

# Natural weathering of plasticized polyvinyl chloride (PVC) Stabilized with Epoxidized Sunflower Oil.

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*Abstract:* - The aim of this work is to study the influence of the weathering conditions on the degradation level of stabilized PVC. Epoxidized Sunflower oil (ESO) was used as a new biodegradable stabilizer for PVC. Flexible plasticized formulations (40% plasticizer) were realized, the natural weathering of the PVC samples was investigated. The samples were exposed in Tizi Ouzou (Algeria) for nine months. The samples were characterized by Fourier transform infrared spectroscopy in order to follow the structural changes. Moreover, the variation of the mass of the samples, the variation of density and mechanical properties (tensile and shore D hardness) were taken into account. Samples were characterized in terms of morphology by SEM. The best results were obtained with the formulation containing DINA and ESO compared to the traditional formulation containing DOP and ESO.

*Key-Words:* - PVC, ESO, natural weathering, DINA, DOP.

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## 1 Introduction

Poly Vinyl Chlorid (PVC), which will be the subject of our study, has a long history of development which began almost 100 years ago with the patenting of the concepts of emulsion and suspension polymerization, the development of the industrial process for synthesizing vinyl chloride, and patents on its plasticization, followed by the development of stabilization about 75 years ago [1]. PVC is one of the most important and widely used thermoplastics due to its many valuable properties such as: low price, good processability, chemical resistance and low flammability. It is approved for use as films and seals for cork bottles in general

contact applications [2]. Phthalates are a class of chemicals substances used as plasticizer for the PVC. They have the particularity to confer certain flexibility to plastics. They are found in products as diverse as paints, synthetic inks and fragrances, drugs, medical devices, food packaging, toys, etc. In 1973, 93% of plasticizers in PVC were phthalates. The most commonly used are: di-ethylhexyl phthalate (DEHP), di-isodecyl phthalate (DIDP) and di-isononyl phthalate (DINP) [3, 4].

Phthalates are toxic substances that compromise immune function, the endocrine and reproductive systems, neural and physical development, as well as the increased risk of cardiovascular disease [5-7].

Stabilizers are indispensable to provide the necessary stability of the PVC against heat, light and weathering [8]. Indeed, When Polyvinyl chloride (PVC) is exposed to high temperatures and/or UV irradiation in the presence of oxygen, free radical chain reactions take place leading to scission and/or crosslinking of the polymer chains and consecutively to a deterioration of the polymer's physical structure [6-10]. The rate of thermal degradation can be reduced by the addition of thermostabilizers to a level which is acceptable from a technological point of view [10-12]. Addition of stabilizers to PVC may improve its photostability [13-15]. Applicable stabilizers are heavy metal and organotin compounds as well as organic co-stabilizers, depending on the desired product properties [16]. Lead is also considered to be an endocrine disruptor and may affect the reproductive function of both men and women. In the human body, this metal is mainly found in the form of inorganic compounds: on the one hand in the respiratory system, in the form of aerosols containing lead (absorption by the lungs) on the other hand through food and drink (absorption from intestine and the stomach). It is a cumulative toxicant that can cause neurological and hematological disorders known as lead poisoning. The risk of lead poisoning is higher in young children, especially 1 to 3 years old [17].

The aim of this work is to pursue the study of the influence of the weathering conditions on the degradation level of pasticized PVC. New formulations based on PVC in order to preserve the environment were realized, di-iso nonyl adipate (DINA) was used as a substitute plasticizer for phthalates and sunflower oil was used in order to replace lead stabilizers.

## 2 Experimental

### 2.1. Materials

#### 2.1.1. PVC resin

Shintech SE 1200 grade 1 is a PVC resin produced by the American company INC-USA, polymerized in suspension.

#### 2.1.2. The plasticizers

The plasticizers (DOP and DINA) used in the preparation of the different formulations are provided by the general society of plasticizers (Tunisia).

### 2.1.3. Epoxidized Sunflower Oil (ESO)

Commercial suspension PVC resin, Shentech 1200 (American company INC-USA), with K value 71.1 according to DIN 53 726 and Mn= 78700 was used. Zn and Ca stearates complex (Reapak BCV/3037) from IACN (Italy) and epoxidized soya bean oil (ESBO) from Akdeniz Kimya A.S. (Turkey) are commercial products used as received. Epoxidation of sunflower oil was carried out at 50 °C in a 250 ml three-necked flask fitted with a condenser, a mechanical stirrer, and a thermometer; using the peracetic acid prepared in situ by reacting 20 ml of hydrogen peroxide (30 % V / V) and 20 ml of commercial sunflower oil (100%) with an excess of glacial acetic acid in the presence of Amberlite IR 120. The reaction medium is stirred and heated for 2 hours. Subsequently, we proceeded to the decantation of the solution and removing the aqueous phase, then washing the oily phase with distilled water until the acid phase is purified (pH = 7) [18].

### 2.2. Preparation of PVC Films

The resin and the additives were mixed: 100 g of PVC, 2 g of Zn and Ca stearates complex, 5 g of ESO or ESBO, 1 g of stearic acid and 40 g of DOP or DINA. The obtained mixture was then introduced into a rotary two- roll mill (Lescuyer S.A, France) heated at 140 ° C for 15 minutes. The mixture is then placed between two trays of a tabletop press (Fontigine BV, Holland) to obtain the desired thickness (2 ± 0.1 mm).

### 2.3. Natural Weathering

The PVC samples were mounted on metallic plates (Tizi-Ouzou, Algeria) placed facing southwards in a 45° angle with the plane of the earth as per ASTM D1435-99 [19]. The PVC samples subjected to the natural weathering exposure (November 2016- July 2017) were cut from a larger sheet measuring 100 mm x 100 mm. The exposure site is located at an elevation of 153.40 m, its latitude North is 36 ° 43' and longitude East 04° 1'. The samples were periodically taken out and characterized. The rate of variation of the mass was determined as a function of time following the relation:

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

Where  $m_0$  is the initial mass sample at the time  $t_0$  and  $m_t$  is the mass of the sample at the time  $t$  (after natural weathering).

## 2.4. Sample Characterization

### 2.4.1. Physical Properties

The density was measured according to the ISO/ R1183, using DSM densimeter (Lhomargy S.A, France).

### 2.4.2. Mechanical Properties

The tensile properties were measured using MTS Criterion model 42 testing machine (MTS Systemes, France), strained at a rate of 100 mm/min according to T51-034 standard. The Shore D hardness was measured using Exacta Bareiss Shore D durometer (Prolabo, Germany) according to NFT 51-109 standard. The results from mechanical testing are presented as average values of three measurements for each type of sample. The determination of the Residual thermal stability at  $200 \pm 1$  °C was carried out according to the standard ISO 182-2. The weight of the samples was 0.5 g. The time required to the appearance of red colour in the pH- paper is associated to the stability determined by (pHs) expressed in minutes.

### 2.4.3. FTIR Analysis

The weathered PVC samples were analyzed directly by FTIR spectroscopy in ATR mode by using a Jasco FT/IR-4200 spectrophotometer (Jasco Inc, Easton MD, USA). Spectra were collected in the spectral range of 4000 to 400  $\text{cm}^{-1}$ , using 60 scans at a resolution of 8  $\text{cm}^{-1}$ .

### 2.4.4. Thermal Properties

#### 2.4.4.1. Residual Thermal Stability

The determination of the Residual thermal stability at  $200 \pm 1$  °C was carried out according to the standard ISO 182-2. The weight of the samples was 0.5 g. The time required to the appearance of red colour in the pH- paper is associated to the stability determined by (pHs) expressed in minutes.

#### 2.4.4.2. Thermogravimetric Analysis.

Thermogravimetric analysis leads to evaluate the mass loss, thermal stability and rate of

decomposition that a sample undergoes during heat treatment as a function of temperature. The thermograms of the various samples were recorded using a LINSEIS STA PT 1600 type thermogravimetric device, controlled by a microcomputer. The mass loss is measured using a thermobalance under an inert nitrogen atmosphere in a temperature range of 20 to 700 ° C with a heating rate of the order of 20 ° C / min.

### 2.4.5. Morphology Analysis

The PHILIPS ESEM XL30 scanning electron microscope with tungsten filament was used. It is coupled with a complete system of microanalysis EDS-X (Energy Dispersive of X-Rays, Belgium). The surfaces were prepared by cutting the samples (5 mm, Rotation:  $n \times 360^\circ$ ). A wet mod at 10 mbar  $\text{H}_2\text{O}$  vapor at the voltage of 20 KV was chosen for observation; the signal was recorded using a detector for backscattered electrons.

## 3 Results and discussion

### 3.1. Variation of mass

According to the mass variation results (table 1), It can be noted a significant increase in mass variation rate as a function of natural ageing time, which explains penetration of water in the different sample; this is due to the quantities of rainfalls measured in the area (table 2).

**Table 1.** Mass variation as a function of natural weathering time

Time (months)	Mass variation (%)		
	DOP, ESO	DOP, ESBO	DINA, ESO
3	1.068	0.2817	0.2983
6	4.87	0.829	1.0369
9	7.262	1.79	1.7194

**Table 2.** Climatic data of the study region (Tizi ousou, Algeria).

	Years									
	2016		2017							
	November	December	January	February	March	April	may	June	July	
Minimum average temperature (°C)	11,4	9,3	5,2	8,6	8,8	10,5	15,2	19,8	22,3	
Maximum average temperature (°C)	21,3	17,6	13,7	18,2	21,2	23	29,6	34,6	37,5	
Medium average Temperature (°C)	16.35	13.45	9.45	13.4	15	16.75	22.4	27.2	29.9	
Precipitations (mm)	68,4	150,1	250	36	29	37	02	8,8	0.4	
Monthly relative humidity (%)	72	85	82	75	72	68	62	58	49	
medium wind m/s	1,5	0,9	1,5	2,2	2.1	2.2	2.2	2.7	2.4	
Sunshine Duration (Hours)	171	140	133	154	273	270	312	341	349	

### 3.2. Variation of Physical and Mechanical Properties

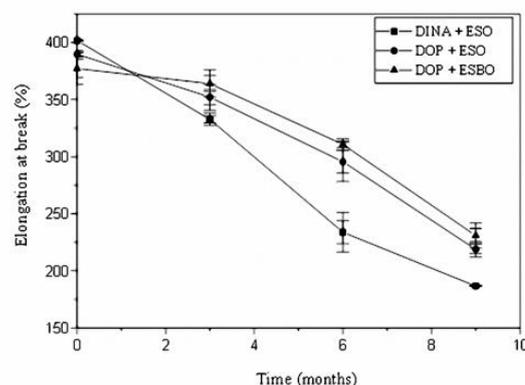
Table 3 shows that the density increases in the case of the three considered formulations, which explain the loss of the plasticizer.

**Table 3.** Variations of density as a function of natural weathering time.

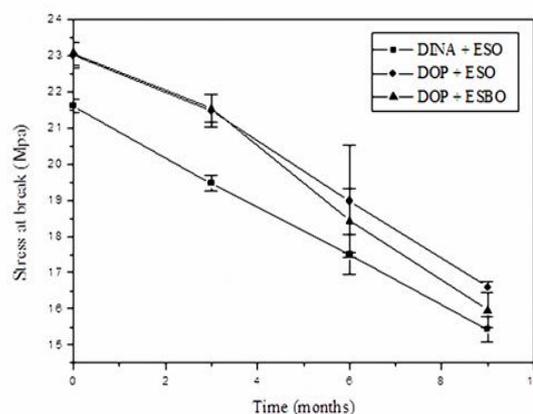
Time (months)	Density (g/cm <sup>3</sup> )		
	P (DOP, ESO)	P (DOP, ESBO)	P (DINA, ESO)
0	1,2 ± 0,000	1,2 ± 0,000	1,16 ± 0,000
3	1,22 ± 0,000	1,22 ± 0,000	1,2 ± 0,000
6	1,22 ± 0,000	1,2 ± 0,000	1,2 ± 0,000
9	1,24 ± 0,000	1,24 ± 0,000	1,24 ± 0,000

Figures 1, 2 and 3 indicate the mechanical properties of the PVC sample as function of natural weathering time. We can see a decline in the elongation rate during the 09<sup>th</sup> month of the natural ageing. These variations may be due to an eventual loss of plasticizer which reduced the flexibility of the samples and/or to the structural modifications that occurred in the polymer backbone upon aging [20]. The decrease of the stress at break induced by the weathering is generalized at all PVC formulations, these results are in agreement with those obtained in similar studies [21-23]. They show that chain scission reactions occurred during the

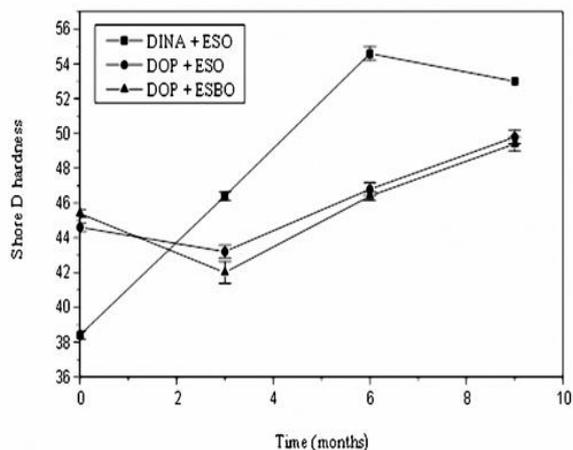
exposure of the samples to natural weathering. However, the shore D hardness decrease during the third months of the natural ageing in the case of the samples containing DOP; this is due probably to the absorption of water (525,3 mm/year) which conferred to the samples a light plasticization [24]. For the samples Containing DINA, the shore D hardnes increased during the period of the natural weathering, which indicate the loss of the plasticizer. The total influence of weathering can be considered as a composite effect of solar UV radiation, moisture and temperature. The climatic data of the study region (Tizi ousou, Algeria) are presented in table 2. Numerous studies indicate that this change is linked to the thermal decomposition and photooxidation of PVC [20]; and to the chemical changes in the surface and internal oxidation [25].



**FIG.1** Evolution of the elongation at break as a function of natural weathering time.



**FIG.2** Evolution of the stress at break as a function of natural weathering time.



**FIG.3** Evolution of the shore D hardness as a function of natural weathering time.

### 3.3. FTIR Analysis

In order to explain the PVC aging results, the samples were analyzed by infrared spectroscopy. The different additives containing in the different samples of PVC were characterized (table 4) [26-29].

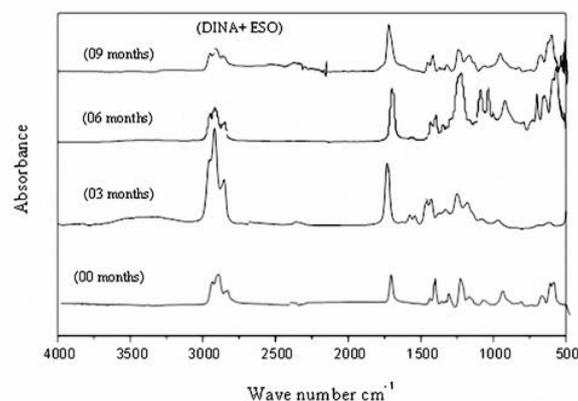
**Table 4** Characteristic bands of the additives present in PVC film

n°	Wave number [cm <sup>-1</sup> ]	Assignment	Additive
1	1726	C = O (ester)	ESO, ESBO, DOP and DINA
2	1466	CH <sub>2</sub> (methyl, methylene)	ESO, ESBO, Zn and Ca stearates complex, DOP and DINA
3	1337	CO <sub>2</sub> <sup>-</sup> (carboxylic acid salts)	Zn and Ca stearates complex
4	1130	C-O-C	ESO, ESBO

The results of the FTIR analysis show the:

- Appearance of a new bands at 1627 cm<sup>-1</sup> and 1667 cm<sup>-1</sup> due to the formation of conjugated double bonds. Our results corroborates with those found by Chaochanchaikul and *al.*, which indicates that the polyene contents of PVC were found to increase with increasing weathering time [30].
- Appearance of a new bands at 1889 cm<sup>-1</sup> in the case of the samples containing DINA and ESO due to the formation of conjugated double bonds (figure 4);

- Appearance of a new band between 3200 and 3500 cm due to hydroxyl compounds (alcohols, carboxylic acids, hydroperoxides) which are associated with chain scissions that occurred during aging of the samples;
- Disappearance of the band at 3455 related to the chain scissions after three months of natural weathering in the case of the samples containing DOP and ESBO, and after six months for the formulation containing DOP, ESO and DINA, ESO;
- increase of the absorbance ratios (table 5) of the new bands formed during aging A1627/A1426 and A1654/ A1426, in the case of samples containing DOP, ESBO and DINA, ESO, which is due to an increase of the concentration of conjugated double bonds and thus indicates that the dehydrochlorination of PVC occurred [20].
- Decrease of the absorbance ratios A1726/ A1436, 1466/1436 and A1337/ A1436 and A1130 /A1436 with time of aging. The decrease can be explained by the loss of additive.



**FIG.4** FTIR spectra of PVC samples containing ESO and DINA after various times of natural weathering.

**Table 5** Variations of absorbance ratios as a function of time of natural weathering.

	00 months	03 months	06 months	09 months
DOP, ESBO				
1726/1436	7.828	2.460	2.315	2.390
1466/1436	0.934	1.000	0.767	0.815
1337/1436	0.934	0.747	0.863	0.684
1130/1436	1.131	1.043	1.821	1.445
1618/1436	-	0.660	0.136	0.434
1654/1436	-	1.130	0.231	0.510
2341/1436	-	1.347	-	0.434
2368/1436	-	0.313	-	0.434
3455/1436	-	1.217	-	-
DOP, ESO				
1726/1436	1.297	2.830	2.67	1.844
1466/1436	0.650	1.000	0.829	0.333
1337/1436	0.505	0.648	0.975	0.688
1130/1436	0.650	0.648	2.207	1.333
1618/1436	-	-	0.682	-
1654/1436	-	0.507	-	-
2341/1436	-	0.804	0.182	1.000
2368/1436	-	0.945	0.207	0.511
3455/1436	-	1.14	0.243	-
DINA, ESO				
1726/1436	2.730	2.781	2.505	2.109
1466/1436	0.915	1.096	0.811	0.619
1337/1436	0.915	0.866	0.905	0.523
1130/1436	0.866	0.866	1.811	0.523
1618/1436	-	0.278	0.529	0.519
1654/1436	-	0.296	0.576	0.571
1984/1436	-	-	-	0.333
2341/1436	-	0.509	0.117	0.285
2368/1436	-	0.545	0.165	0.271
3455/1436	-	1.23	0.211	-

On the other hand, DOP contains steric hindrance linked to the presence of an aromatic ring in its structure, resulting in less efficient homogenization of the constituents of the formulation, less efficiency of the stabilizing system and a greater quantity of still active thermal stabilizers, which resulted in the increase in residual thermal stability. In addition, it can be noted that the residual thermal stability decreased in the case of all the considered formulations, which suggests that the phenomena of degradation of the thermal stabilizers was occurred [3, 31, 32].

**Table 6** Variation of residual thermal stability at 200°C as function of natural weathering time.

residual thermal stability (min)			
Time, months	P (DOP, ESO)	P (DOP, ESBO)	P (DINA, ESO)
Control	7,00	8,00	5
3	6,25	7,5	4,37
6	5,34	6,25	4,00
9	5,15	6,10	3,7

### 3.4. Thermal Properties

#### 3.4.1. Residual Thermal Stability

The residual thermal stability varied as a function of the weathering time in the case of all the considered formulations. The thermal stability of samples plasticized by DOP is relatively greater compared to samples plasticized by DINA (table 6). This difference can be explained by the amount of heat stabilizers still active in the sample. In fact, during the preparation of the formulations, a certain amount of stabilizers is consumed following chemical reactions with the HCl released by the PVC and is transformed into an inactive form (ZnCl<sub>2</sub>, CaCl<sub>2</sub>, -CHCl-CHOH-). Therefore, the determination of the residual thermal stability provides information on the amount of thermal stabilizer still active in the PVC sample. It is known that the plasticizer allows better homogenization of the constituents of the formulation and, consequently, better efficiency of the stabilizing system. Thus, the obtained results show that because of its linear structure and its low viscosity, the DINA allowed the best homogenization of the constituents of the formulation and the best efficiency of the stabilizing system, hence the smaller amount of active thermal stabilizers and the lowest residual thermal stability.

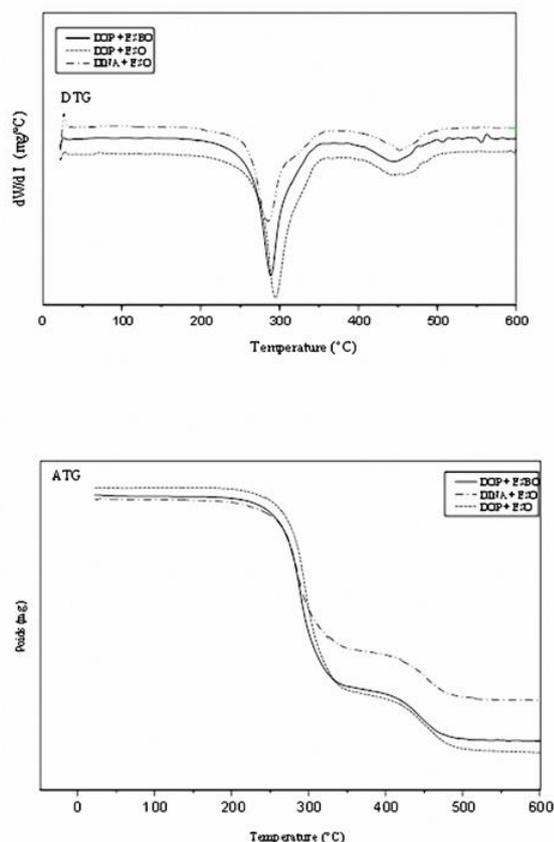
#### 3.4.2. Thermogravimetric Analysis (TGA)

The derivatograms recorded under a nitrogen atmosphere (Figure 5) for plasticized samples after nine months of natural weathering are similar. The mass loss was recorded at 205 °C for the samples plasticized by DOP and 208 °C in the case of the samples plasticized by DINA, the mass loss accelerated at 286-450 °C. The first stage (200-250) corresponds to the dehydrochlorination of the polymer [33, 32]. In the first step the temperature of maximum weight loss is important in the case of the samples plasticized with DINA compared to the samples containing DOP, this result leads to say that the formulation based on DINA and ESO is more stable. The peak at 450 is produced by PVC decomposition [34].

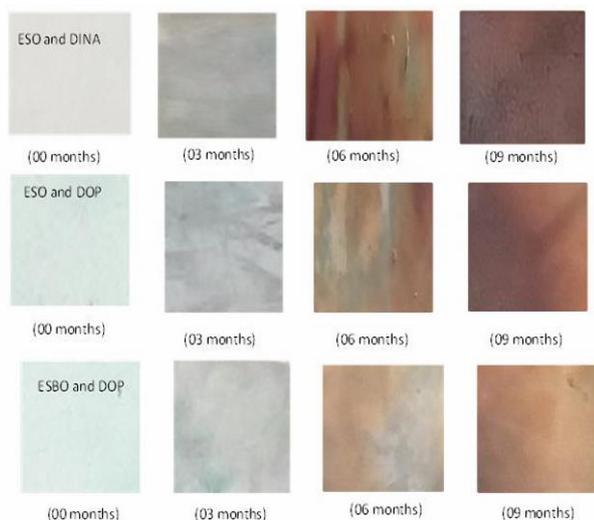
#### 3.5. Visual Observation

After various time of natural weathering (figure 6), a gradual change in colour can be observed in the case of the three plasticized samples probably related to the degradation, dehydrochlorination of PVC, and dust buildup on samples during natural weathering [35]. Furthermore, there is a considerable change for samples containing the DINA and epoxidized

sunflower, which shows the degradation of the polymer by the phenomenon of photo oxidation [36].



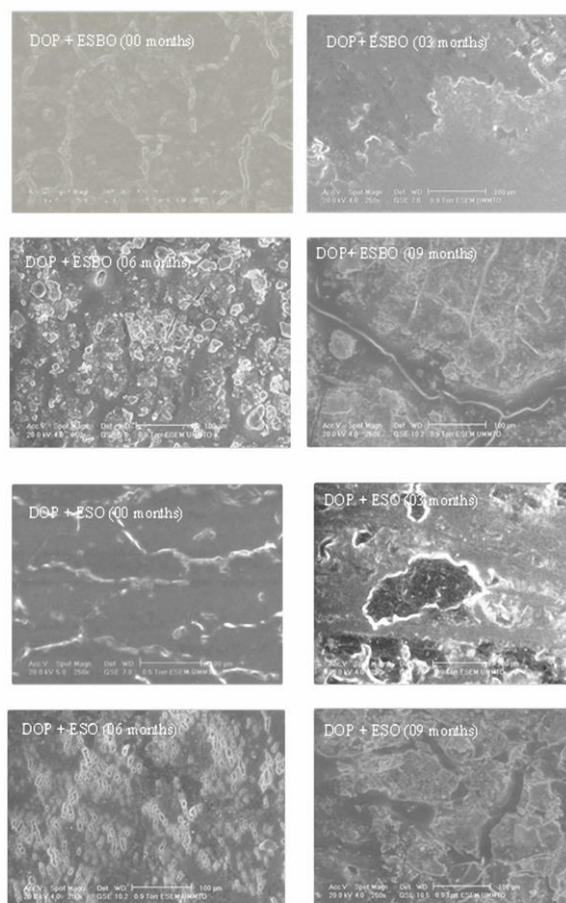
**FIG.5** ATG and DTG curves recorded under a nitrogen atmosphere for the PVC samples after nine months of natural weathering.



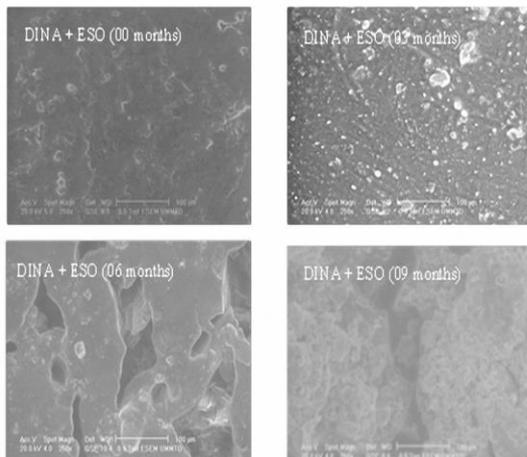
**FIG.6** Photographs of the samples as function of time of natural weathering.

### 3.6. Analysis by Scanning Electron Microscopy

Analysis of the plasticized samples by scanning electron microscopy (figure 7) reveals holes at various locations that are due to the migration and degradation of additives. In addition, the obtained results can be explained with the fact that the area of degradation in PVC consists of two layers. The surface layer which is subjected to oxidation grows old because of tear of macromolecular chains. Below the surface layer down to some depth, the hydrogen chloride is eliminated and conjugation polyene chain's dominate [37].



**FIG.7** Scanning electron microscopy analysis of the PVC samples containing DOP, ESO or ESBO after various time of the natural weathering.



**FIG.8** Scanning electron microscopy analysis of the PVC samples containing DIN and ESO after various time of the natural weathering.

## 4 Conclusions

The results from this study showed a modification of the mechanical properties after natural weathering. The results show that chain scission reactions occurred during the exposure of the samples to natural weathering;

The FTIR spectra reveals the appearance of a new bands at  $1627\text{ cm}^{-1}$  and  $1667\text{ cm}^{-1}$  due to the formation of conjugated double bonds and appearance of a new band between  $3200$  and  $3500\text{ cm}^{-1}$  due to hydroxyl compounds (alcohols, carboxylic acids, hydroperoxides) which are associated with chain scissions that occurred during aging of the samples. The absorbance ratios of the new bands formed during aging  $A_{1627}/A_{1426}$  and  $A_{1654}/A_{1426}$  increase in the case of samples containing DOP, ESBO and DIN, ESO, which is due to an increase of the concentration of conjugated double bonds and thus indicates that the dehydrochlorination of PVC occurred. This result is confirmed by Thermogravimetric Analysis (TGA) and Residual Thermal Stability;

Analysis of the plasticized samples taken after various time of natural weathering by scanning electron microscopy reveals holes at various locations that are due to the migration and degradation of additives;

Finally, it seems that ESO-based formulations offer very interesting prospects.

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### **Contribution of individual authors to the creation of a scientific article (ghostwriting policy)**

**FARID HAMITOUCHE:** Carried out the practical part of this work;

**NADIA LARDJANE:** Supervised the PhD student Farid Hamitouche during the realization of his work and the preparation of the article;

**YVES GROHANS:** Contributed in the preparation of the article taking into account these relevant remarks;

**HASSIBA LARIBI-HABCHI:** Supervised the PhD student Farid hamitouche during the realization of his work;

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She is the laboratory director; she contributed in the supervision of the PhD student Farid Hamitouche and the preparation of the article.

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