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P.A. Christensen, T.A. Egerton, S.M. Martins-Franchetti, Changqing Jin
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Photodegradation of Poly (caprolactone)/Poly(vinyl chloride) Blend.

P.A.Christensen², T.A.Egerton², S.M. Martins-Franchetti^{1*}, Changqing Jin², and
J.R.White²

^{1*} Department of Biochemistry and Microbiology, University State “Júlio de Mesquita
Filho”- UNESP, Rio Claro, SP, Brazil

² School of Chemical Engineering & Advanced Materials,
University of Newcastle, Newcastle upon Tyne NE1 7RU, UK

Abstract

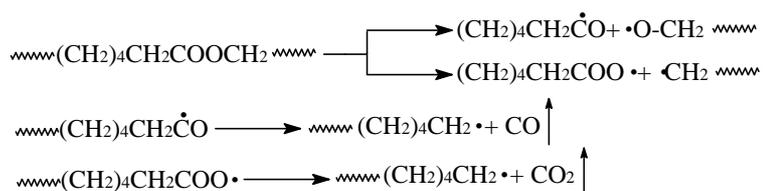
The photodegradation of a 1:1 blend of poly (caprolactone) and poly(vinyl chloride) has been studied by following carbon dioxide emission during UV exposure. Similar measurements were made on poly(caprolactone) and poly(vinyl chloride) homopolymers prepared and irradiated in the same way. It was found that the blend gave lower CO₂ emission than either of the two homopolymers, indicating that the interaction of the two components in the blend provided a beneficial reduction of photodegradation. It is therefore deduced that the detailed morphological characteristics of the blend have a controlling influence over the photo-oxidation.

* Corresponding author. Tel.: +55-19-35264189 Fax: +55-19-35264176
E-Mail address: samaramf@rc.unesp.br

1. Introduction

Poly(caprolactone) (PCL), an aliphatic polyester, is able to form blends with a wide range of polymers. It is biocompatible and has excellent permeability to drug molecules [1]. It is completely biodegraded within the human body [2] and therefore can be used as a carrier for controlled release drug delivery systems. Although its relatively low melting point, 60°C, limits its structural applications, its excellent blending properties allow it to be blended with poly(vinyl chloride) (PVC) to produce materials with higher melting points. Karal et al [3] have reported that the two components are compatible over a wide range of compositions and that PCL can plasticize PVC at certain dilutions. Even though PVC and PCL are believed to be mixed completely at the molecular level in the melt, they show phase separation when solidified, the exact morphology depending on composition and the presence in the blend of any third polymer or any additive [4-6]. Blending with PVC does not compromise the desired properties of PCL for many potential applications but it is necessary to know more about the degradation characteristics of the blends in aggressive environments in order to increase the range of applications. The current paper describes a study of the photodegradation of selected PCL/PVC blends.

Few reports on the photodegradation of PCL/PVC blends are to be found in the literature. Bei *et al* [1] studied the photodegradation of a poly(caprolactone)/poly(ethylene glycol) block copolymer (PCL/PEG). They proposed that the carbonyl groups present in the PCL photodegraded to form CO₂ and $-(CH_2)_4CH_2\cdot$ radicals which then broke down the poly(ethylene glycol) by a series of free radical reactions (Scheme 1).



Scheme 1. PCL photodegradation reactions

Earlier studies by the present authors and co-workers [7,8] and by Worsley and co-workers [9,10] have shown that FTIR assay of the carbon dioxide formed during the photodegradation of unpigmented and TiO₂ pigmented films can be used to monitor their photodegradation. The *in situ* FTIR technique used by the present authors was originally developed to study pigmented paints [11] and its use was then extended to the study of photochemical degradation of 100 µm thick polyethylene (PE) film and of PVC extrudate [7,8]. The current paper reports its application to monitor the photodegradation of PCL/PVC blends

2. Experimental

2.1. Materials

PCL films (100 µm thick) were prepared by casting PCL solutions which had been made by stirring 0.1 g of PCL powder in 15 ml dichloroethane at 60°C for 30 minutes. They were then evaporated in a Petri dish for 48 h at 25°C before drying in a vacuum desiccator [12]. 100 µm films of PVC and PCL/PVC 1:1 (50/50 w/w %) blends were prepared in a similar way.

2.2. Film characterization

The films thickness were measured with a manual thickness gauge (Mitutoyo, Japan). The UV spectra of PCL and blends were measured from 200 – 800 nm using a Shimadzu 2401 spectrometer. X-ray diffraction measurements were made with CuK_α radiation (wavelength 0.1542nm) using a Philips X-PERT Plus X-ray diffractometer.

2.3. FTIR measurement of photo-generated carbon dioxide.

Discs of 12 mm diameter were cut from the film and were positioned opposite a CaF₂ window in a specially built infrared cell. Samples were enclosed in the cell for the duration of

the experimental run. The starting atmosphere was set up by flushing with wet oxygen, provided by bubbling cylinder oxygen through water, prior to sealing the cell. From the measurements made it was deduced that the atmosphere remained almost unchanged for the duration of the experiments, i.e. the oxygen consumption was not sufficient to alter markedly the gaseous reaction atmosphere. The CaF_2 window was irradiated by the output of a 150 W xenon lamp as described earlier [10]. The lamp output was filtered by 100 mm of water, to remove infrared, and an AM0 filter (Oriel), to remove radiation below ~ 275 nm. IR measurements were made using a Bio Rad FTS 60A spectrometer using the procedure described previously [11]. The progressive accumulation of carbon dioxide was normally monitored during an irradiation time of 3 h and was then followed for a further 1 h after irradiation ceased.

3. Results

3.1. UV absorption spectra

The UV absorption spectra of PCL, PVC and PCL/PVC films given in Fig. 1 indicate that although the PVC does not absorb in the range 800-220 nm the PCL shows an absorption at 320 - 260 nm on a background which gradually increases as the wavelength decreases from 750 nm to the sharp absorption rise below 250 nm. This 320 - 260 nm absorption is also present, though more weakly because of the lower PCL content, in the spectrum of the 1:1 PCL/PVC blend and is assigned to an $n \rightarrow \pi^*$ transition of the carbonyl group.

3.2. X-ray diffractograms

More extensive discussion of the X-ray analyses is given elsewhere [13]. The X-ray diffractograms of the PVC film gave very broad reflections at $2\theta \sim 17^\circ$ and 24° , characteristic of a predominantly amorphous film with a small crystalline or quasi-crystalline fraction

(figure 2). The PCL film showed relatively sharp peaks at positions close to the orthorhombic PCL reflections at $2\theta = 21.4^\circ$ and 23.8° [13,14], and an amorphous halo under the crystalline reflections. The ratio of the crystalline and amorphous reflections indicated significant crystallinity. The 1:1 blend showed evidence of crystallinity, with peaks in the positions for the PCL orthorhombic crystalline phase, together with a strong amorphous halo from the amorphous phase, which was probably a mixed PCL-PVC phase.

3.3. Carbon dioxide emission under UV irradiation

The results of UV irradiation of PCL are shown in Fig. 3. During an initial 60 minutes dark period no carbon dioxide was generated. At the end of this time the film was exposed to UV and after only 30 minutes irradiation, CO_2 was detected. The amount of CO_2 increased with irradiation time but further generation stopped when irradiation ceased. The 100 μm PCL film has a similar thickness to the 100 μm PE films that were used in earlier studies [6, 7]. Increasing the effective film thickness by using a sample composed of 5 PCL layers approximately doubled the rate of CO_2 generation. Fig. 4 shows a similar pattern of results for the 100 μm cast films of PVC. Again, increasing the sample thickness by using 5 layers of film increased the rate of CO_2 formation. However, although the PVC films have the same thickness as the PCL films, the rate of CO_2 generation was less. It is also noticeable that, as in the earlier study of PVC plaques [8], the generation of CO_2 from PVC did not stop immediately UV irradiation ceased. A direct comparison of the rate of CO_2 formation from single films of PCL and PVC showed that a single 100 μm PCL film emitted CO_2 at about twice the rate of the 100 μm PVC film (absorbances of 80×10^{-4} and 40×10^{-4} respectively after 180 minutes UV exposure.) Photogeneration of CO_2 from multiple layers of PCL and PVC have also been measured, and the results (Fig. 5) show that the CO_2 photogeneration continues to be greater from PCL than from PVC.

Finally (Fig. 6) we have compared CO₂ photogeneration from films of PCL, PVC and PCL/PVC blend. It is clearly seen that the photogeneration from the PCL/PVC blend is less than that from either of the single components.

4. Discussion

This study has used the FTIR measurement of evolved CO₂ to compare the photoactivity of PVC, PCL and PVC/PCL. Earlier work has demonstrated clearly the relevance of the CO₂ measurement to the photodegradation of polyalkenes [7] and, especially, PVC [8-10]. Although it would be useful to compare the FTIR results of PCL degradation with those from other techniques, such as GPC measurements of molecular weight (MW) distributions, the CO₂ method provides a convenient comparison of the activities of polymer blends in which the individual components may have very different MW distributions.

4.1. The effects of sample thickness

In the simplest case, increased sample thickness would increase formation of photodegradation products *pro rata*, as was the case in our earlier studies of carbonyl development [15] and carbon dioxide generation [7] in multilayer samples of unpigmented PE films. This implies that CO₂ is generated at the same rate at all depths within the sample and that the diffusion coefficient is sufficiently high for it to escape quickly. However, this would be modified if the commonly observed oxygen-diffusion limited reaction conditions prevail [16-20] or if strong UV attenuation reduced the effective UV flux at the reaction locus, as occurs in pigmented films [15].

The use of polycaprolactones for controlled drug delivery utilises their permeability to molecules which are large in comparison with oxygen and it was anticipated that the results for multi-film PCL samples would be controlled not by oxygen diffusion but by UV

attenuation. In a recent publication [22], the diffusivity of oxygen in a polycaprolactone sample is given as $23.4 \times 10^4 \text{ cm}^2 \text{ s}^{-1}$ and it has been suggested [23] that the reason for the extraordinarily high gas transport in PCL is the presence of pores and surface defects in films produced by casting from solution. The diffusion coefficients of O_2 in PVC (given variously as $0.41 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ [24] and $0.84 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ [25]), are much less. On the other hand, from Fig 1, an approximate estimate of the 290 nm absorbance of a single PCL film is ~ 0.25 (i.e. $\sim 45\%$ of the 290 nm radiation is absorbed). From this value it can be calculated that for five films ca 94% of the 290 nm radiation would be absorbed – and if photo-oxidation is assumed to be proportional to the amount of 290 nm radiation absorbed the CO_2 photogeneration would increase by a factor of ~ 2 . This estimate is in tolerable agreement with the measured factor of 1.75 (based on an increase from 80 to 142×10^{-4} , see figure 3) and the agreement implies that UV attenuation is the main factor which limits the CO_2 evolution from the multilayer PCL sample. For PVC the UV absorption is much less than for PCL, and as expected, CO_2 generation from multilayer PVC films increases by a bigger factor, ~ 2.5 . If UV attenuation were solely responsible for this reduction in rate (from the 5 expected for the *pro rata* case) ca 20% of the incident UV would have to be absorbed by each film. As this is much less than the measured absorbance it is concluded that for multilayer PVC samples reduced availability of oxygen is probably significant in this case.

It is concluded that, although significant photogeneration of CO_2 probably occurs throughout the depth of the 100 μm PCL and PVC films, in PCL the rate of oxidation is reduced progressively through the depth due to UV absorption whereas oxygen diffusion probably limits the oxidation in PVC.

4.2. Photodegradation of PVC/PCL blends

The CO₂ generated by irradiating the PVC/PCL blend was significantly less than the amount that would be expected if there were no interaction between the two components. This result is particularly significant because the optical attenuation of the PVC/PCL blend is intermediate between that of its components (Fig. 2). At long wavelengths this attenuation is primarily due to scattering but at shorter wavelengths is dominated by absorption. Therefore, we do not consider that differences in the optics makes are the primary cause of the low photoactivity of the PVC/PCL blend. Instead, two possible explanations for this are proposed. Firstly, if, as suggested above, the PVC phase is more prone than PCL to oxygen starvation under the conditions of the experiments conducted here, the oxidation of the PCL in the interior of the blend samples could be limited as a result of reduced oxygen levels due to the slower diffusion of oxygen through the PVC, if a phase-separated PVC component is present. The second explanation is that, in the blend, the degree of order in one, or possibly both, of the phases is greater than in single component films prepared and treated in the same way, leading to slower oxidation. This idea is explored in the following paragraph.

The excellent miscibility of PCL and PVC offers the possibility of forming a mixed phase with zero crystallinity. The composite was blended and dried at room temperature, which is below the PCL crystal melting temperature, and PCL crystals will be stable if formed. However, their growth will be kinetically rather than thermodynamically limited. Although there is likely to be competition to locate PCL in PCL crystals in the mixed phase, it is not surprising that evidence for the formation of PCL crystals was obtained. In pure PCL, crystallinity is limited mainly by entanglements that prevent the macromolecules from arranging into crystal formation. In the 50/50 (w/w %) blend the stoichiometry suggests that initially there are approximately 1.6 Cl atoms for each ester group. Spectroscopic studies (to be published separately) suggest that the presence of PVC perturbs the C=O vibration of pure PCL, possibly as result of Cl--C=O interactions. It is possible that the PVC molecules

plasticize the PCL, enhancing the mobility of the PCL molecules and allowing a greater extent of crystallization than occurs in pure PCL. The degree of plasticization would depend on the proportions of each component in the blend. The X-ray measurements are not sufficiently accurate to verify this though the data cannot rule it out. If PCL were more crystalline in the blend than in pure PCL, then the contribution of the PCL to CO₂ emission would be reduced if photo-oxidation occurs almost exclusively in the amorphous regions. The increased crystallinity of PCL would cause oxygen diffusion to occur less readily and would therefore reduce oxygen availability for PVC oxidation also. In a similar manner, ordering in any phase-separated PVC present in the PVC/PCL blend may be more developed than in pure PVC, due to the plasticizing effect of the PCL. If, as is suspected, some PVC phase-separates and forms partly crystalline (or highly ordered if not truly crystalline) domains, oxidation in these domains will not occur as readily as in pure PVC. If this is the case the CO₂ emission contributed by the PVC in the blend will be less than would be predicted from the measurements on the pure PVC. It should be noted that if either component in the PCL/PVC blend phase-separates and forms crystalline (or highly ordered) domains, the overall diffusion of penetrants such as oxygen will be reduced, causing reduced oxidation rates in both phases. If both components phase separate into crystalline domains this effect will be further enhanced.

The effect of changes in morphology on the optical properties of the polymers and their blends should be considered. The presence of crystalline domains will cause light scattering: a majority of the scattered radiation will pass obliquely through the sample, increasing its opportunity to cause photooxidation events of the kind that lead to the generation of CO₂. If this effect were to dominate it would cause CO₂ emission from the blends to be higher than from the single polymers, contrary to observation.

5. Conclusions

The results reported above indicate that CO₂ photogeneration from PCL/PVC blends is less than from either of the pure components when irradiated under the same conditions. The carbonyl groups in PCL have been reported to sensitise PCL/PEG composites [1] but in PCL/PVC the blend is more, not less, photo-stable. This observation was not anticipated because the UV spectrum of the blend demonstrates that the UV absorption characteristic of the single component PCL is retained in the PCL/PVC blend. It is therefore deduced that the detailed morphological characteristics of the blend has a controlling influence over the photo-oxidation. Complementary studies using a different UV source and post-irradiation analyses by UV-Vis, FTIR and scanning electron microscope observation also indicated that the degradation of the blend was not a simple addition of the changes observed with the component homopolymers [13].

Acknowledgements

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Figure Captions

1. Transmission spectra of 100 μm films of poly(caprolactone), (PCL) ; Poly(vinyl chloride), (PVC) and of a 50:50 blend of the two components.
2. X-ray diffractograms of 100 μm films of poly(caprolactone), (PCL) ; Poly(vinyl chloride), (PVC) and of a 50:50 blend of the two components. For clarity, the diffractograms have been displaced vertically with respect to one another.
3. Carbon dioxide evolution from a single PCL film and from a stack of 5 PCL films when UV irradiated PCL in a humidified O_2 atmosphere.
4. Carbon dioxide evolution from a single PVC film and from a stack of 5 PVC films when UV irradiated PCL in a humidified O_2 atmosphere.
5. A comparison of carbon dioxide evolution from a stack of 5 PCL films with that from a stack of 5 PVC films during UV irradiation in a humidified O_2 atmosphere. UV .
6. A comparison of carbon dioxide evolution from 100 μm films of poly(caprolactone), (PCL) ; Poly(vinyl chloride), (PVC) and of a 50:50 blend of the two components.
(These measurements were made with a different, but same model, lamp to that used for the results in Figs. 3- 5).

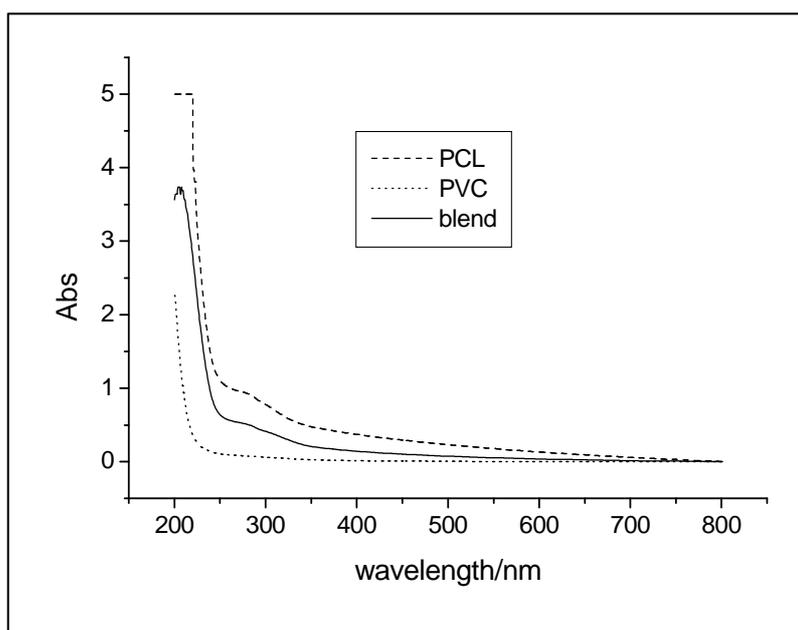
Fig 1

Fig. 2

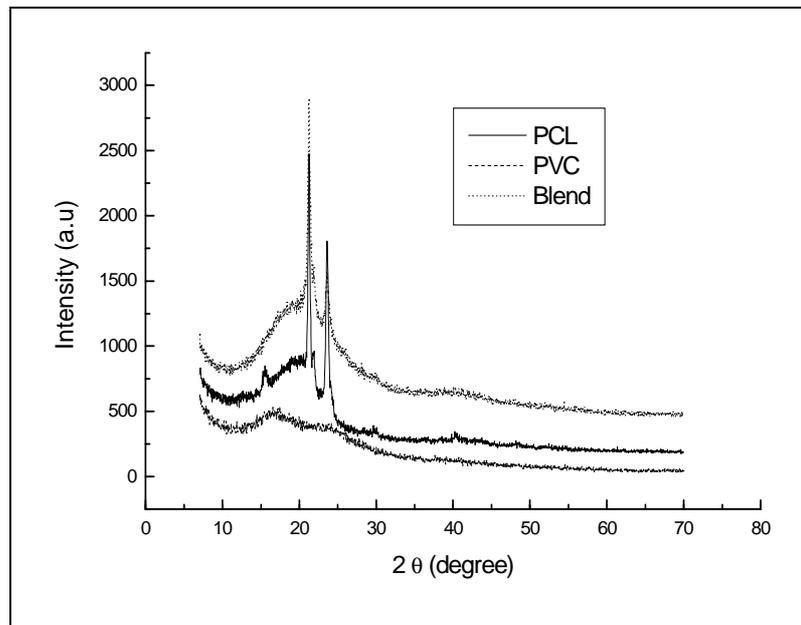


Fig.3

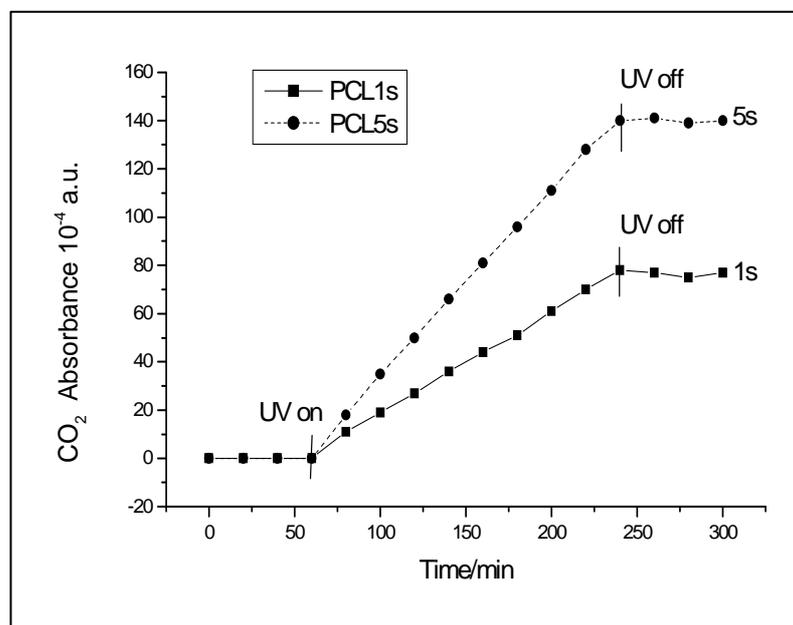


Fig. 4

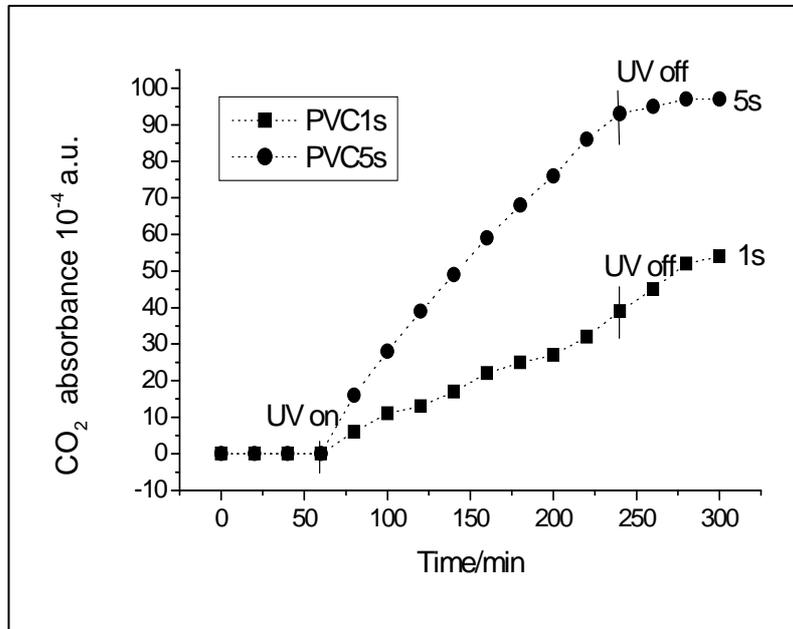


Fig 5.

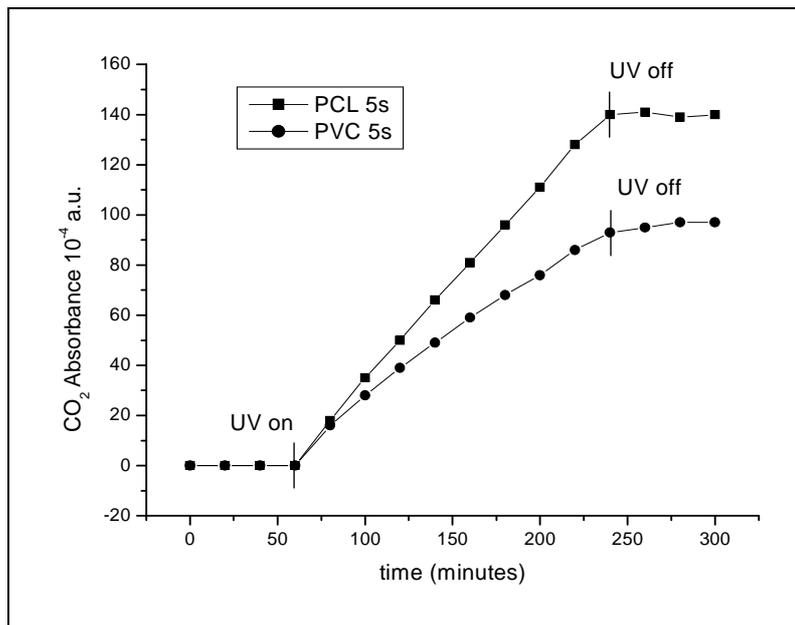


Figure 6

