

# Influence of Polluted Atmospheres on the Natural Aging of Poly(vinyl chloride) Stabilized with Epoxidized Sunflower Oil

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**ABSTRACT:** Semirigid and plasticized poly(vinyl chloride) (PVC) samples, stabilized with epoxidized sunflower oil (ESO), Zn, and Ca stearates, were exposed in Algiers (hot, Mediterranean climate) for 12 months in three sites where the concentrations of atmospheric pollutants ( $\text{NO}_x$ ,  $\text{O}_3$ , hydrocarbons) are known. The evolution of the mechanical properties (tensile test and shore D hardness) was followed according to the aging time. The modification structure of polymer was investigated

by Fourier transform infrared spectroscopy. The results have shown that all the considered properties were affected. Furthermore, it seems that the  $\text{O}_3$  exerted the most deleterious effect, followed by hydrocarbons and then by  $\text{NO}_x$ . © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1973–1978, 2008

**Key words:** PVC; epoxidized sunflower oil; aging;  $\text{O}_3$ ;  $\text{NO}_x$ ; hydrocarbons

## INTRODUCTION

Plastics materials suffer changes in appearance and properties on weathering. The main weather parameters and their effects, which were investigated, are UV radiation, heat, and humidity.<sup>1–7</sup> Industrial pollutants are playing, regrettably, an ever increasing role in our environment and up to now less attention has been paid to their effect on the weatherability of polymers.<sup>8,9</sup> Air pollution is usually defined as the presence in the outdoor atmosphere of substances put there directly or indirectly by an act of man, in amounts, which are detrimental to health and safety or interfere with the full use of materials or property, for example, made from polymeric materials.<sup>10</sup> Man is not the only agent able to pollute the atmosphere. There are many natural processes that do so such as pollination of plants, volcanic emptions, dust storms, and forest fires. There are also secondary pollutants in the atmosphere, formed in the air from primary pollutants, due to acts by man; for example, smoke, industrial pollutants, and photochemical smog formed in the air from substances emitted from automobile, exhaust, and other sources. The major air pollutants are particulate matter, sulfur oxides, nitrogen oxides, hydrocarbons, and photochemical oxidants such as ozone, atomic oxygen,

singlet oxygen, and peroxyacetylnitrate.<sup>11</sup> The concentration of air pollutants is very important for long-term properties of polymeric materials.

Poly(vinyl chloride) (PVC) is a widely used polymer due to its excellent properties. Nevertheless, the low-thermal stability is one of its main disadvantages. The problem can be solved by the use of thermal stabilizers that must perform at least two basic functions: substitute stable groups for allylic and tertiary chlorine atoms and neutralize HCl.<sup>12,13</sup> Epoxidized vegetable oils are of great importance in polymer industry. They are essentially used as stabilizers and/or plasticizers for chlorine-containing polymers.

In previous studies,<sup>14,15</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. It was found that ESO acts as an acceptor for the liberated HCl and a retardant for the apparition of discoloration.<sup>14</sup> Synergistic effects were found when ESO is used in combination with metal carboxylates.

It is known that the products of thermal degradation often increase the vulnerability of a polymer to weathering and thermal stabilizers are required to limit this type of degradation. Thermal stabilizers do not directly protect the polymer against natural weathering but are of crucial importance in determining weatherability because they limit degradation during processing.

The aim of this work is to study the natural aging of PVC stabilized with ESO in presence of Zn and

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Ca stearates. For that purpose, the PVC samples have been exposed in Algiers for 12 months in three (03) sites in which the concentrations of atmospheric pollutants ( $\text{NO}_x$ ,  $\text{O}_3$ , and hydrocarbons) are known. Various analytical techniques were used to evaluate the variations of the mechanical and chemical properties resulting from the environmental corrosion.

## EXPERIMENTAL

### Materials

Commercial PVC suspension resin, Petvinil S3971 from Petkim (Turkey) was used. Zn stearate from Aldrich, Ca stearate from Prolabo, dioctylphthalate (DOP) from SGP (Tunisia), and stearic acid from SO. G. I. S. SPA (Italy) was employed. ESO was especially prepared as described previously.<sup>14</sup> The level of oxirane oxygen was 6.4%.

Two formulations containing 1 wt % of Zn stearate, 1 wt % of Ca stearate, 5 wt % of ESO, 1 wt % of stearic acid, 10 wt % (semirigid PVC), and 50 wt % of DOP (plasticized PVC) were prepared based on the polymer weight. PVC and additives were mixed in a two-roll mill at 140 and 170°C, respectively, for plasticized and semirigid formulations. The blends were then melt compressed at 170°C and 340 KN/m<sup>2</sup>. The thickness of the samples was about (2 ± 0.1) mm.

### Natural exposure in Algiers

The specimens to perform all measurements were exposed to outdoor weathering in Algiers (hot, Mediterranean climate), according to the standard ISO 4607(1985), for 1 year in three sites where the concentrations of atmospheric pollutants are known.

#### Site I

It is situated in the center of the town. This stuffy site is characterized by a heavy traffic (1400–1700 vehicles/day), which permits the accumulation of pollutants. The levels of  $\text{NO}_x$  are high.<sup>16</sup>

The  $\text{NO}$  average content/day is about 60 ppb with average content/hour of 300 ppb sometimes.

The  $\text{NO}_2$  average content/day is about 30 ppb with average content/hour higher than 60 ppb sometimes.

#### Site II

It is representative of an urban area. The amount of aromatic hydrocarbons is high. The average contents of benzene and toluene are, respectively, about 28 and 38  $\mu\text{g}/\text{m}^3$ . The total amount of aromatic hydrocarbons (benzene, toluene, ethyl benzene, and xylene) is about 100  $\mu\text{g}/\text{m}^3$ .<sup>17</sup>

#### Site III

It is situated in the suburbs and is characterized by a weak traffic, which results in low levels of hydrocarbons and  $\text{NO}_x$ . The level of  $\text{O}_3$  is high. The average amount of  $\text{O}_3$  is about 50 ppb/day, while the amounts of  $\text{NO}_x$  are relatively weak (10–15 ppb).<sup>16</sup>

The weathered samples were taken every 3 months and characterized. On the other hand, samples were kept in an interior ambience to serve as control. They were characterized in the same manner than the weathered ones.

### Experimental methods of characterization

#### Mechanical properties

Measurements of tensile properties were undertaken using an Instron 1185 machine according to the standard AFNOR NF T51-034. A shore D type durometer was used for the determination of the hardness of the samples according to the standard AFNOR T51-109. All the reported values of mechanical properties are averaged by five measurements on the specimens.

#### Fourier transform infrared spectroscopy

The Fourier transform infrared spectroscopy (FTIR) analysis was carried out on purified PVC samples with a JASCO FTIR-430 spectrophotometer. The polymer was purified by five cycles of dissolution in tetrahydrofuran (THF) and precipitation with methanol. Then, it was dissolved in THF. After evaporation of the solvent at 40°C during 24 h, a polymeric film was recovered and analyzed.

## RESULTS AND DISCUSSION

### Mechanical properties

Figures 1 and 2 illustrate, respectively, the variations of stress and strain at break as a function of the exposure time in months for semirigid and plasticized PVC. They show clearly that the properties at break in the three sites decreased with exposure time while they remained practically constant for the control. Although the variations were relatively weak, the effect of exposure site was evidenced. It seems that the  $\text{O}_3$  exerted the most deleterious effect, followed by hydrocarbons and then  $\text{NO}_x$ . The decrease of the mechanical properties at break is due to the fact that several complex chemical changes take place in PVC during weathering, including dehydrochlorination and oxidation, which in turn lead to changes in color, cross linking, chain scission, and general deterioration of the physical properties.<sup>3–15</sup>

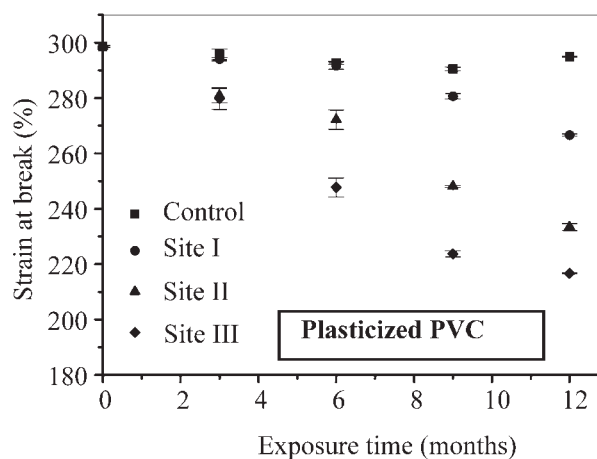
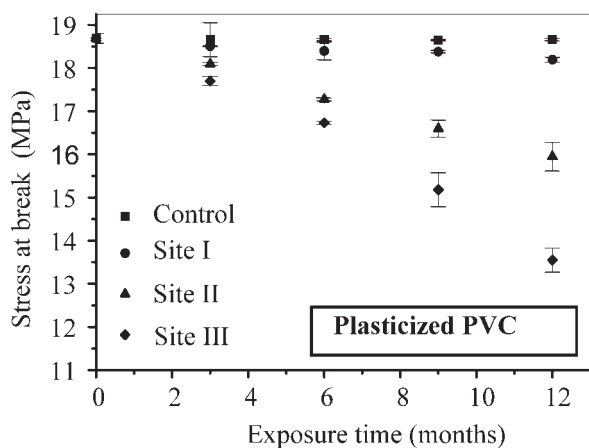
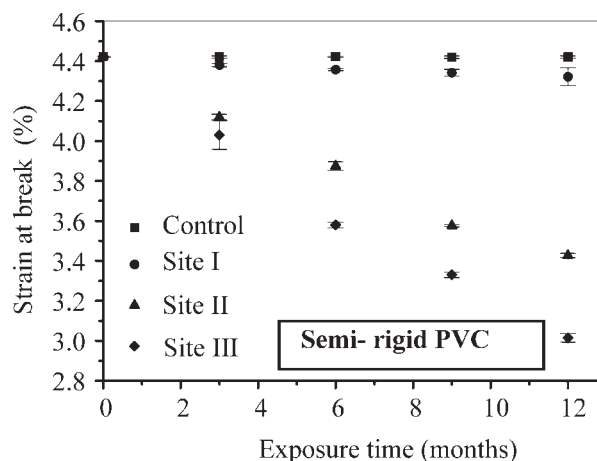
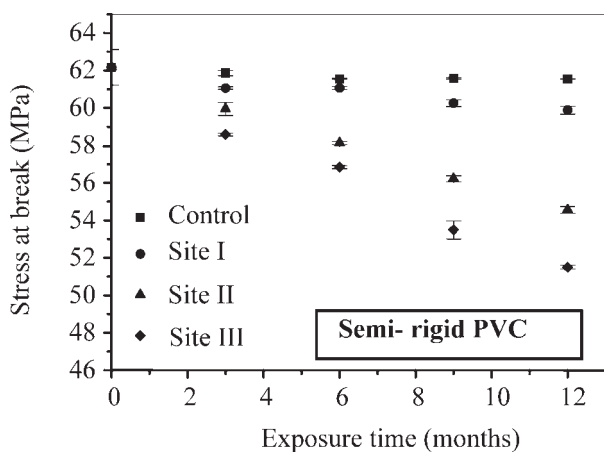


Figure 1 Stress at break evolution with time.

Figure 2 Strain at break evolution with time.

To compare the three sites, the variation rates of stress and strain at break were estimated according to the following relations:

$$\Delta\sigma_r(\%) = \frac{\sigma_{ro} - \sigma_{ri}}{\sigma_{ro}} \times 100 \quad (1)$$

$$\Delta\varepsilon_r(\%) = \frac{\varepsilon_{ro} - \varepsilon_{ri}}{\varepsilon_{ro}} \times 100 \quad (2)$$

where  $\Delta\sigma_r$  (%) is the variation rate of stress at break,  $\sigma_{ro}$  the stress at break obtained at the time  $t_o$ ,  $\sigma_{ri}$  the stress at break obtained at the time  $t_i$ ,  $\Delta\varepsilon_r$  (%) the variation rate of strain at break,  $\varepsilon_{ro}$  the strain at break obtained at the time  $t_o$ ,  $\varepsilon_{ri}$  the strain at break obtained at the time  $t_i$ .

In Tables I and II, the values of  $\Delta\sigma_r$  and  $\Delta\varepsilon_r$  are reported, respectively. Globally, it can be seen that stress and strain at break decreased for the three sites considered. However, the most noticeable decrease occurred in site III, followed by site II and then site I. The total influence of weathering can be considered as a composite effect of solar UV radi-

ation, moisture, temperature, and pollutants. It must be noted that the three sites are not very distant, and they were submitted to the same climatic variations. The only difference is the composition and the concentration in atmospheric pollutants, which accelerated the degradation of the polymer. From the

TABLE I  
Variation of  $\Delta\sigma_r$  with Exposure Time

Time (months)	Site I	Site II	Site III
Semirigid PVC			
00	0.00	0.00	0.00
03	1.78	3.58	5.77
06	1.77	6.50	8.57
09	3.08	9.57	13.95
12	3.67	12.24	17.16
Plasticized PVC			
00	0.00	0.00	0.00
03	0.99	3.18	5.28
06	1.57	7.67	10.48
09	1.65	11.20	18.78
12	2.64	14.67	27.50

**TABLE II**  
Variation of  $\Delta\epsilon_r$  with Exposure Time

Time (months)	Site I	Site II	Site III
Semirigid PVC			
00	0.00	0.00	0.00
03	0.94	6.84	8.85
06	1.46	12.38	19.05
09	1.82	19.13	24.70
12	2.27	22.49	31.82
Plasticized PVC			
00	0.00	0.00	0.00
03	1.55	6.23	6.29
06	2.34	8.86	17.05
09	6.03	16.93	25.10
12	10.73	21.84	27.46

results of Tables I and II, it seems that PVC is more sensitive to the effect of ozone than hydrocarbons and  $\text{NO}_x$ . Ozone may abstract hydrogen and form polymer peroxy radicals or add to double bonds with formation of ozonides, which are unstable and easily decomposed into aldehydes and acids. Organic-free radicals formed from hydrocarbons in a photochemical process may initiate free radical oxidation of the polymer. Furthermore, aromatic polynuclear hydrocarbons are sensitizers and accelerate photooxidation. On the other hand, the main reaction of  $\text{NO}_2$  with polymers is abstraction of hydrogen from the polymer molecules. The polymer alkyl radical formed can further react with molecular oxygen and produce polymer peroxy radical. As a result of all these reactions, tensile properties are lost.

The shore D hardness values are given in Table III for semirigid and plasticized PVC. It can be noted that the hardness was subjected to a little increase for both formulations and in the three sites considered. However, the increase is relatively more noticeable for plasticized PVC and particularly in site III. These variations may be due to the structural modifications that occurred in the polymer backbone upon weathering and to an eventual loss of the

**TABLE III**  
Variation of Shore D Hardness with Exposure Time

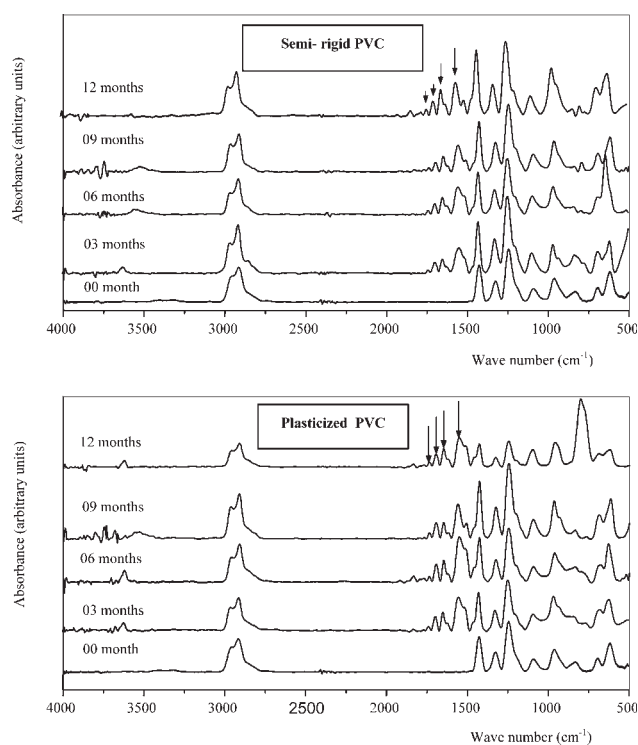
Time (months)	Site I	Site II	Site III
Semirigid PVC			
00	79.00 ± 0.82	79.00 ± 0.82	79.00 ± 0.82
03	80.00 ± 0.71	79.00 ± 0.58	79.00 ± 0.57
06	80.00 ± 0.55	79.00 ± 0.58	80.00 ± 0.71
09	80.00 ± 0.50	80.00 ± 0.82	80.00 ± 0.58
12	80.00 ± 0.58	80.00 ± 0.48	80.00 ± 0.71
Plasticized PVC			
00	37.0 ± 0.44	37.0 ± 0.44	37.00 ± 0.44
03	38.00 ± 0.58	39.00 ± 0.58	39.00 ± 0.58
06	39.00 ± 0.58	39.00 ± 0.50	40.00 ± 0.50
09	39.00 ± 0.58	39.00 ± 1.00	40.00 ± 0.58
12	39.00 ± 0.85	39.00 ± 0.58	40.00 ± 0.50

plasticizer. These changes are concentrated at the exposed surface.

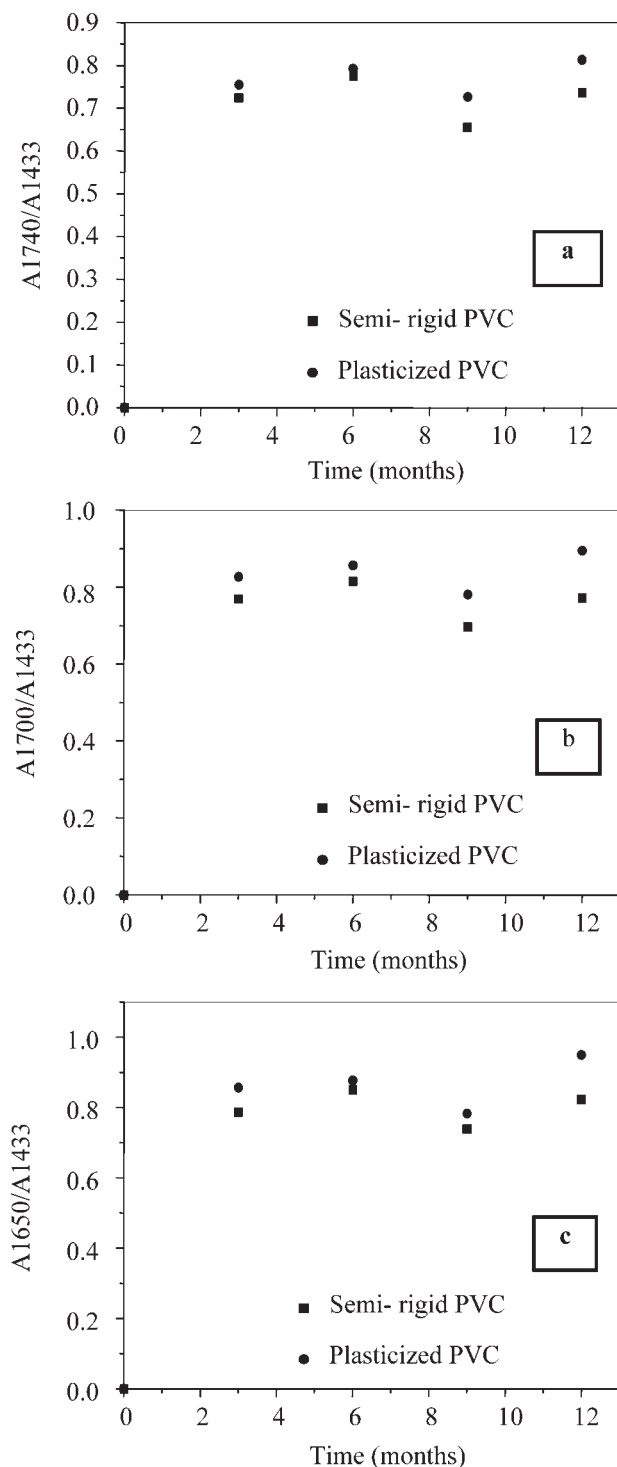
### FTIR analysis

To check the presence of degradation structures in the PVC backbone after weathering, the samples were purified and analyzed by FTIR spectroscopy. Figure 3 shows the FTIR spectra of semirigid and plasticized PVC after various times of exposition in site III, which is the site the most reach in ozone and where the mechanical properties were the most affected. The FTIR spectra showed significant changes with aging, particularly, between 1500 and 1800  $\text{cm}^{-1}$ . It can be noted the presence of several bands located at 1740  $\text{cm}^{-1}$ , 1700  $\text{cm}^{-1}$ , 1650  $\text{cm}^{-1}$ , and 1556  $\text{cm}^{-1}$ . Different types of oxygenated structures appear in the PVC chain on photolysis in the presence of oxygen. The C=O groups are characterized by their infrared absorption in the range 1700–1800  $\text{cm}^{-1}$ .<sup>18,19</sup>

On the other hand, as the main characteristic feature of the photolysis of PVC is the dehydrochlorination reaction, conjugated polyenes sequences are formed with concomitant evolution of HCl. The polyenes structures absorb generally between 1600 and 1650  $\text{cm}^{-1}$ .<sup>7,18</sup> The spectral range 1500–1600  $\text{cm}^{-1}$  contains the absorption band of the stretching vibration of the  $\text{COO}^-$  group.<sup>18</sup> The band at 1556  $\text{cm}^{-1}$  is due to complexation form of residual metal stearates,



**Figure 3** Evolution of FTIR spectra with exposure time (months) for plasticized PVC in site III.



**Figure 4** Variation of absorbances ratios as a function of exposure time.

which are not eliminated by the purification.<sup>15</sup> To eliminate the effect of uneven film thickness, absorbances were calculated as normalized indices. The following absorbance ratios were evaluated and plotted against the exposure time (Fig. 4) to investigate the level of degradation:

$A_{1740}/A_{1433}$  : C=O content

$A_{1700}/A_{1433}$  : C=O content

$A_{1650}/A_{1433}$  : C=C content

The band at  $1433\text{ cm}^{-1}$  is due to the vibration of  $\text{CH}_2$  of PVC.<sup>12</sup> It can be noted that the more rapid increase of the three ratios occurred during the first months of exposure. After that, the evolution of these ratios is relatively weak. These results indicate that the degradation process develop primarily in the top layer of the weathered samples. This leads to the formation of degradation structures containing C=O groups, which absorb the UV light and then protect the deep layers. However, this highly degraded top layer constitutes the starting point of the rupture and then explains the observed deterioration of the mechanical properties.

On the other hand, Figure 4 shows that all the absorbance ratios of the plasticized samples are higher than those of the semirigid ones. This means that the increase in the concentration of the plasticizer increases the sensitivity of PVC to the combined action of UV light and atmospheric pollutants.

## CONCLUSIONS

The results from this study showed a deterioration of the mechanical properties: a decrease in the properties at break since the first months of exposure and an increase of the shore D hardness. These variations were due to the chemical modifications induced by the photo dehydrochlorination and the photooxidation of PVC (HCl evolution, polyenes formation, chains scissions, and crosslinks). The migration of the plasticizer also contributed to these variations to some extent. Finally, this article evidenced the influence of air pollutants on the long-term properties of PVC. It was found that  $\text{O}_3$  exerted the most deleterious effect, followed by hydrocarbons and then  $\text{NO}_x$ .

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