

Contamination of water by the poly vinyl chloride additives

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Abstract— The contact of PVC waste with leachate from landfills leads to the phenomenon of migration of the additives present and the contamination of soils and groundwater. The aim of this part of our work is to study the behavior of new formulations based on poly chloride of vinyl in contact with liquid media. For this, rigid and plasticized sheets were realized, two plasticizers were considered: di-octyl phthalate (DOP) and di-iso nonyl adipate (DINA). Epoxidized sunflower oil (ESO) was used as a heat stabilizer in combination with Zinc and Calcium stearates, epoxidized soybean oil (ESBO) was used for comparison. Migration tests were carried out in two media simulating landfill leachate and rainwater, namely, an acetic acid solution and distilled water at 25°C and 50°C. The evolution of the mass in contact with the two simulator medium was considered. PVC films were characterized by Fourier transform infrared spectroscopy. The different simulator mediums were analyzed by atomic absorption spectrometry (SAA). The results showed that the nature of the plasticizer and the thermal stabilizer influence the properties of the PVC as well as the migration phenomena.

Key words: PVC, Plasticizer, ESO, ESBO, migration, leachate, landfill.

I INTRODUCTION

Polyvinyl chloride (PVC) is the second most consumed plastic in the world; it is associated with the great technological innovations of the 20th century. It covers all sectors of economic activity, with a global consumption of more than 20 million tons, this is due to all its mechanical and physical properties and its ability to be modified [1] Any implementation of PVC requires the incorporation of additives: thermal stabilizers, plasticizers, lubricants, fillers, pigments, etc. In this study, we will focus on plasticizers and thermal stabilizers. Plasticizers are incorporated into the polymer in order to modify the properties of the resin and to develop new properties absent in the case of the resin itself [2]. Among the most used plasticizers are phthalates. The most commonly used are di ethyl hexyl phthalate (DEHP), di iso decyl phthalate (DIDP), and di iso nonyl phthalate (DINP). All phthalates in use today are ubiquitous in the environment. Air emissions and leaching from some applications appear to be the primary pathways through which phthalates enter the environment. Air emissions and leaching from certain applications appear to be the main routes by which phthalates enter the environment. Furthermore, the accumulation of phthalates in the human body can cause adverse health effects. DEHP affects male and female fertility [3,4]. An epidemiological study conducted in Italy revealed an excess of lung cancers in subjects exposed to various phthalates, including bis(2-ethylhexyl) phthalate [5] Therefore, the current trend in Europe is to reduce the use of phthalates. Thermal stabilizers are products that provide protection against thermal degradation caused by oxidation or solar radiation [6]. The objective of our work is the study of the behavior and migration of additives of new formulations based on polyvinyl chloride (PVC) in water experience was carried out by evaluating the parameters of three formulations: mass variation, analysis by FTIR and SEM.

II MATERIALS

A. PRODUCTS

1. Plasticizer

The plasticizers used in the preparation of the various formulations are supplied by General Society of Plasticizers (Tunisia). They are dioctyl phthalate (DOP) and diiso nonyl adipate (DINA), with molar masses of 390.6 g/mol and 398.6 g/mol, respectively.

2. Thermal Stabilizers

The thermal stabilizer used is epoxidized sunflower oil combined with zinc and calcium stearates. Epoxidation of sunflower oil was carried out at 50 °C, using peracetic acid prepared in situ by reaction of hydrogen peroxide (30% V/V) with excess glacial acetic acid in the presence of Amberlite IR 120 ion exchange resin. The oxirane oxygen (O.O) content is 6.4% [7].

B. FORMULATIONS PRODUCED AND PREPARATION METHOD

Three plasticized formulations were developed: P (DINA, ESO), P (DOP, ESO), and P (DOP, ESO). The resin and additives were cold-mixed. The resulting mixture was then introduced into a twin-roll mixer heated to 140 °C for 15 to 20 minutes. The gelled mixture was then placed between two plates of a Fontigine tabletop press at 170 °C under a load of 300 kN for 5 minutes to obtain the desired thickness (approximately 2 mm).

C. MIGRATION TESTS

Rectangular specimens, 25 mm long and 10 mm wide, were cut from each plate and placed in tubes, each containing 20 ml of acetic acid solution (5000 ppm) adjusted to pH=5 with sodium hydroxide (NaOH) solution. This simulant medium has been proposed as a simulant of leachate from domestic waste [8]. The same number of samples was introduced into tubes containing 20 ml of distilled water, for comparison and as a simulant of rainwater in contact with landfill waste. The test was carried out in an oven at 25 ± 2 °C and 50 ± 2 °C. Each experiment lasted 30 days. Regular samples were taken every five days. The specimens were weighed before and after immersion to monitor the change in mass. A SARTORIUS balance was used for this purpose. The accuracy is 0.001 g.

1) SPECTROSCOPIC CHARACTERIZATION

The samples were prepared as very thin films. To do this, a mass of 0.15 ± 0.05 g of sample was dissolved in tetrahydrofuran (THF). The resulting solution was spread onto a watch glass in the form of a very thin film and dried at 40 °C for 24 hours. The PVC films were characterized by Fourier transform infrared spectroscopy using a SHIMADZU FTIR-8400 instrument with a resolution of 2 cm⁻¹.

2) Atomic Absorption Spectrometry Analysis

After 30 days of immersion in acetic acid and distilled water, the various simulant media were analyzed by atomic absorption spectrometry in accordance with standard NF V05-113-1972. The study focused on Cd, Zn, and Ca.

II RESULTS AND DISCUSSION

A. PRELIMINARY STUDY BASED ON MASS VARIATION RATE

The rate of change of mass of the specimens as a function of contact time was monitored using the following formula:

$$\zeta (\%) = \frac{m_t - m_0}{m_0} \times 100 \quad \dots\dots\dots(1)$$

Where: m_t represents the mass of the sample taken at time t after wiping.
 m_0 represents the initial mass of the sample.

1. EFFECT OF THE NATURE OF THE PLASTICIZER

Table 1 shows the evolution of the mass variation rate as a function of contact time with acetic acid and distilled water at 25 °C and 50 °C. We note that, for the same plasticizer rate, the mass variation is relatively greater in the case of DINA, and this, for the two simulating media and the two temperatures considered. This result is explained by the greater polarity of this plasticizer and its lower steric hindrance compared to DOP, these results are in agreement with those illustrated in reference [9], found by Gächter and Müller (1990) in a study carried out on the migration of three plasticizers: DINP, DIDP and DINA. On the other hand, in their study on the migration of two plasticizers DOA and DOP in olive oil, reference [10] related to Kondili et al who observed that the migration of DOA is more important compared to that of DOP, this result can be explained by the difference in solubility of the two plasticizers as well as by their molecular weight.

2.EFFECT OF THE NATURE OF THE SIMULATOR MEDIUM

Table 1 shows that the mass variation is slightly greater in acetic acid than in distilled water, which is due, overall, to the greater polarity of the first simulator medium [11; 12; 13]

3.EFFECT OF TEMPERATURE

The mass variations are greater at 50 °C than at 25 °C (table 1). This is directly linked to the fact that temperature increases the mobility of molecules and promotes their migration [11; 14; 15].

Table 1: Evolution of the rate of mass variation as a function of time.

a) Acetic acid, 25 °C

Time (days)	P (DOP,ESO)	P(DINA,ESO)
0	0	0
5	0	0
10	0	0
15	0	0
20	0	0
25	0,0065	0,0208
30	0,0121	0,0096

b) Distilled water , 25 °C

Time (days)	P (DOP,ESO)	P (DINA, ESO)
0	0	0
5	0	0
10	0	0
15	0	0
20	0	0
25	0	0
30	0,0120	0,0166

c) Acetic Acid, 50 °C

Temps (jours)	P (DOP,ESO)	P(DINA,ESO)
0	0	0
5	0	0
10	0	0
15	0	0
20	0	0
25	0,0126	0,0172
30	0,0131	0,0370

d) Distilled water, 50 °C

Temps (jours)	P (DOP ESO)	P (DINA,ESO)
0	0	0
5	0	0
10	0	0
15	0	0
20	0	0
25	0,0128	0,0123
30	0,0170	0,0169

4. STUDY OF PVC FILMS AFTER CONTACT WITH THE SIMULATING ENVIRONMENTS

Figure 1 represents the infrared spectrum of the DINA-plasticized formulation stabilized with ESO before immersion and after 30 days of immersion in acetic acid (I) and distilled water (II) at 25 °C. The absorbance ratios of the different additives present in each formulation after 30 days of immersion in acetic acid (I) and distilled water (II) at 25 °C and 50 °C are illustrated in Tables 2 and 3. We note, overall, that all absorbance ratios decreased after 30 days of contact with the two simulant media, for all formulations and for the two considered temperatures. These results confirm the migration of the additives present in the considered formulations (DOP, DINA, Ca and Zn stearate, ESO and ESBO).

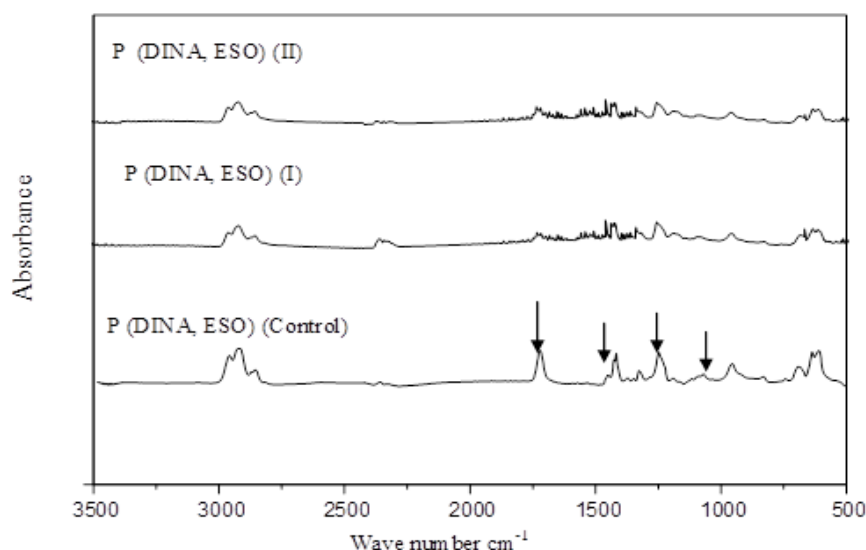


Figure 1: Infrared spectra of formulations containing DINA and ESO after 30 days of immersion in acetic acid (I) and distilled water (II) at 50 °C.

Table 2: Absorbance ratios of the different additives present in each formulation after 30 days of immersion in acetic acid (I) and distilled water (II) at 25 °C.

	A1726/A1433		A1466/A1433		A1337/A1433		A1130/A1433	
	t = 0 days	t = 30 days	t = 0 days	t = 30 days	t = 0 days	t = 30 days	t = 0 days	t = 30 days
P (DOP, ESO) (I)	0,110	0,061	0,088	0,047	0,082	0,043	0,068	0,035
P (DOP, ESO) (I)	0,123	0,073	0,092	0,057	0,098	0,049	0,086	0,039
P (DINA, ESO) (I)	0,163	0,0781	0,136	0,0534	0,135	0,053	0,121	0,037
P (DOP, ESO) (II)	0,110	0,073	0,088	0,0558	0,082	0,0445	0,068	0,040
P (DOP, ESO) (II)	0,123	0,112	0,092	0,070	0,098	0,070	0,086	0,067
P (DINA, ESO) (II)	0,184	0,163	0,169	0,136	0,158	0,135	0,158	0,121

Table 3: Absorbance ratios of the different additives present in each formulation after 30 days of immersion in acetic acid (I) and distilled water (II) at 50 °C.

	A1726/A1433		A1466A1433		A1337/A1433		A1130/A1433	
	t = 0 days	t = 30 days	t = 0 days	t = 30 days	t = 0 days	t = 30 days	t = 0 days	t = 30 days
P (DOP, ESO) (I)	0,110	0,108	0,088	0,084	0,082	0,077	0,068	0,071
P (DOP, ESO) (I)	0,123	0,061	0,092	0,044	0,098	0,041	0,086	0,040
P (DINA, ESO) (I)	0,163	0,065	0,136	0,055	0,135	0,048	0,121	0,035
P (DOP, ESO) (II)	0,110	0,109	0,088	0,065	0,082	0,064	0,068	0,063
P (DOP, ESO) (II)	0,123	0,104	0,092	0,077	0,065	0,068	0,086	0,098
P (DINA, ESO) (II)	0,163	0,069	0,136	0,052	0,135	0,048	0,121	0,036

5. APPLICATION OF ATOMIC ABSORPTION SPECTROMETRY TO THE STUDY OF PVC/SIMULATING MEDIA INTERACTIONS

The metal concentrations of the different additives included in the plasticized formulations after 30 days of immersion in acetic acid (I) and distilled water (II) at 25 °C and 50 °C are shown in Tables 4 and 5. The results show that the Ca and Zn contents increase after 30 days of immersion in acetic acid (I) and distilled water (II) for both formulations and both considered temperatures, which confirms the influence of temperature as well as the nature of the simulating medium on the migration phenomenon [16]. As for Cd, the concentrations remained below the detection limit of the device.

Table 4: Heavy metal contents in plasticized formulations after 30 days of immersion in acetic acid (I) and distilled water (II) at 25°C

	[Cd] en mg/l		[Ca] en mg/l		[Zn] en mg/l	
	t = 0 jours	t = 30 jours	t = 0 jours	t = 30 jours	t = 0 jours	t = 30 jours
P (DOP, ESO) (I)	< 0,01	< 0,01	< 0,05	8	0,5	7
P (DOP, ESO) (I)	< 0,01	< 0,01	< 0,05	3	0,5	1,9
P (DINA, ESO) (I)	< 0,01	< 0,01	< 0,05	3	0,5	1,9
P (DOP, ESO) (II)	< 0,01	< 0,01	< 0,05	8	0,2	7
P (DOP, ESO) (II)	< 0,01	< 0,01	< 0,05	3	0,2	0,2
P (DINA, ESO) (II)	< 0,01	< 0,01	< 0,05	4	0,2	0,2

Table 5: Heavy metal contents in plasticized formulations after 30 days of immersion in acetic acid (I) and distilled water (II) at 50 °C.

	[Cd] mg/l		[Ca] mg/l		[Zn] mg/l	
	t = 0 days	t = 30 days	t = 0 days	t = 30 days	t = 0 days	t = 30 days
P (DOP, ESO) (I)	< 0,01	< 0,01	< 0,05	34	0,5	9,4
P (DOP, ESO) (I)	< 0,01	< 0,01	< 0,05	80	0,5	14
P (DINA, ESO) (I)	< 0,01	< 0,01	< 0,05	48	0,5	4,2
P (DOP, ESO) (II)	< 0,01	< 0,01	< 0,05	<0,05	0,2	1,3
P (DOP, ESO) (II)	< 0,01	< 0,01	< 0,05	<0,05	0,2	1,3
P (DINA, ESO) (II)	< 0,01	< 0,01	< 0,05	2	0,2	1,3

III Conclusion

Migration tests showed that interactions take place between the considered formulations and the used simulators and that factors such as temperature, the nature of the plasticizer, the nature of the simulator medium as well as the nature of the thermal stabilizer have a direct influence on the migration phenomenon of the different additives (DOP, DINA, Ca and Zn stearate, ESO and ESBO). This phenomenon was highlighted by Fourier transform infrared spectroscopy (FTIR) and atomic absorption spectrometry (AAS).

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