

## UV radiations effects on the mechanical and physicochemical properties of a polycarbonate

Sonya REDJALA<sup>1</sup>, Rabah FERHOUM<sup>1</sup>, Said AZEM<sup>1</sup>, Nourredine AIT HOCINE<sup>2</sup>

- <sup>1</sup>. Laboratoire d'Élaboration, de Caractérisation et de Modélisation des Matériaux (LEC2M), University Tizi Ouzou, Algeria
- <sup>2</sup>. INSA Centre Val de Loire, LMR 3, Rue de la Chocolaterie – BP 3410 41034 Blois Cedex – France

**ABSTRACT —** This work is devoted to the experimental study of UV irradiation effects on the microstructure and mechanical behavior of a polycarbonate (PC). Simple compression tests, X-ray diffraction, Scanning Electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) were carried out in order to characterize the response of the specimens material before and after UV irradiation with a wavelength of 253 nm at room temperature and for several maintained durations of 72, 144 and 216 hours. These investigations showed a decrease of the intrinsic properties of polycarbonate (Young modulus, yield stress, etc.). The superposition of spectra FTIR shows that the intensity of chemical connections is influenced by the duration of UV irradiation; in addition, an increase of diffractogram peaks intensity of the samples after 216 hours of ageing has been noticed. Our objective in this work is to find correlations between the time of maintenance, microstructure and mechanical properties of our materials

**Keywords:** *Amorphous polymer; polycarbonate; UV irradiation; photo-degradation*

### I. Introduction

Under ambient conditions, polymers are known to undergo degradation, a process which results in the deterioration of polymer properties, characterized by an uncontrolled change in its molecular weight [1]. A polymer can undergo degradation in two stages during its lifetime, one during its manufacture and the other during its daily use. The different ways in which the gross properties of polymeric materials are affected by environmental conditions are innumerable. The degradation at molecular level is mainly caused by energetic agencies and chemical agencies. This article deals with the experimental study of the viscoelastoplastic responses of amorphous polymers after UV irradiation.

Correlations between the amorphous morphology and the mechanical properties of

*Corresponding author: FERHOUM Rabah,  
Research field: Mechanics and Materials  
Address: University of Mouloud Mammeri Tizi-Ouzou  
E-mail:ferhoum@yahoo.fr*

polymers have attracted considerable attention over the last decade [2–5]. Numerous publications concerning the degradation mechanisms of PC have recently been reported [6-10]. In the meantime, it is well known that ultraviolet (UV) irradiation induces significant physicochemical changes in polymers involving a reduction in molecular weights and therefore a decrease in their mechanical performances [11-12]. The present work focuses on the effect of UV irradiation on microstructure evolution; the challenge is to identify the relationship between holding time, UV wavelength and mechanical properties.

### *Background on photo degradation*

The degradation of polymers has a great influence on their behavior. Two types of processes can be distinguished, physical and chemical, and the two are strongly related. Degradation can be induced, for example, by UV irradiation, temperature, physicochemical attacks (water, oxygen, etc.) and mechanical

stress. UV irradiation is known to accelerate both oxidative and mechanical degradation.

This material exhibits a significant increase in the refractive index after irradiation with deep ultraviolet light (DUV), as first reported by Tomlinson et al. [12]. Planar optical waveguides can be created in PMMA by exposure to ionizing radiation [13, 14] and deep UV radiation [10, 14]. This also makes it possible to obtain simple components for the communication of visible data, as well as small strain and temperature sensors by inscribing Bragg gratings in these planar waveguides.

### Scope of this work

The present work is devoted to the experimental study of the viscoelastoplastic responses of amorphous polymers after UV irradiation. Our objective is to understand the evolution of the structure of this polymer during UV irradiation and its effects on its mechanical behavior. The chemical modifications that occur in the material during irradiation are examined by Fourier Transform Infrared Spectroscopy (FTIR).

The article is organized as follows. In Sect. 1, experimental research on PMMA in the unpainted state is done and commented on. Section 2 presents the effect of UV irradiation on the microstructure and the mechanical properties. Finally, the final remarks are given in Sect.

## II. Experimental Investigation

### II.1. Materials and methods

The study material is polycarbonate bisphenol, the chemical structure of which is shown in FIG. 1.

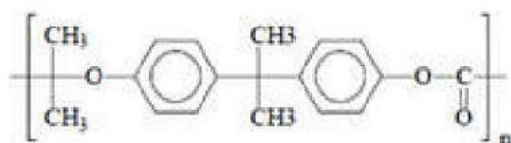


Fig. 1. Chemical Polycarbonate PC formula

The PC exhibits interesting properties; high impact strength, high transparency and hardness of about 45 HK.

The first series of tests was carried out to check the initial isotropy of the material. Compression tests were performed at a nominal

strain rate of  $10^{-3} \text{ s}^{-1}$  in two directions. The results of these tests are given in FIG. 3, illustrating the evolution of stress-strain curves. It can be seen that the polymer tested has a quasi-isotropic behavior since the differences between the curves, at least under quasi-static compression conditions and at ambient temperature, are almost similar.

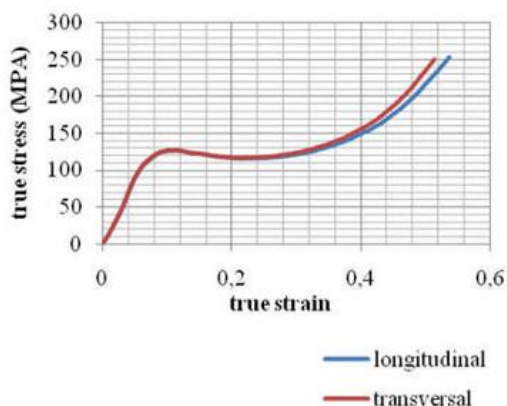


Fig. 2. Comparison of strain–stress curves in uniaxial direction.

The characterization of the material in the virgin state with FTIR analysis, illustrate the chemical construction of the material; where the bonds of C-O, CH<sub>3</sub>, C=O and C-H, characterized by bands: 1200, 1400, 1740 and 2800  $\text{cm}^{-1}$  respectively were displayed.

The position of the vibration bands FTIR will depend in particular on the difference in electronegativity of the atoms and their mass.

Consequently, a chemical composition of material and data structure generates a set of absorption bands characteristic of the nature of the chemical bonds, their proportion and their orientation. FIG. 3 shows the analysis of the FTIR spectra of the virgin polycarbonate.

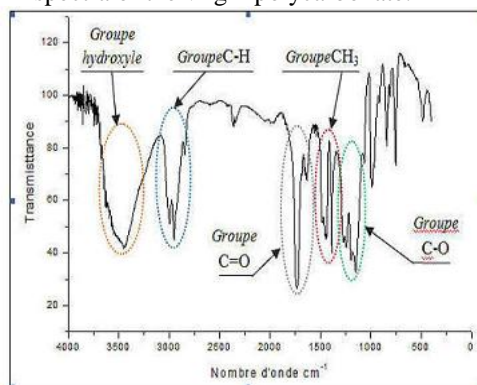


Fig. 3. Chemical analysis of polycarbonate in a virgin state by FTIR.

## II.2. Mechanism of degradation UV

The UV irradiation of the samples was carried out using a monochromatic light source of 253 nm wavelength from a Cole-Parmer low-pressure mercury lamp (25W) at various times (72 to 216 h). The UV lamp was positioned at a distance of 10 cm from the sample. A low speed air flow from an electric fan was used to keep the sample at room temperature during irradiation.

## II.3. Compression test

The uniaxial compression tests were carried out by a universal hydraulic machine *IBERTEST* with a capacity of 50 kN. The tests were carried out at ambient temperature and with a strain rate of 2 mm / min. All specimens, Figure 4, were obtained by laser cutting from a 4.4 mm thick calendered polycarbonate plate, Figure 5.

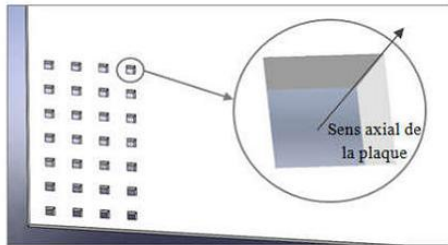


Fig. 4. The polycarbonate plate and traces of cutting.

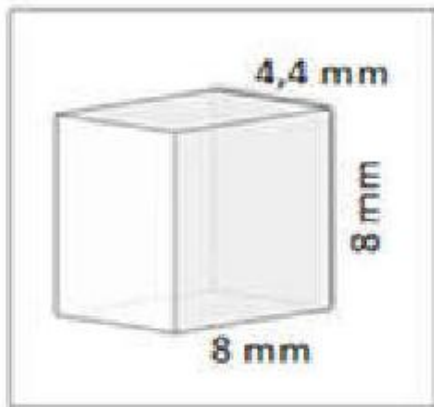


Fig. 5. Compression sample

## III. Results and discussion

### III.1 Mechanical behavior before and after degradation

Figure 6 shows variation of the stress versus the strain. At the beginning, the material shows an elastic expansion related to Poisson's ratio of the material. When the material becomes plastic, a slight contraction is observed near the yield stress. Plastic compaction (contracting volume

strain for intermediate stretching ratio) is in competition with dilatation.

This phenomenon appears when the mobility of the amorphous chains and the time to accommodate macroscopic deformation are favored. At higher strains, microstructural rearrangements and orientation mechanisms gradually occur in PC.

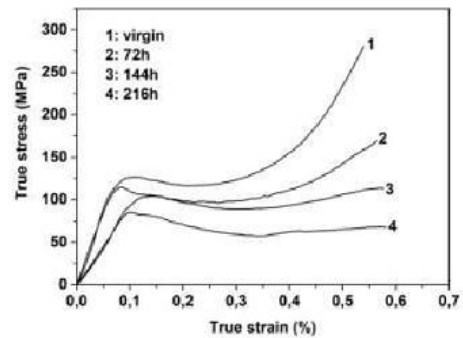


Fig. 6. Stress-strain curves in a virgin state and after ageing under radiation UV

Comparison stress-strain curves of PC before and after degradation is shown in Fig. 7. It appears that most of the mechanical properties of PC are affected by degradation.

Indeed, significant changes in Young's modulus, yield stress, and strain at failure are observed. Particularly, yield and maximal stresses decrease with degradation.

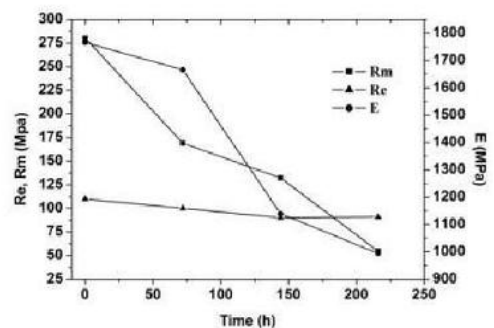


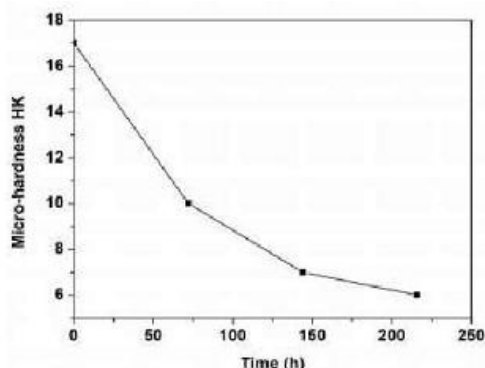
Fig.7. Mechanical properties evolution after UV degradation

### III.2 Hardness measurement

In this case, measurements of micro-hardness Knoop with a load of 25 gf and a holding time of 20 s were carried out on our samples before and after various degradation times.

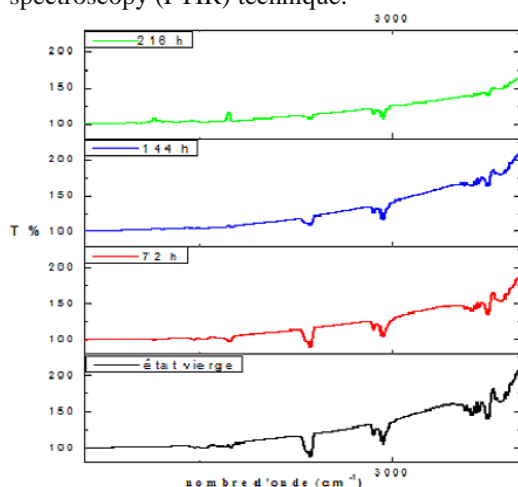
A mechanical property that may be important to consider is hardness, which is a measure of a material's resistance to localized plastic deformation [1]. In this case, measurements of

micro-hardness KNOOP with a load of 25gf and time maintain of 20s were carried out on our samples before and after various degradation times. We can see in figure 8 a decrease of the order of 70%, 17 HK in the virgin state at 6 HK at 216 hours of aging, which was confirmed by [5]. This decrease in micro-hardness has been attributed to the formation of various oxidation products.



**Fig. 8** Micro-hardness as a function of aging time

In order to reveal all the chemical modifications that can cause the mechanical properties change mentioned above, we make use of the Fourier transform infrared spectroscopy (FTIR) technique.



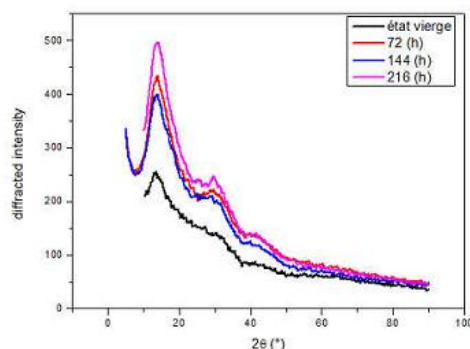
**Fig. 8.** Superposition of IRTF spectra at virgin state and after degradations

FIG. 8 illustrates the effect of aging by UV irradiation on the microstructure by reducing the intensity of all the chemical bonds of the polycarbonate (C-O, CH 3, C = C and C-H); this modification is already clearly observed at 72 hours. We can explain the phenomenon by a

break of chemical chains and the formation of oxidation products [11]. The high energy of the UV irradiation makes it possible to have the chain scission of the polymer [12].

### III.3 X-ray diffraction analysis (XRD)

The X-ray diffraction patterns of the virgin PC and the irradiated PC are shown in FIG. 9.



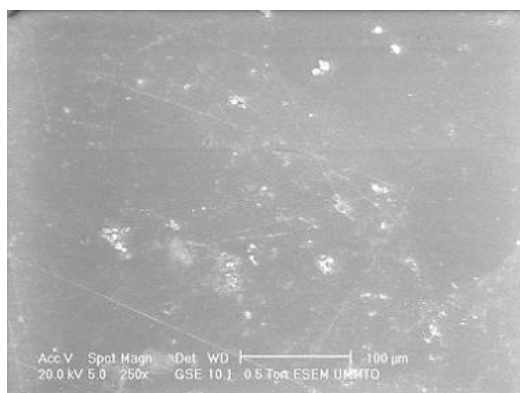
**Fig. 9.** X-ray diffraction patterns of virgin and irradiated PC

In this figure, it appears a regular rearrangement of the chains in the irradiated PC which is manifested by an increase in the intensities of the peaks with the UV exposure time. The profile of the halos shows that the PC is an amorphous polymer with a partial order [12-13].

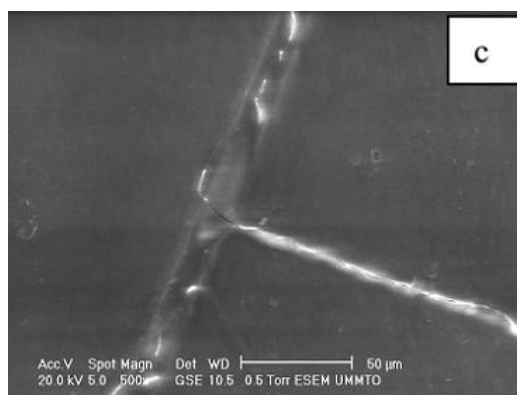
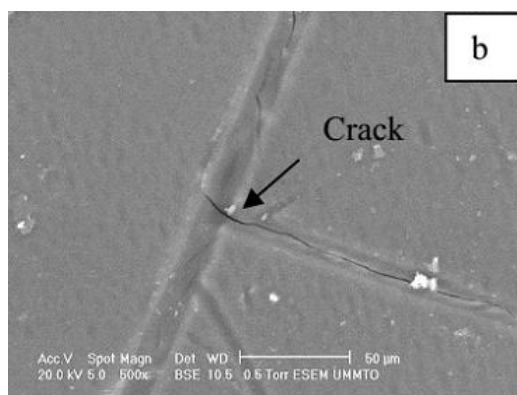
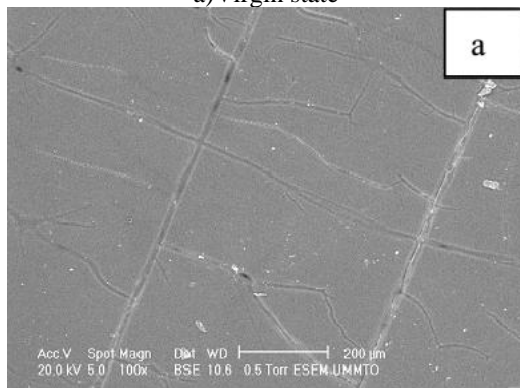
### III.4 scanning electron microscopy (SEM)

The samples of polycarbonate, in the virgin state and after degradation with different UV exposure times, were examined using a scanning electron microscope (SEM) of the Philips XL30 environmental type. For degraded samples, only directly exposed faces are analyzed in backscattered electron (BSE) mode to reveal any chemical contrast due to structure modification and secondary electron mode to observe surface defects such as pores and Cracks. Figure 11a shows the microstructure of the polycarbonate in a virgin state, which reveals only superficial scratches and pores of varying sizes. These defects are probably due to the handling of the material. However, the degraded material reveals a multitude of microcracks which are more numerous than the degradation time is higher as shown in figures 11c, f, i recorded the GSE mode. It appears that these cracks form "cells" which tend to

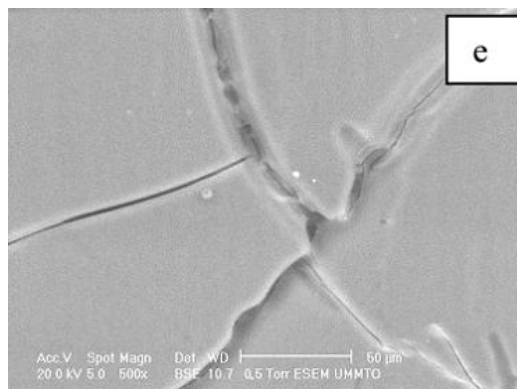
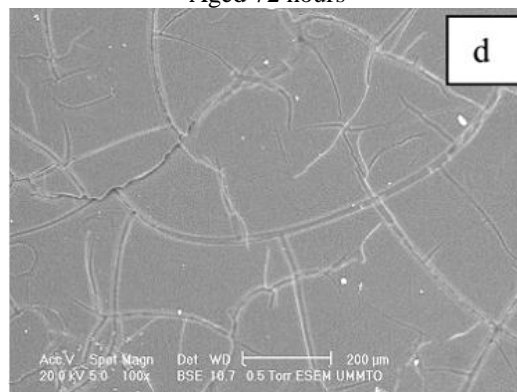
propagate at high exposure times as shown in Figure 11. The figure 11 g, recorded in BSE mode, also reveals a chemical contrast (white areas and dark areas ) Probably due to a reorganization of the molecular chains causing a change in the density of the material. This does not appear for durations of 72 and 144 hours of exposure (Figure 11a and d). The relatively bright areas refer more backscattered electrons which suggest a rise in relative density to that of the darkest areas. We also see a contrast along the cracks as if these areas increased the density. This could be explained by the loss of atoms (such as hydrogen and oxygen) by rupture of the C-H and C-O bonds, which increases the relative density. This phenomenon is in agreement with the results of IR spectroscopy, which showed chemical bond breaking. A SEM observation with a higher magnification clearly shows this phenomenon which is manifested by a chemical contrast on either side of the crack as shown in figure 12.



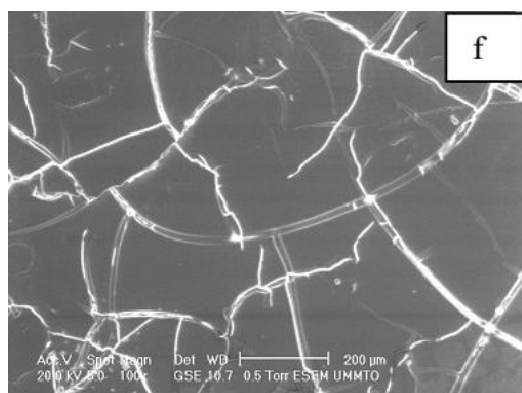
a) Virgin state



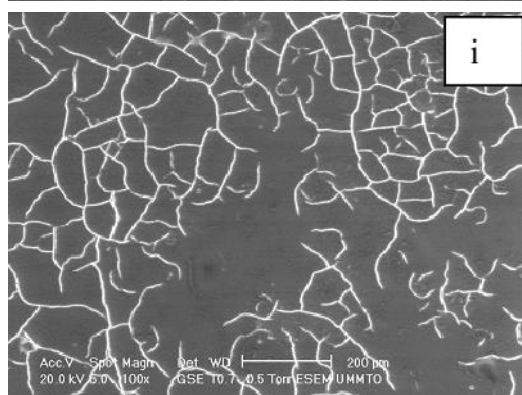
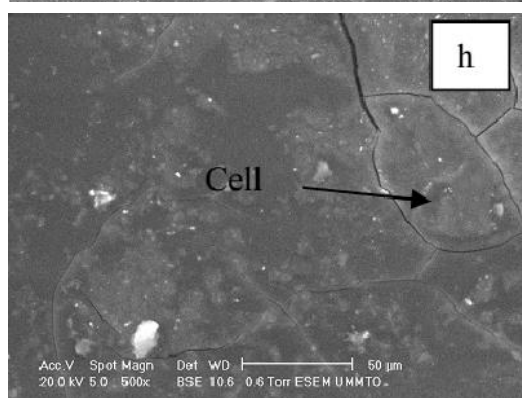
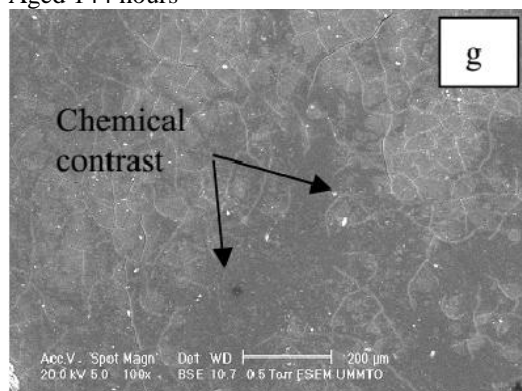
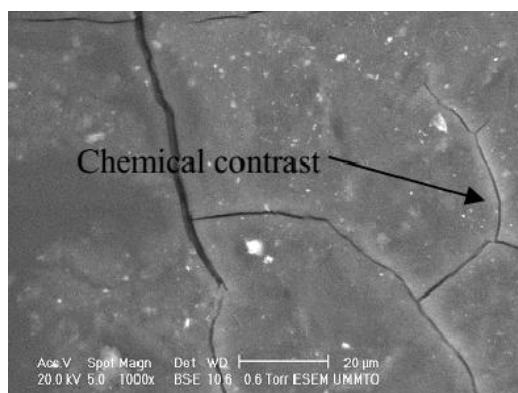
Aged 72 hours





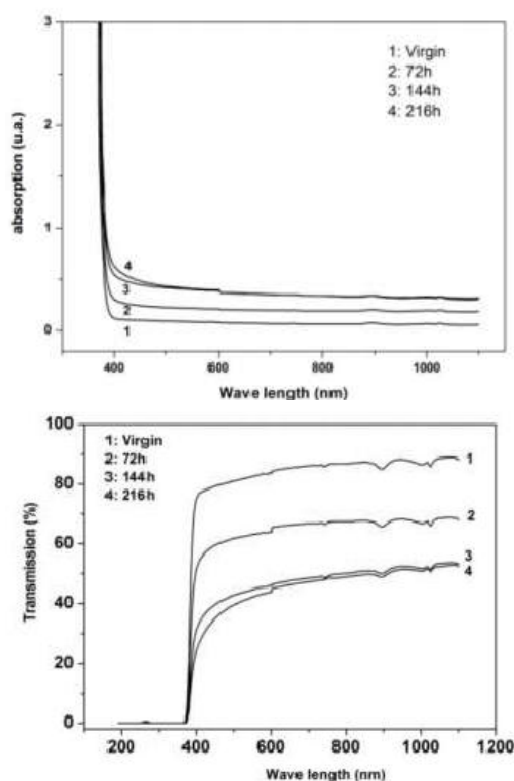


Aged 144 hours

**Fig. 11.** Microstructure evolution depending on material aging**Fig. 12.** Microstructure of the material after aging 216 hours

### III.5 Absorption and transmittance spectra

The ultraviolet-visible (UV / VIS) absorption and transmission spectra of the samples studied were performed in the wavelength range 190-1100 nm using a Perkin-Elmer spectrophotometer. Irradiation of the samples was carried out using a monochromatic light source of wavelength 253 nm from a low pressure mercury lamp Cole-Parmer (25W). The distance between the light source and the sample was 10 cm. The thermal effects of the UV lamp were compensated by adjusting the sample temperature around 298K. The Ultraviolet-visible (UV/VIS) spectrophotometric scans were measured in the wavelength range 190–1100 nm before and after UV-irradiation. The absorption and transmission spectra of the irradiated PC at different durations are shown in FIG. 13a. This figure shows that the absorbance is constant for all the samples in the low wavelengths (between 200 and 380 nm). After this interval, a sharp drop in absorbance is observed in 380 nm while it remains almost constant up to 1100 nm for all the samples. However, it should be noted that within this range (380 to 1100 nm) the absorbance is relatively higher for longer irradiation times. It appears that exposure under UV increases the absorbance of the material and decreases the transmittance (FIG. 13b), which results in a decrease in the transparency of the polycarbonate. Indeed, the figure 14 shows a gradual decrease of the transparency of samples according to the duration of ageing.



**Fig.13.** Absorption and transmittance spectra for PC before and after UV irradiation



**Fig. 14.** transparency of the material as a function of the irradiation time

#### IV. Conclusion

In this work, we have characterized the effects of UV aging on the mechanical behavior

and microstructure of polycarbonate. Compression tests, micro-hardness measurements, FTIR analyzes and X-ray diffraction were performed. The results showed that photodegradation at the wavelength of 253 nm and for three different durations (72, 144 and 216 hours) have an influence on the chemical formula, the physical state (it adopts the yellowish color) and the mechanical behavior of our material. Indeed, evolutions of micro-hardness, elastic limits, resistance to rupture were recorded. There is therefore a good correlation between the modification of the microstructure of the aged material and the reduction of the mechanical characteristics and the absorbance. A chemical contrast is revealed on both sides of the microcracks. This is a consequence of a displacement of the molecular chains after the rupture of the secondary chemical bonds. This movement of the chains causes a change in the density of the material which is manifested by a chemical contrast revealed by SEM (FIG. 12). The structural rearrangement generates an increase in absorbance of the material.

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