

# *Study of the photo-oxidation and photolysis of unsaturated and cross-linked polyesters in the presence of inorganic photo-active pigment as Titanium Oxides*

Zahi KHALIL<sup>(1,2)</sup>

<sup>(1)</sup>Laboratoire de Photochimie Moléculaire and Macromoléculaire, Université de Clermont II- Ensemble Universitaire de Cézeaux 63177 Aubière Cedex France.

<sup>(2)</sup>Laboratory of materials, catalysis, environmental and analytical methods (MCEMA) Lebanese university Beirut, Lebanon

[zahi.khalil@hotmail.com](mailto:zahi.khalil@hotmail.com)

Bachar KOUBAISSY<sup>(2)</sup>, Mariam AKIL<sup>(2)</sup>,

<sup>(2)</sup>Laboratory of materials, catalysis, environmental and analytical methods (MCEMA) Lebanese university Beirut, Lebanon

## **Abstract**

The chemical evolution involved in the photolysis and in the photo-oxidation at long wavelengths higher than 300 nanometer of polypropylene glycol-maleatophthalate cross-linked by the styrene caused by the addition of photoactive pigment such as titanium oxides have been examined using Fourier Transform Infrared Spectroscopy and Ultra Violet spectrophotometry.

The evolution of photo-oxidation observed by Infrared spectrophotometry of the polymer in the presence of titanium oxides leads to the same photoproducts as the photo-oxidation of the virgin polymer. The nature and percentage of the incorporated titanium oxides (rutile I, rutile II, Anatase) have an important influence on the oxidation rate of the polymer. Changings of the speed of oxidation of the polymer regarding to the rate of titanium oxides was observed.

The examination of trends related of pigmented and virgin polymers shows a significant difference in the zone of 400-500 nanometer .with the presence of titanium oxides in the polymer, the concentration of photoproducts absorbing in this zone of wavelengths is high. The variation of optical density in the Ultra Violet - Visible region can be interpreted by the internal filter effect associated to these highly absorbent pigments. Very absorbent photo-chemically unstable products, especially the photolysis products, are protected by an absorbing screen.

## **Keywords**

Polyesters, titanium oxides, photo-oxidation, photolysis, polymerization, pigment

### I. INTRODUCTION

The history of polyesters began from synthesis research of aliphatic polyester [1]. Polyester fibers have an excellent basic properties, such as mechanical properties and chemical resistance [2]. Several recent studies reported the potential of titanium oxides (TiO<sub>2</sub>) as Nano photo-catalyst [3]; [4]; [5]; [6].

Surface modification of inorganic nanoparticles is essential for the fine dispersion in organic and polymeric matrices. Attachment of polymers onto surfaces of nanoparticles is mostly the preferred way of their surface modification [7].

The compatibility of TiO<sub>2</sub> nanoparticles (NPs) surface with fiber surface chemical functionalities is one of the most important prerequisites for obtaining stable composite system and long-term durability effects [8].

The inorganic fillers which are introduced in the polymeric materials can be either absorbent, such as photo-active pigments [9]; [10] or non-absorbent as calcium carbonate [11] or alumina "tri-hydrate [12]; [13]. The introduction of absorbent loads presents on the fundamental level, an essential interest; they cause disturbances that are often used to analyze the mechanism of photo-oxidation of polymers. The introduction of a photoactive pigment such titanium oxides in cross-linked polyesters (UP) have several

consequences on the photochemical evolution which are examined.

Pigments such as titanium oxides or zinc oxide, absorbing light at wavelengths superior to 380 and 350 nanometers (nm) respectively, are likely to cause reactions of photo-catalytic oxidation. The character of photo-catalytic compound is bound to photo-conduction properties possessed by this substance.

Indeed, the excitement of a photoactive pigment causes the formation of active species likely to initiate photo-oxidation reactions in the polymer ( $O_2^*$ ,  $O^*_{(ads)}$ ,  $O^*_{(ads)}$ ,  $OH^*$ ,  $OH^*_2$ ) [14];[15]. Currently, no definitive mechanism of production of excited species can be retained; there is no data on the energy of the different species in chemisorbed phase. Among the species cited, most authors retain per-hydroxyl and hydroxyl radicals ( $OH^*$ ) and ( $OH^*_2$ ) as responsible for most of photo-catalytic phenomena.

In conclusion, the overall effect of a pigment pro-oxidant or stabilizer depends on the polymer base percentage and pigment dispersion matrix. The internal filter effects and photo-catalysis will compete and only the experience will give us information on the preponderant phenomenon.

We have mainly discussed the cross-linked unsaturated polyesters (UP) which are polymers of the class of thermosets, whose implementation leads to cross-linked un-melted materials. They are easy to build by charges and glass fibers. They are very appreciated for their flexibility of implementation and their properties: These materials can compete with metals in several areas and especially in the transportation industries.

## II. EXPERIMENTAL

The cross-linked unsaturated polyesters (UP) are mainly polymers of the class of thermosets. They are very easy to build by charges and glass fiber. They are very appreciated for their properties. These materials can compete with metals in several areas and especially in the transportation industries.

The development of cross-linked unsaturated polyesters involves two steps:

- A poly-esterification between di-acids (Isophthalic acid/maleic anhydride) and glycols (1,2 propylene glycol)
- A radical co-polymerization with styrene

Cross-linked unsaturated polyesters were provided as homogeneous film of variable thickness, and the introduced absorbent fillers are: Titanium oxides with treated surface Rutile type I, II and anatase.

Two types of mixtures have been realized containing either 2.5% or 10%. For such pigment concentrations, we examined using a UV spectrophotometer equipped with integrating sphere absorption spectra and determined the following table (1):

Table 1: Different mixtures of polyesters-TiO<sub>2</sub> and their properties

Mixtures of polymer (UP) -TiO <sub>2</sub> Thickness (e) =110 micrometers (μm)	Properties		
	Absorption domain of photons by the pigment	Optical density at 325 nm (2.5%) of pigment	Scattered light and backscattered at λ higher than
type Rutile I	300-390 nm	1.5	390 nm
type Rutile II	300-390 nm	1.25	390 nm
type Anatase	300-370 nm	1	370 nm

The study of the evolution of the material has required the use of multiple of irradiation and analysis equipment's:

### ***Irradiation conditions***

- A long-wavelength: polychromatic irradiation apparatus, called SEPAP (12-24) [16] consists of four mercury vapor lamps "medium pressure", the type MY MAZDA 400 Watt, whose budget allows only radiation of wavelength greater than 300 nm. The central of the chamber, located 25 centimeter (cm) from the lamps, is equipped with a turret samples (24) animated by a regular and circular movement. The temperature is controlled continuously by a thermocouple contact and can be stabilized at 2°C between 40 and 80°C.
- A short wavelength irradiation apparatus SEPAP (254) [16] consists of a cylindrical reflector. The source, a monochromatic tube mercury vapor "low pressure" emitting at 253.7 nanometer (nm), embodies one of its focal axes. The other focal axis coincides with the axis of a sample turret (24) driven in a regular and circular movement of rotation Irradiation was performed at room temperature.

## Analysis

Changes in chemical structure of polymers is followed by (UV) analysis on a Perkin Elmer 554 equipped with an integrating sphere, and by (IR) on a Perkin Elmer 682 spectrophotometer and a Fourier transform Infrared (FTIR) Nicolet 20 SX.

## Titration of hydro-peroxides

The determination of hydro-peroxides concentration is performed according to the method implemented and described by [17], which is based on the ambient temperature oxidation of iron II ( $\text{Fe}^{2+}$ ) and coordination of iron III ( $\text{Fe}^{3+}$ ) with thiocyanate ions ( $\text{SCN}^-$ ).

## III. RESULTS

### III.1. Study of the photo-catalyzed oxidation of the polymer (UP) pigmented with titanium oxides.

#### III.1.1. Analysis of photoproducts absorbing in (IR)

The irradiation of polymer (UP) samples containing 2.5% and 10% of pigment is made in the equipment SEPAP (12-24) at Temperature ( $T$ ) = 60 °C. The evolution of the polymer during photo-oxidation was examined regarding to the nature and rate of titanium oxides.

As shown in "Fig. 1", the photo-oxidation of (UP) polymer containing titanium oxides leads to an evolution of IR spectra quite similar to that one of virgin polymer, In the field of hydroxyls, there is an increase in absorbance between 3100-3600  $\text{cm}^{-1}$  and the appearance of three bands at 3465, 3300 and 3400  $\text{cm}^{-1}$ . In the field of carbonyls, one observes the expansion of the initial band. Also, the evolution of (IR) spectra is not affected by the rate of titanium oxides. Moreover, the addition of titanium oxides to the polymer (UP) does not protect the hydro-peroxides. Also, the study of photochemical and thermal stability of hydro-peroxides in the pigmented polymer (UP) does not detect any presence of hydro-peroxide groups.

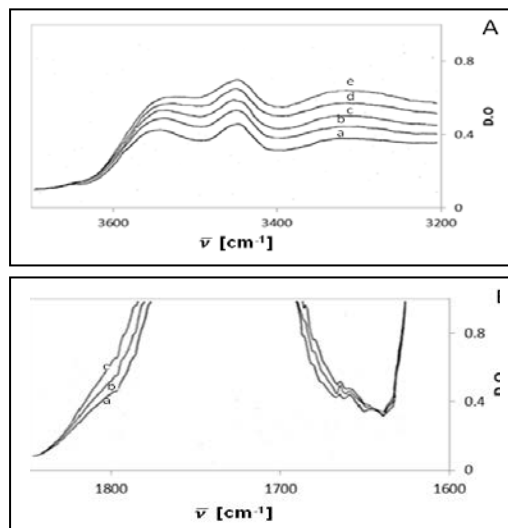


Figure 1: Evolution the (IR) spectrum of a polymer (UP+10%  $\text{TiO}_2$  Rutile I), irradiated in SEPAP 12-24. ( $e = 125 \mu\text{m}$ ).  
 - a: original b: 65 hours (h), c: 131 h, d: 221h, e: 314 h

The kinetics of formation of photo-oxidation products is significantly affected by the rate of titanium oxides in the polymer, as shown in "Fig. 1", which represent the variations of the optical density at 3300  $\text{cm}^{-1}$  versus the irradiation time of virgin and pigmented samples. For a given titanium oxide type, the oxidation rate increases with low rate (2.5%), particularly with oxides of rutile type I or Anatase, while a significant inhibition of photo-oxidation at high rates (10%) is observed. Also, the type of titanium oxide affects the oxidation rate of the polymer. Actually, at equal percentage of  $\text{TiO}_2$ , the oxidation rates of pigmented samples with titanium oxides type rutile I or II are always lower than that one of samples pigmented with titanium oxide of anatase type.

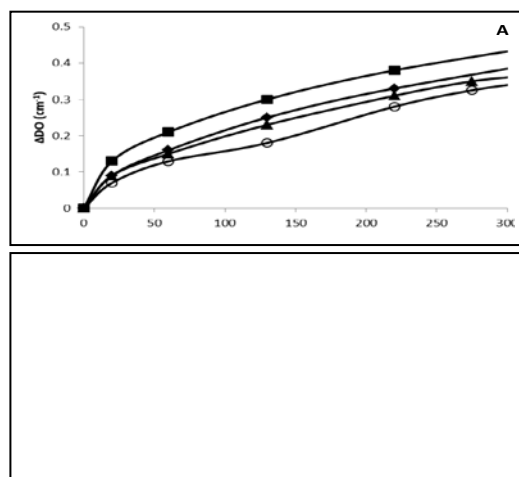


Figure 2: Increase in optical density at 3300  $\text{cm}^{-1}$  of a pigmented polymer (UP), versus the duration of irradiation. ( $e = 120 \mu\text{m}$ ).  
 A: (+ 2.5%  $\text{TiO}_2$ ) rutile I - B: (+ 10%  $\text{TiO}_2$ ) rutile I:  
 (○) virgin, (▲)  $\text{TiO}_2$  rutile I, (■)  $\text{TiO}_2$  rutile II, (◆)  $\text{TiO}_2$  anatase

### III.1.2. Analysis of photoproducts absorbing in (UV)

The introduction of titanium oxides causes an increase of absorption observed by (UV). So, the ability to accurately track the spectral variations will be limited to  $\lambda > 390$  nm for samples pigmented with TiO<sub>2</sub> rutile type I or II, and  $\lambda > 370$  nm for samples pigmented with TiO<sub>2</sub> anatase type. In this area, as shown in Figures 4, there is an increase of the concentration of absorbent photoproducts, depending on the type of oxide and its percentage. At low percent (2.5%), the increase of the optical density between 300-390 nm "Fig. 3" and "Fig. 4" and its decay between 250-300 nm is observed, while, at high percent (10%), the high absorption does not allow to observe accurately changes in (UV) spectra. The kinetic study of formation of photoproducts absorbing (UV) is difficult because of the strong absorption of titanium oxide. However, we examined the evolution of the optical density between 400 -500 nm regarding to the duration of irradiation. The comparison of changings (UV) spectra of virgin and pigmented samples showed that the addition of titanium oxides to the polymer (UP) increases significantly the rate of formation of photoproducts absorbing in the domain of visible light; this increase appears to be independent of the type titanium oxide introduced, as well as its percentage.

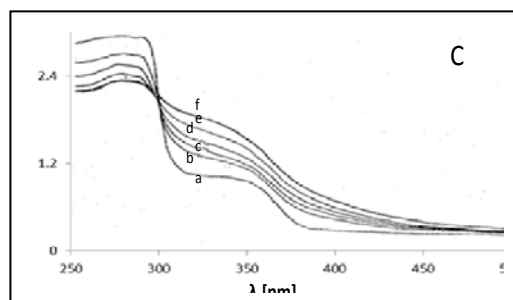


Figure 3 : Evolution the (UV) spectrum of a polymer (UP +(2.5% TiO<sub>2</sub>) .  
 a: original , b: 25 h , c: 65 h , d: 131h , e: 221 h , f: 314 h  
 A : + TiO<sub>2</sub> rutile I ( e = 112 μm ) - B : + TiO<sub>2</sub> rutile II ( e = 128 μm ) -  
 C : + TiO<sub>2</sub> anatase ( e = 112 μm )

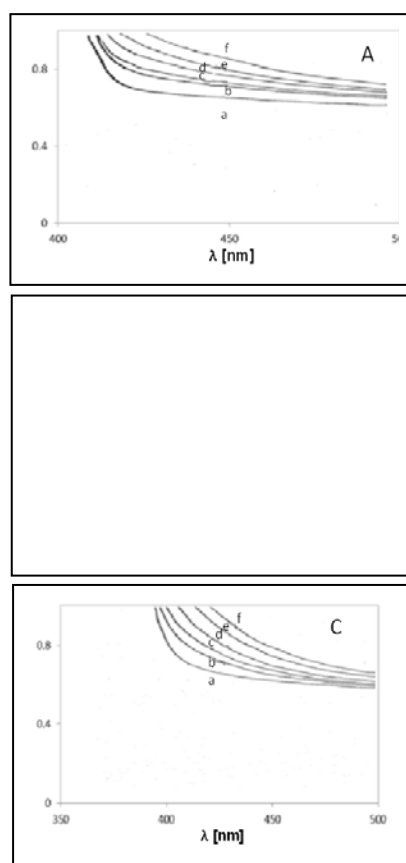


Figure 4 : Evolution the (UV) spectrum of a polymer UP (+10% TiO<sub>2</sub>) , irradiated in SEPAP (12-24)  
 a: original , b: 25 h , c: 65 h , d: 131h , e: 221 h , f: 314 h  
 A : + TiO<sub>2</sub> rutile I ( e = 125 μm ) - B : + TiO<sub>2</sub> rutile II ( e = 135 μm ) -  
 C : + TiO<sub>2</sub> anatase ( e = 122 μm )

### III.2-Study of the photolysis of polymer (UP) pigmented with titanium oxides

The polymer (UP) was the seat of very important phenomena of photolysis, characterized in (IR) by the appearance of a broad band around 3300 cm<sup>-1</sup> and (UV). by changings of optical density between 300-500 nm. When samples containing titanium oxides are irradiated without oxygen, the pigment may act as an inner filter, leading to a significant inhibition of the formation of photoproducts.

The irradiation of samples of polymer (UP) containing (0%), (2.5%), and (10%) titanium oxide of rutile type I under vacuum at  $\lambda > 315$  nm and  $45^\circ\text{C}$  shows that the observed photoproducts in the hydroxyls field are identical either for virgin and pigmented samples, by the appearance of a broad band around  $3300\text{ cm}^{-1}$  "Fig. 5". But as shown in "Fig. 6", the incorporation of titanium oxides in the polymer (UP) decreases the rate of formation of photoproducts; as important as the percentage of oxides is higher.

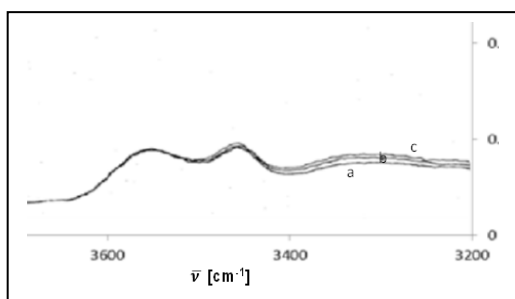


Figure 5: Evolution of the (IR) spectrum of a polymer (UP +10%  $\text{TiO}_2$ ) Rutile II, irradiated under vacuum. ( $e = 138\ \mu\text{m}$ ).  
 - a : original , b : 235 h , c : 424 h.

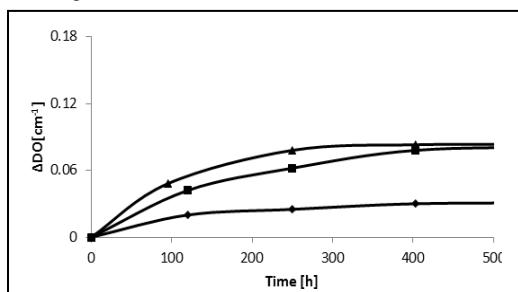


Figure 6 : Increase in optical density at  $3300\text{ cm}^{-1}$  of a pigmented polymer (UP), versus the duration of irradiation. ( $e = 125\ \mu\text{m}$ ).  
 (▲) Virgin, (■) 2.5%  $\text{TiO}_2$  I, (◆) 10%  $\text{TiO}_2$  rutile II.

Analysis of the spectra absorption in UV - visible range of the samples irradiated in vacuum shows a significant evolution in optical density between 400-500 nm, attributed to photolysis products highly absorbent "Fig. 7", and the rate of formation of photolysis products. We have noticed that this evolution of the (UV) spectrum is not proportional to the rate of titanium oxides; the optical density between 400-500 nm is increasing faster when the polymer is pigmented with 2.5%.

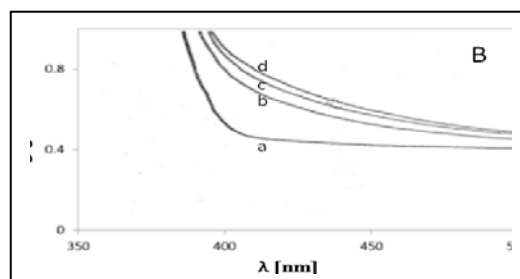
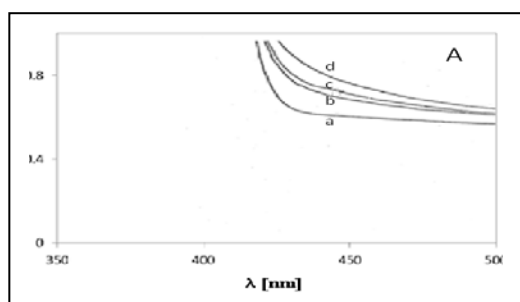


Figure 7: Evolution of the (UV) spectrum of a polymer (UP), irradiated under vacuum at  $\lambda \geq 315$  nm.  
 A : +10%  $\text{TiO}_2$  rutile I ( $e = 138\ \mu\text{m}$ ) - B : +2.5%  $\text{TiO}_2$  rutile II ( $e = 130\ \mu\text{m}$ )  
 a: original , b: 123 h , c: 235 h , d: 424h

We studied the photo-stability of photolysis products in the presence of oxygen. For this, we irradiated in SEPAP (12-24) at  $T = 60^\circ\text{C}$  pre-photolyzed samples containing 2.5% and 10% of titanium oxide. The IR spectrum does not change during irradiation, especially in the field of hydroxyls. The presence of oxygen leads to the decrease in absorbance between 400-500 nm. Products of photolysis photo-oxidize and turn into less absorbent products "Fig. 8". But we find that the speed of photo-oxidation of photolysis products in the pigmented samples is lower than that observed in blank samples.

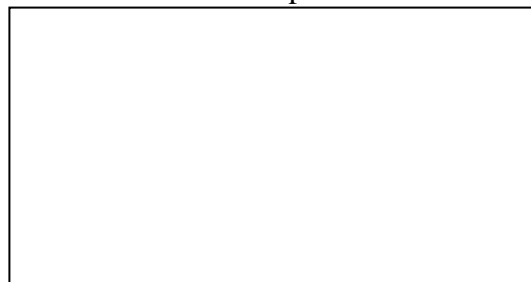


Figure 8: a) original, b) photolysis 424 h at  $\lambda \geq 315$  nm, c) post photo-oxidation 17h, d) post photo-oxidation 68h

#### IV. CONCLUSION:

The consequences of the addition of titanium oxides and in general photoactive pigments on the chemical evolution of a polymer are resumed as follows:

1 - It allows to control the priming photochemical oxidation reactions, either primary or secondary. In a polymer which contains no chromophoric groups that absorb between 300 - 400 nm, the kinetic parameters of the photo-thermal oxidation depend on the nature of impurities and absorbing content, at least in the first phases. In the presence of photoactive pigment, the nature of the absorbent sites is known and the speed of light absorption is controlled by the concentration of the pigment. In a polymer containing absorbing chromophoric groups

in the solar spectra, the absorption of light is controlled by the absorption spectra of the polymer and the concentration of pigment.

2 - In the presence of a pigment, the light is absorbed in the first microns of the sample. Photo-thermal oxidation reactions will be limited to the surface of the polymer. In this case, the diffusion of oxygen is ever the process controlling the oxidation kinetics.

3 - In a pigmented polymer, the light is mainly absorbed by the pigment. The effect of the inner filter results in an inhibition of the direct photo-oxidation of the polymer. The quality of protection will depend on the absorption properties of the polymer and pigment.

4 - The pigment can also act as a protective shield of intermediate photoproducts, if these products are photo chemically unstable. These photoproducts accumulate in the matrix, allowing their analysis. Finally, in practical terms, an introduced pigment into a polymer can protect the additives, which are normally involved in their ground state (anti - oxidant, hydro-peroxides reducer ...).

The understanding of the mechanisms of photochemical evolution of the virgin and pigmented polymer (UP) with titanium oxides, allowed to suggest a system of photo-stabilizing additives of the composite materials used primarily in the transportation, taking into account the disturbances caused by mineral fillers, fibers and additives.

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