Macromol. Symp. ***180,*** *181–189 (2002)*

Study of the Influence of Atmospheric Pollutants on the Natural Ageing of Rigid Polyvinyl Chloride

Naïma Belhaneche- Bensemra, Naïma Ouazene

Laboratoire de recherche en sciences et techniques de l'Environnement, Ecole
Nationale Polytechnique, BP 182, El-Harrach, Alger, ALGERIE
(E- mail: nbelhaneche@yahoo.fr)

Summary: The aim of this work is to study the natural ageing of rigid polyvinyl chloride (PVC) used in building and construction areas. For that purpose the PVC bars have been exposed in Algiers for 24 months in three sites where the concentrations of atmospheric pollutants (NO_x, O_3, hydrocarbons) are known. Samples were taken every three months. The evolution of mechanical properties was followed by tensile and hardness tests whereas the modification structure of polymer was followed by Fourier transform infrared spectroscopy (FTIR) and UV-visible spectroscopy.

The results have shown a little drop in strain at break and stress at break, whereas hardness remains practically constant.

IR and UV- visible analysis have shown apparition of chemical structures due to the polymer degradation (carbonyl and hydroperoxide groups and polyenes) since the first months of exposure in the three sites.

Introduction

Most commercial polymers undergo chemical and physical modifications when they are exposed for a long time to the combined action of sunlight, atmospheric oxygen, moisture and pollutants [1].

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 the health and safety or interfere with the full use of materials or property, e.g. made from polymeric materials [2]. 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 eruptions, 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, e.g. 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 [3].

The concentration of air pollutants is very important for the long term properties of polymeric materials. Polyvinyl chloride (PVC) is a polymer of considerable commercial importance.

CCC 1022-1360/00/$ 17.50+.50/0

A wide variety of applications in outdoor constructions such as doors, down spouts, shutters, sash window, exterior cladding and advertising signs, where impact resistance, transparency, color, corrosion resistance and water repellency are of extreme considerations have been developed. However PVC is very susceptible towards discoloration during as well as after the processing of polymer. When PVC is exposed to long term outdoor environment, it undergoes very slow long term photochemical degradation. It is subjected to various atmospheric effects including exposure to rain, fungus, mechanical stress, pollutants and exposure to ultraviolet radiation. The ultimate result is then reflected in a marked loss of additives, discoloration, embrittlement and finally loss in mechanical properties [4].

The aim of this paper is to study the natural weathering of rigid PVC used in building and construction areas. For that purpose, the PVC bars have been exposed in Algiers for 24 months in three sites were the concentrations of atmospheric pollutants (NO_x, O_3 and hydrocarbons) are known. Samples were taken every three months. The evolution of mechanical properties was followed by tensile and hardness tests whereas the modification structure of polymer was followed by Fourier transform infrared spectroscopy (FTIR) and UV-visible spectroscopy.

Experimental

- **Materials**

This study of weatherability was carried out on industrial samples manufactured by ENPC-PROFIPLAST (ALGERIA). Commercial grades of additives listed in Table 1 were used in the formulation. The percentages of components were not given by the producer.

This rigid PVC is used to produce various articles such as doors, windows and shutters.

Table 1. Compounds used.

Compound	Chemical nature
Heat and light stabilizer	Lead bibasic phosphite
External lubricant	Lead stearate
Impact modifier	Acrylic resin
Pigment	TiO_2
Filler	$CaCO_3$

- **Exterior Weathering in Algiers**

The samples (100×6×4 cm) were exposed to exterior weathering according to the standard ISO 4607 (1985).

They were deposited in spring 1998 for two years in three sites where the concentrations of atmospheric pollutants are known:

Site I:

It is representative of an urban area.The amount of aromatic hydrocarbons is about 140 $\mu g/m^3$.

Site II:

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 NO_x are high (NO and NO_2 average contents/hour are respectively 10-100 PPb and 10-60 PPb).

Site III:

It is situated in the suburbs and is characterized by a weak traffic. The level of O_3 is high (O_3 average content/hour = 20-90 PPb).

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

- **Mechanical Characterization**

Measurements of tensile properties were undertaken using an ADAMEL LHOMARGY DY 25 testing machine according to the AFNOR NF T51-034. A shore D type durometer was used for determining the hardness of the samples according to the AFNOR NF T51-109.

- **Spectroscopic Characterization**

Before spectroscopic characterization a sample was cut in a cross- section of the whole bar and was purified by dissolution in tetrahydrofuran (THF), centrifugation, filtration, precipitation with methanol and then filtration and drying in vacuum at 40°C during 24 hours.

The infrared spectra were recorded with a Philips type PU 9800 FTIR spectrophotometer at a resolution of 2 cm^{-1} using KBr pellets (1wt %).

The UV-visible spectra were recorded with a SECOMAM ANTHELIE LIGHT UV-visible spectrophometer. Solutions of the samples were prepared in freshly distilled THF (1 g/l) and analyzed immediately.

Results and Discussion

Figures 1 and 2 illustrate the variation of stress and strain at break as a function of the time of exposure in months, respectively. They show clearly that the properties at break in the three sites decreased with exposure time while they remained practically constant for the reference. Although the variations were relatively weak, the effect of exposure site was evidenced. It seems that the O_3 exerted the most nocuous effect, followed by hydrocarbons and then NO_x.

The decrease of the mechanical properties at break can be related to the chains scissions due to the photooxidation of PVC [5].

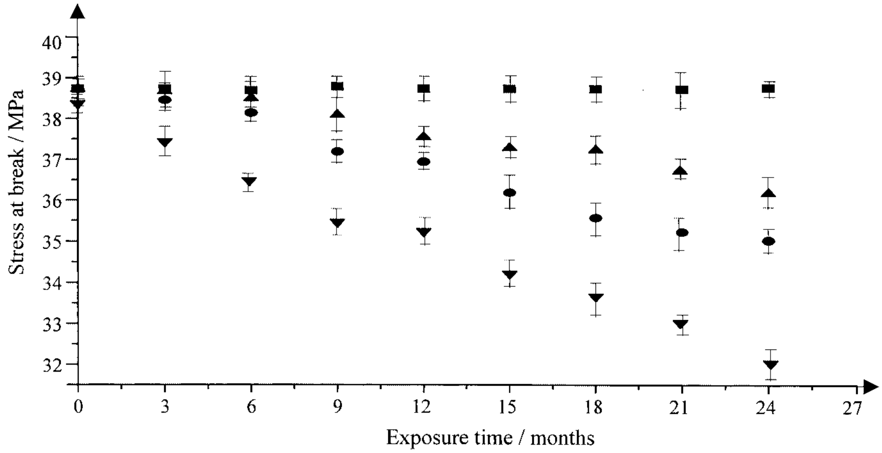

Figure 1. Effect of exposure site on the evolution of stress at break :
■ Reference, ● Site I, ▲ Site II, ▼ Site III

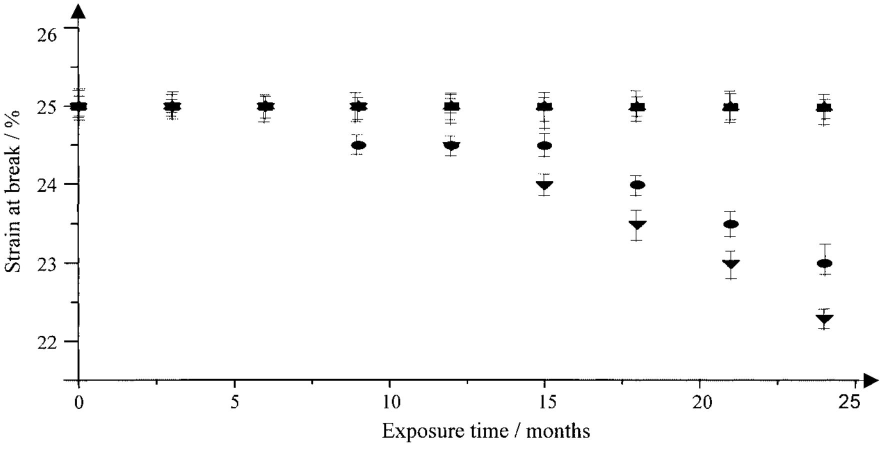

Figure 2. Effect of exposure site on the evolution of strain at break :
■ Reference, ● Site I , ▲ Site II, ▼ Site III

The Shore D hardness values obtained for all the weathered samples in the three sites are reported in Table 2. It can be noted that hardness remained practically constant for all the samples and in the three sites. The considered time exposure and the low level of degradation have not affected the hardness of the samples.

Table 2. Shore D hardness.

Time (months)	00	03	06	09	12	15	18	21	24
Reference	75	75	75	75	75	75	75	75	75
Site I	75	75	75	75	74	75	75	75	75
Site II	75	75	74	74	75	75	75	75	75
Site III	75	75	75	75	74	75	74	75	75

It is known that several complex chemical changes take place in PVC during weathering, including dehydrochlorination and oxidation which in turn lead to changes in color (both coloration and bleaching), crosslinking and chain scission, and general deterioration of physical properties [1,4]. FTIR and UV-visible spectroscopy were used, after purification of the samples, to evaluate the effects of the degradation in the three sites. The FTIR spectra (Figures 3, 4 and 5), showed significant changes with ageing. A carbonyl peak centered around 1733 cm^{-1} and a very broad hydroxyl peak at 3200-3600 cm^{-1} developed after exposure in the three sites since the first months.

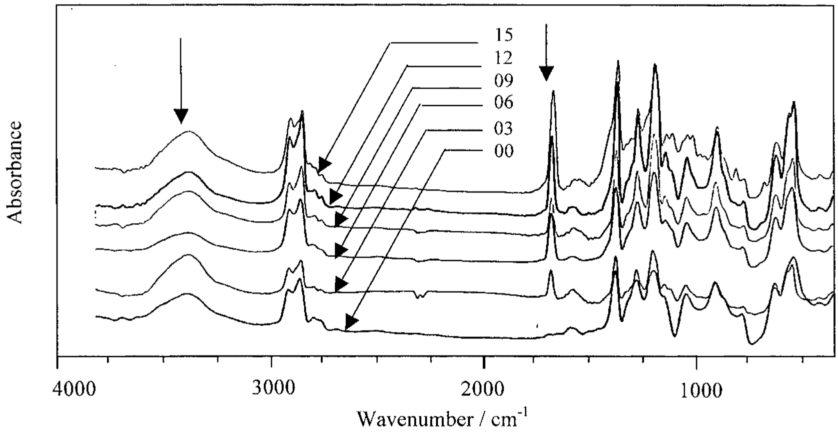

Figure 3. Evolution of FTIR spectra with exposure time (months) in site I.

These different types of oxygenated structures appear in the PVC chain on photolysis in the presence of oxygen [1,2]. The very broad hydroxyl band can be attributed to hydroperoxide and alcohol functions [1,6]. The carbonyl band was suggested to be mainly due to α and β-chloroketones [1,6].

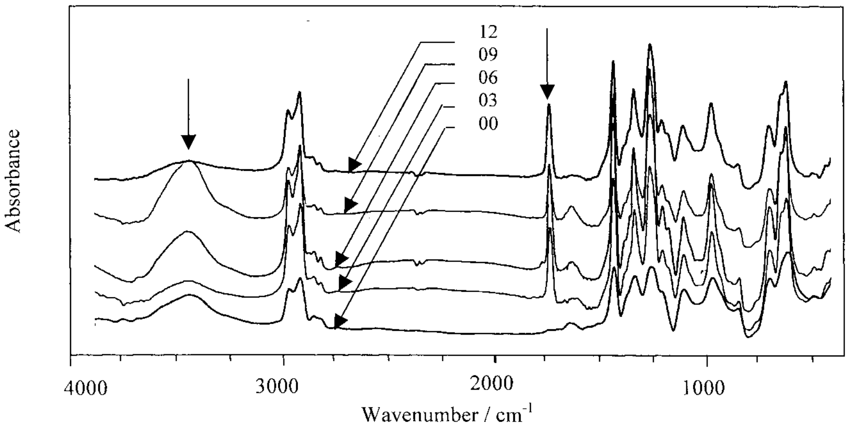

Figure 4. Evolution of FTIR spectra with exposure time (months) in site II.

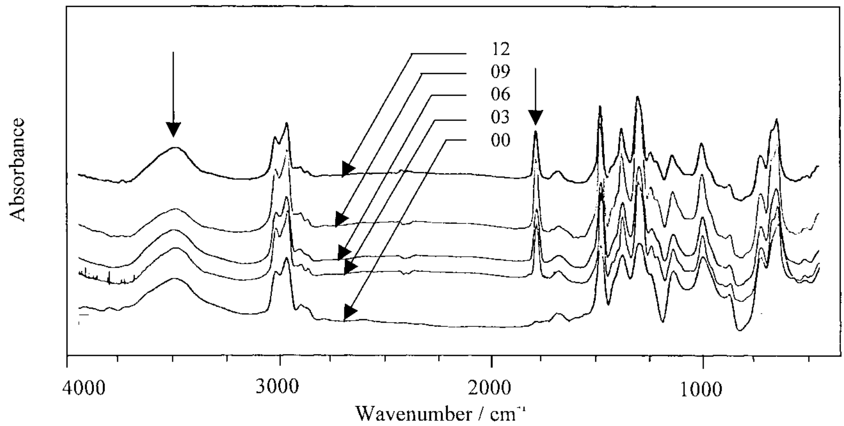

Figure 5. Evolution of FTIR spectra with exposure time (months) in site III.

In Tables 3 and 4 are reported the relative variations of carbonyl and hydroxyl bands, respectively, with the exposure time. The reference band at 1434 cm^{-1} is due to the $-CH_2-$ groups of PVC. It can be seen that the more rapid increase of the ratios A_{1733} / A_{1434} and A_{3430} /A_{1434} occured during the first months of exposure. After that, the evolution of these ratios is relatively weak. These results indicate that the oxidation process develop primarily in the top layer of the weathered material. This leads to the formation of oxygenated structures which absorb the UV light and then protect the deep layers.

Table 3. Evolution of the ratio A_{1733}/A_{1434} with exposure time.

Time (months)	00	03	06	09	12	15
Site I	00	0.61	0.67	0.70	0.69	0.72
Site II	00	0.59	0.60	0.60	0.64	0.66
Site III	00	0.59	0.63	0.65	0.66	0.74

Table 4. Evolution of the ratio A_{3430}/A_{1434} with exposure time.

Time (months)	00	03	06	09	12	15
Site I	0.08	0.32	0.32	0.35	0.41	0.45
Site II	0.08	0.10	0.20	0.61	0.10	0.15
Site III	0.08	0.94	0.23	0.21	0.24	0.34

On the other hand, it is known that the main characteristic feature of the photolysis of PVC is the dehydrochlorination reaction, which develops extensively, as in the thermal degradation, and which leads to the formation of conjugated polyene sequences with concomitant evolution of HCl [1,7,8]. These polyene structures can be easily characterized by their UV-visible absorption, which ranges from 230 nm for dienes to ≈ 400 nm for n=8 [9]. Figures 6, 7 and 8 shows the UV-visible spectra obtained after purification of the aged samples in the three sites. Similar spectra were given in the literature on the photooxidation of PVC [10-12].

Contrary to the non aged PVC which has no absorption band, all the aged samples presented different absorption bands below 350 nm. These bands are representative of the formation of conjugated polyenes with $n \leq 6$ [9].

Furthermore, the corresponding absorbances increased with the exposure time in the three sites indicating the increase of the concentration of these various polyenes. As degradation proceeds, these chromophores concentrate closer to the surface of the exposed material, leading to the appearance of a highly degraded superficial layer which acts as a UV screen and partly prevents the bulk of the PVC sheet from further deterioration. In the presence of oxygen, oxidation develops simultaneously with the zip-dehydrochlorination with formation of carbonyl and hydroperoxide groups on the polymer chains which in addition suffer cleavages and crosslinking leading to the deterioration of mechanical properties.

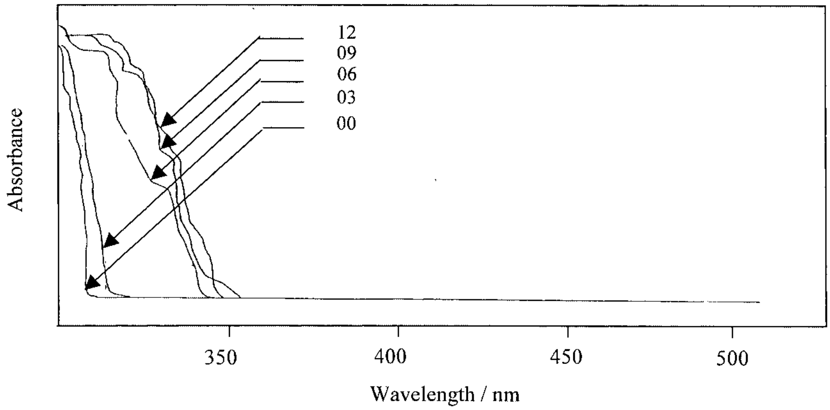

Figure 6. Evolution of UV-visible spectra with exposure time (months) in site I.

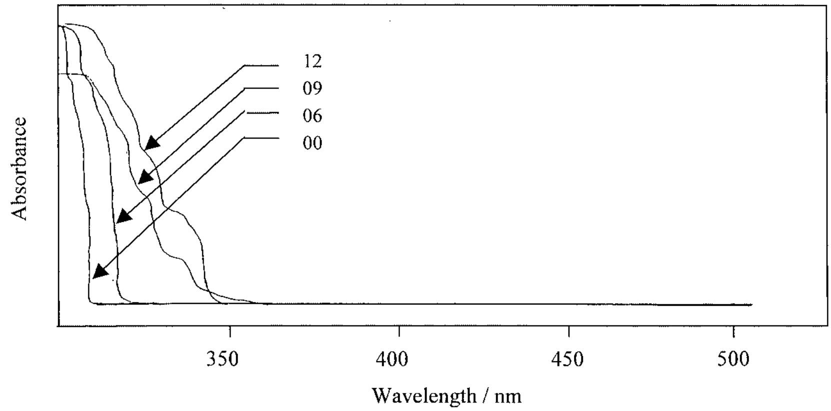

Figure 7. Evolution of UV-visible spectra with exposure time (months) in site II.

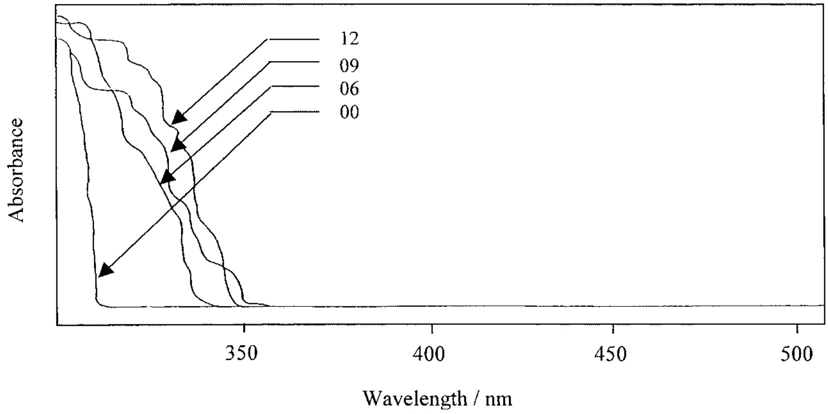

Figure 8. Evolution of UV-visible spectra with exposure time (months) in site III.

Conclusion

The investigation of the influence of atmospheric pollutants(O_3, NO_x, hydrocarbons) on the weatherability of rigid PVC was carried out. The samples were exposed for two years in three sites. Every one of them was characterized by a relatively high level of a specific atmospheric pollutant.

The results showed a decrease in the properties at break of the samples since the first months of exposure. It was found that O_3 exerted the most deleterious effect, followed by hydrocarbons and then NO_x. However, shore D hardness remained practically constant for all the samples in the three sites. The considered time exposure and the level of degradation have not affected the hardness of the samples.

FTIR and UV-visible analysis showed the formation of chemical structures due to the polymer photoxidation (carbonyl and hydroperoxide groups and polyenes) since the first months of exposure. During the oxidation, chains scissions and crosslinking reactions occurred leading to the gradual loss of the mechanical properties .

This paper evidenced the influence of air pollutants on the long-term properties of PVC. The need of more research is amply verified, both on the effects and their prevention.

[1] C. Decker, "Degradation and stabilization of PVC ", Elsevier Applied Science Publishers, London and New York **1984**, p81.
[2] J. R Hollum,"Topics and terms in environmental problems", Wiley, New York **1978**, p52.
[3] S. Garner, G. Stahl, The effects of hostile environment on coatings and plastics, *American Chemical Society* **1983**, p291.
[4] B.D Gupta, J. Verdu, *J. Polym. Eng* , Nos 1-2, **1988**, 8, 73.
[5] C. Decker, M. Balandier, *Eur. Polym. J.* **1982**, 18, 1085.
[6] G.Scott, M. Tahan, *Eur.Polym.J.* **1975**, 11, 535.
[7] F. Mori, M. Koyama, Y. Oki, Die Angew. *Makromol. Chem.*, **1979**, 75, 113.
[8] J. L. Gardette, J. Lemaire, *Polym. Degr. Stab.* **1989**, 25, 293.
[9] V. D. Daniels, H. H. Rees, *J. Polym.Sci.*, *Polym. Chem.* Ed. **1974**, 12, 2115.
[10] M. Balandier, C. Decker, *Eur. Polym . J.* **1978**, 14, 995.
[11] C. Decker, M. Balandier, *Eur. Polym.* J. **1982**,18, 1085.
[12] J. L. Gardette, J. Lemaire, *Polym. Degr.Stab.* **1986**, 16, 147.