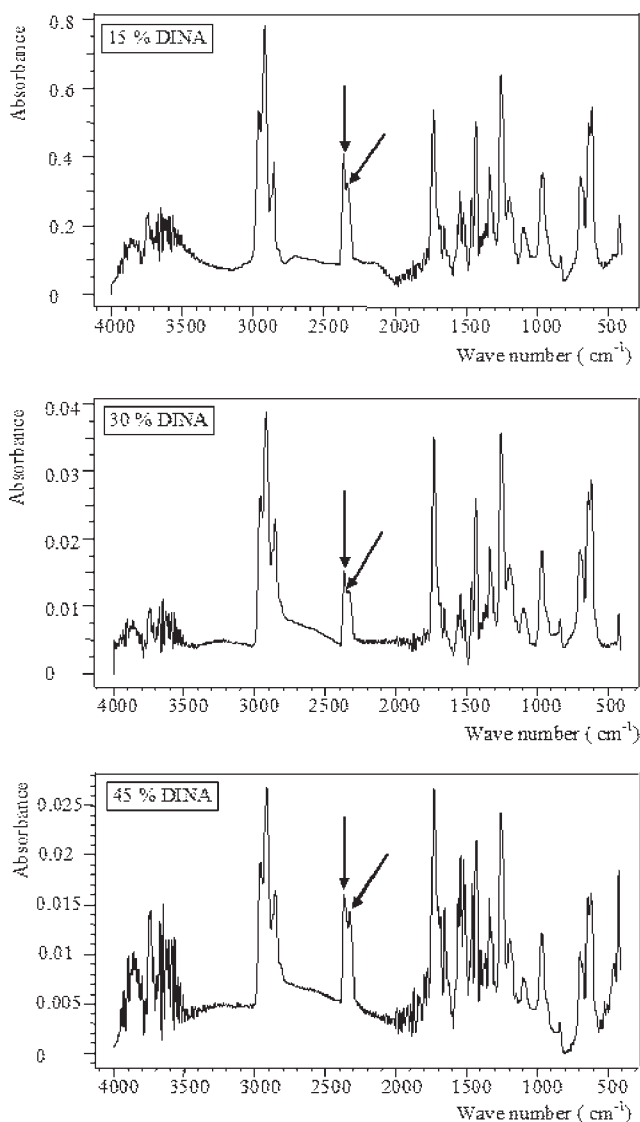
The density of the samples was measured according to the ISO/R1183.

#### Tensile properties

Measurements of tensile properties were undertaken using an INSTRON model 1185 (France) testing machine according to the ISO/R27 at a crosshead speed of 100 mm/s.



**Figure 4** FTIR spectra of the samples plasticized with DIDP after 6 months of soil burial.



**Figure 5** FTIR spectra of the samples plasticized with DIN A after 6 months of soil burial.

### Shore D hardness

Shore D hardness was measured according to ISO 868.

## RESULTS AND DISCUSSION

### Leaching test

The rates of mass variation ( $\tau$ ) as a function of time gives information's about the phenomenon which occurred between the samples and the two model leachates considered. An increase means that the leachates penetrated the samples, whereas a decrease means that some additives migrated in the leachates. The mass variation data corresponding to the various formulations considered with time of contact with acetic acid (simulant for domestic waste leachate) and distilled water (simu-

lant of rainfall on wastes deposited in bulk) at 25 and 50°C are given in Figures 1 and 2, respectively. It can be noted that  $\tau$  increases with time of contact in the two model leachates considered. This means the penetration of leachates in the PVC samples. Globally, Figures 1 and 2 show that  $\tau$  increases with the rate of plasticizer. This can be explained by the fact that the presence of the plasticizer increases the free volume between the PVC chains which facilitates the penetration of the leachates. On the other hand, it can be noted that, for a same concentration of plasticizer, the highest values of  $\tau$  are obtained for DIN A. This result is due to the lower steric hindrance of DIN A in comparison with DOP and DIDP.

Furthermore, the variation of  $\tau$  is relatively more important in the case of acetic acid [Figs. 1, 2(a)] in comparison with distilled water [Figs. 1, 2(b)] for all the considered formulations which is due to the higher polarity of acetic acid which favors its penetration in the PVC samples.

The comparison of Figures 1 and 2 shows that the variation of  $\tau$  is more pronounced at 50°C than at 25°C. It is obvious that the increasing of temperature leads to a higher mobility of the molecules and favors the interactions between PVC samples and leachates. In previous studies,<sup>10–12</sup> we have shown that the penetration of the simulants in the PVC samples favors the mobility of the additives present in the formulation and then their migration in the surrounding medium.

### Soil burial degradation test

#### FTIR characterization

After 6 months of soil burial near a landfill, the PVC samples were characterized. Figures 3–5 show the FTIR spectra of the samples containing 15, 30, and 45% of DOP, DIDP, and DIN A, respectively.

The appearance of two bands located at 2350 and 2300 cm<sup>-1</sup> can be observed on the PVC spectra containing 15, 30, and 45% of DIN A (Fig. 5), whereas these two bands are observed only for the concentrations of

**TABLE I**  
Characteristic Bands of the Used Additives Present in PVC Film<sup>10,12,13</sup>

Wave number (cm <sup>-1</sup> )	Assignment	Additive
1722	C=O (ester)	DOP, DIDP or DIN A
1578	CO <sub>2</sub> <sup>-</sup> (carboxylic acid salt)	Ca stearate
1537	CO <sub>2</sub> <sup>-</sup> (carboxylic acid salt)	Zn stearate
1460	CH <sub>2</sub> (methyl, methylene)	ESO, Zn stearate, DOP, DIDP or DIN A



TABLE II  
Variation of Absorbances Ratios as a Function of Time

	A1722/A1428	A1578/A1428	A1537/A1428	A1460/A1428
15% DOP (control)	1.008	0.989	0.984	0.990
15% DOP (6 months)	1.270	0.409	0.308	0.500
30% DOP (control)	1.009	0.989	0.989	0.994
30% DOP (6 months)	1.480	0.530	0.690	0.740
45% DOP (control)	1.012	0.991	0.989	0.994
45% DOP (6 months)	1.450	0.316	0.957	0.873
15% DIDP (control)	1.005	0.993	0.991	0.996
15% DIDP (6 months)	1.140	0.460	0.400	0.600
30% DIDP (control)	1.007	0.991	0.990	0.993
30% DIDP (6 months)	1.660	0.708	0.625	0.790
45% DIDP (control)	1.022	0.991	0.991	0.997
45% DIDP (6 months)	1.820	0.195	0.639	0.678
15% DINA (control)	0.998	0.989	0.988	0.991
15% DINA (6 months)	0.105	0.215	0.596	0.543
30% DINA (control)	1.005	0.993	0.994	0.994
30% DINA (6 months)	1.330	0.177	0.448	0.518
45% DINA (control)	1.010	0.998	0.989	0.992
45% DINA (6 months)	1.230	0.200	0.942	0.814

30 and 45% of DIDP (Fig. 4) and 45% of DOP (Fig. 3). These two bands are related to structures of the type  $X = Y = Z$  (where X, Y, Z can represent atoms of C, N, O, and S).<sup>13</sup> Their presence indicates that some biodegradation of the plasticizers occurred, and they are probably due to metabolites of plasticizers degradation by microorganisms which use them as source of carbon and energy.<sup>14,15</sup> The obtained results let suppose that the DINA because of its simplest structure is more easily attacked by the microorganisms.

To investigate the eventual modifications which occurred, the spectra of PVC alone and of additives present in the various formulations were compared with the spectrum of PVC with additives. This allowed the identification of some characteristic bands which are related to the additives present in the formulation as shown in Table I. A semiquantitative estimation of the modifications which occurred was done. For that purpose, the following absorbance's ratios were calculated:

$A_{1722}/A_{1428}$ : DOP, DIDP, or DINA.

$A_{1578}/A_{1428}$ : Ca stearate.

$A_{1537}/A_{1428}$ : Zn stearate.

$A_{1460}/A_{1428}$ : ESO, Zn stearate, DOP, DIDP, or DINA.

The band at  $1428\text{ cm}^{-1}$  is due to the vibration of  $\text{CH}_2$  of PVC<sup>16</sup> and was taken as a reference band. The variations of these four ratios of absorbances as a function of time are given in Table II.

Globally, the results show that:

- The absorbances ratios  $A_{1578}/A_{1428}$ ,  $A_{1537}/A_{1428}$ , and  $A_{1460}/A_{1428}$  decreased with the time of soil burial for all the formulations considered. This means that the concentrations of the corresponding additives (Ca stearate, Zn stearate, ESO, and the plasticizers) decreased in the PVC samples. This decrease may be due to a migration of these additives in the soil or to micro-organism attack.

TABLE III  
Variation of Density and Mechanical Properties with Time

Rate of plasticizer	Density ( $\text{g}/\text{cm}^3$ )		Elongation at break (%)		Stress at break (MPa)		Shore D hardness	
	Control	6 months	Control	6 months	Control	6 months	Control	6 months
15% DOP	1.29	1.31	125	50	4.21	7.89	78	80
30% DOP	1.25	1.28	305	290	2.37	2.58	60	63
45% DOP	1.22	1.24	350	295	2.16	2.20	46	48
15% DIDP	1.29	1.30	75	45	4.48	7.69	76	78
30% DIDP	1.24	1.29	262	240	2.71	2.74	65	68
45% DIDP	1.21	1.23	263	250	1.63	1.73	48	52
15% DINA	1.27	1.29	225	165	3.12	5.56	72	75
30% DINA	1.23	1.28	275	266	2.22	2.27	55	64
45% DINA	1.19	1.27	358	310	1.89	2.16	38	54

- The absorbances ratios  $A_{1722}/A_{1428}$  increased with time of soil burial for all the formulations considered. This fact is probably due to the metabolites of the plasticizers, whose presence was already evidenced by the appearance of the two bands at 2350 and 2300  $\text{cm}^{-1}$  in the spectra of Figures 3 and 4.

#### Variation of density and mechanical properties

Table III shows the variations of density and mechanical properties (elongation at break, stress at break, and shore D hardness) with time of soil burial. It can be noted that all the densities increased after 6 months of contact with soil. This means that the samples became more rigid and confirms the loss of the plasticizers due to various mechanisms such as extraction, migration, and bio deterioration as evidenced previously by FTIR analysis. Elongation at break decreased with time, whereas stresses at break and shore D hardness's increased. These variations can be explained by the loss of the plasticizers which reduced the flexibility of the samples. On the other hand, the void spaces (pores) resulting from the loss of the plasticizers are filled with water in soil. The 6 months of soil burial seem to be long time to allow the penetration of water through the PVC mass. The structure of PVC filled with water could also explain the results of mechanical properties given in Table III.

#### CONCLUSIONS

The rates of the mass variations increased for both model leachates considered indicating their penetration in the PVC samples. The phenomenon is

influenced by the plasticizer concentration, the temperature, the nature of the model leachate, and the nature of the plasticizers.

The soil burial test showed the loss of additives by migration and biodegradation which lead to the modification of the density and mechanical properties of the PVC samples.

Finally, it seems that the simple structure of DINA favors its biodegradation in comparison with phthalate plasticizers, and then, the tested alternative formulations are more environmentally compatible.

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